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Grégorio Crini · Eric Lichtfouse *Editors*

Green Adsorbents for Pollutant Removal

Innovative materials

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Preface

> A further aspect of water pollution control is the treatment methods by which this control is to be achieved. The term BATNEEC is now used and means Best Available Technology Not Entailing Excessive Cost. It is likely that adsorption will find its way into this group of water treatment technologies. (Gordon McKay 1995)

Over the past three decades, there has been an increasing interest in the phenomenon of contaminant sequestration by nonconventional green adsorbents using oriented-adsorption processes. This phenomenon has a high potential for applications in water and wastewater treatments. Liquid-solid adsorption using green adsorbents can be simply defined as the removal of contaminants from solutions using products and by-products of biological, agricultural, and industrial origin. Green adsorbents represent cheap filter materials often with high affinity, capacity, and selectivity to interact with contaminants. They are abundant and already available in most places in large quantities. The list of green adsorbents is extremely extensive, including carbons from agricultural solid wastes and industrial by-products; agro-food wastes; industrial by-products; natural products, e.g., clays, hemp, flax, and cotton; and biological materials such as dead biomass, living plants, algae, biopolymers, and fungi.

Cultivation of *Lepista nuda*, named “blue foot” in French, an edible mushroom, on a composted substrate. (Copyright: INRA, Jacques GUINBERTEAU 2018)

This book is the second volume of two volumes on *Green Adsorbents for Pollutant Removal* published in the series *Environmental Chemistry for a Sustainable World*.

Written by 80 international contributors coming from 23 different countries who are leading experts in the adsorption field, these two volumes show a typical selection of green materials used in wastewater treatment, with emphasis on industrial effluents. The first volume provides an overview of fundamentals and design of adsorption processes.

This second volume focuses on innovative materials. The first chapter by Nadia Morin-Crini et al. presents hemp-based materials for metal removal. The second chapter by Leticia B. Escudero et al. describes the biosorption of metals and metalloids on various materials. In Chap. 3, Ioannis Anastopoulos et al. present the use of leaves for metal removal. Then, Anita George Varghese et al. discuss the recent advances in cellulose-based adsorbents used in environmental purposes in Chap. 4. Ramonna Kosheleva et al. (Chap. 5), Liliana Giraldo et al. (Chap. 6), and Viraj Gunarathne et al. (Chap. 7) review activated carbons from food wastes, aerogels and bones, and municipal solid waste biochar as efficient materials for pollutant removal, respectively. Biosorption of dyes onto microbial biosorbents is presented by Uttariya Roy et al. in Chap. 8. In Chap. 9, Shweta Kulshreshtha discusses the use of mushroom biomass to remove pollutants. A detailed review of green adsorbents for removal of antibiotics, pesticides, and endocrine disruptors is given by Akeem Adeyemi Oladipo et al. in Chap. 10. In Chap. 11, Prashant Pandey and Vipin Kumar Saini review the use of pillared interlayered clays as innovative materials for pollutant removal. Finally, in Chap. 12, Dharmendra K. Gupta et al. discuss the use of green adsorbents for radioactive pollutant removal from natural water.

The audience for this book includes students, environmentalists, engineers, water scientists, and civil and industrial personnel who wish to specialize in adsorption technology. Academically, this book will be of use to students in chemical and environmental engineering who wish to learn about adsorption and its fundamentals. It has also been compiled for practicing engineers who wish to know about recent developments on adsorbent materials in order to promote further research toward improving and developing newer adsorbents and processes for the efficient removal of pollutants from industrial effluents. However, the book is not meant to be an extensive treatise on adsorption and adsorbents. For example, particular aspects on modeling or biosorption are not considered because the reader can find abundant information on these topics in the literature. The book will serve two main functions: a readable and useful presentation not only for undergraduate and postgraduate students but also for the water scientists and engineers and a convenient reference handbook in the form of numerous recent examples and appended information.

The editors extend their thanks to all the authors who contributed to this book for their efforts in producing timely and high-quality chapters. The creation of this book would not have been possible without the assistance of several friends deserving acknowledgment. They have helped by choosing contributors, by reviewing chapters, and in many other ways. Finally, we would like to thank the staff at Springer Nature for their highly professional editing of the publication.

Besançon Cedex, France Grégorio Crini
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Eric Lichtfouse 58, is a biogeochemist at the University of Aix-Marseille, CEREGE, Aix-en-Provence, France. He got a PhD in organic geochemistry at the University of Strasbourg in 1989 for the discovery of new fossil steroids in sediments and petroleum. He has invented the ^{13}C-dating method allowing to measure the dynamics of soil organic molecules. He is chief editor of the journal Environmental Chemistry Letters and former chief editor of the journal Agronomy for Sustainable Development. He has published the book *Scientific Writing for Impact Factor Journal*, describing the micro-article, a new tool to identify the novelty of experimental results. He has published 85 research papers, with an h-index of 23, and edited more than 50 books. He got the Analytical Chemistry Prize of the French Chemical Society, the Grand University Prize of Nancy University, and a Journal Citation Award by the Essential Science Indicators.

Chapter 1

Hemp-Based Materials for Metal Removal

Nadia Morin-Crini, Sonia Loiacono, Vincent Placet, Giangiacomo Torri, Corina Bradu, Mirjana Kostić, Cesare Cosentino, Gilles Chanet, Bernard Martel, Eric Lichtfouse, and Grégorio Crini

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Abstract With the increasing focus on renewable materials and sustainability issues, the development of non-conventional materials from natural resources and possessing complexing properties is currently an area of extensive research due to their potential applications in biosorption processes for pollutant removal. Among them, the hemp plant, an annual high yielding industrial crop grown for its fibres and seeds, is one of the most promising material for biosorption of metal ions from diluted waste streams. In this chapter, an extensive list of hemp-based biosorbent literature has been compiled and discussed. After a brief description of hemp and its properties and applications, the chapter gives a general overview of liquid-solid biosorption processes for metal removal from aqueous solutions onto hemp-based materials.

Abbreviations

AC	activated carbons
CAC	commercial activated carbons
DSC	differential scanning calorimetry
EDX	energy-disperse X-ray spectroscopy
FT-IR	Fourier transform infra-red spectrophotometry
MFA	microfibrils angle
NMR	nuclear magnetic spectroscopy
SEM	scanning electron microscopy
SPE	solid-phase extraction
TGA	thermogravimetric analysis
THC	delta-9-tetrahydrocannabinol
XPS	X-ray photoelectron spectroscopy
ΔG	Gibbs free energy change
ΔH	enthalpy change
ΔS	entropy change

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1.1 Introduction

Many wastewaters contain significant levels of organic and mineral contaminants which are toxic or otherwise undesirable because they create, in particular, odor, bad taste and color. Amongst the numerous techniques of contaminant removal, liquid-solid adsorption is the procedure of choice as it can be used to efficiently remove different types of contaminants (Manes 1998; Cooney 1999; Liu and Liptak 2000; Dąbrowski 2001; Yang 2003; Crini and Badot 2008; Sharma and Sanghi 2012). Furthermore, adsorption can produce high quality water while also being a process that is both technologically simple and economically feasible. So, adsorption processes from aqueous solutions are important techniques in water purification, wastewater decontamination, and many other areas such as recovery and separation applications.

Carbons are one of the oldest and most widely used adsorbents in industry (Manes 1998). Indeed, due to their great capacity to adsorb contaminants, commercial activated carbon (CAC) are the most effective adsorbents, and if the adsorption system is properly designed they give a good-quality output, with concentrations under the legal limits for discharge waters. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to improve their properties. The processes that use these usual adsorbents are often carried out in a batch mode, by adding activated carbon (AC) to a vessel containing the contaminated solution, or by feeding the solution continuously through a packed bed of carbon. Adsorption processes using AC are also interesting because of convenience, easy operation, and their simplicity of design (Manes 1998; Radovic et al. 2000).

However, although these commercial materials are preferred conventional adsorbents for contaminant removal, their widespread industrial use is restricted due to high cost (Crini 2005; Kyzas and Kostoglou 2014). As such, alternative non-conventional adsorbents including products and by-products of biological and agricultural origin, and from forest industries were proposed, studied and employed as inexpensive and efficient adsorbents – in this case called biosorbents due to their natural origin and property to bind and concentrate metal ions from aqueous solutions (McKay 1996; Volesky 2004; Blackburn 2004; Crini 2006; Oliveira and Franca 2008; Crini and Badot 2010; Rezić 2013; Michalak et al. 2013; Vijayaraghavan and Balasubramanian 2015; Sharma 2015; Muya et al. 2016; Okenicova et al. 2016; Khalaf 2016; Zhao et al. 2016).

Indeed, the past three decades have shown an explosion in the development of new materials proposed as biosorbents for metal removal in biosorption-oriented processes using various contacting systems. These include living organisms (e.g. algae, bacteria, fungi, and yeasts) and dead biomass (e.g. bark, sawdust, peat, natural fibres such as cotton and flax, plants, and other organic substances such as biopolymers or polysaccharides). Polysaccharides include starch, cellulose, alginate and chitin and their derived products such as chitosan and cyclodextrins. These

Table 1.1 Examples of biosorbents used in biosorption-oriented processes for metal removal from water/wastewater with special attention to polysaccharide-based biosorbents (selected reviews)

Biosorbent	Reference(s)
Agricultural wastes (sawdust, bark, peat, coffee, date pits…)	Novoselova and Sirotkina (2008); Crini and Badot (2010); Dulman and Cucu-Man (2010); Fomina and Gadd (2014); Kyzas and Kostoglou (2014); Westholm et al. (2014); Suba and Rathika (2016); Tapia-Orozco et al. (2016); Ahmed (2016); De Gisi et al. (2016); Raval et al. (2016); Anastopoulos et al. (2017a)
Algae (seaweeds)	Fomina and Gadd (2014); He and Chen (2014); Kumar et al. (2015); Dabbagh et al. (2016)
Alginate	Nastaj and Przewlocka (2014); Vandenbossche et al. (2015)
Biomass	Mudhoo et al. (2012); Gorska et al. (2014)
Cellulose and derivatives	Hubbe et al. (2011); Mudhoo et al. (2012); Rezić (2013); Vandenbossche et al. (2015); Salman et al. (2015); Tran et al. (2015); Ummartyotin and Pechyen (2016); Kumar et al. (2017)
Chitin, chitosan and derivatives	Mudhoo et al. (2012); Westholm et al. (2014); Tran et al. (2015); Ummartyotin and Pechyen (2016); Zhang et al. (2016); Anastopoulos et al. (2017b)
Composts	Anastopoulos and Kyzas (2015)
Eggshell	Ummartyotin and Pechyen (2016)
Extracellular polymeric substances	More et al. (2014); Li and Yu (2014)
Microbial materials (fungi, bacteria, yeasts…)	Dhankhar and Hooda (2011); Srivastava et al. (2015); Shakya et al. (2016); Ayangbenro and Babalola (2017)
Pectin	Vandenbossche et al. (2015); Zhao and Zhou (2016)
Plant materials	Fomina and Gadd (2014); Srivastava et al. (2015)
Starch and derivatives	Crini and Badot (2010); Morin-Crini and Crini (2013); Vandenbossche et al. (2015); Sharma (2015); Haroon et al. (2016)

materials are interesting due to the fact that they are abundant in nature, available in large quantities, inexpensive, and may have potential as biosorbent materials due to their physicochemical characteristics and particular structure (Volesky 2004; Blackburn 2004; Crini 2005, 2006). Abundant data can be found in the literature. Table 1.1 reports some examples of materials used in the biosorption process with special attention to polysaccharide-based adsorbents.

Actually, numerous works are being conducted on the use of hemp-based materials as biosorbents. Hemp is a fast growing, annual herbaceous (Fig. 1.1) and multipurpose plant. In particular, its bast fibres are natural, cheap, strong, stiff and lightweight, and have been not only identified as attractive reinforcements for composites (thermoplastic polymers…) and material for wool insulation but also as useful chelating materials.

An analysis of the Web of Science database reveals that 104 publications containing both the keywords ‘hemp’ and ‘metal’ in the topic category have been published from 2002 to 2016. Figure 1.2 clearly shows an increase of citations. Each publication has been cited 15.98 times on the average. Overall this finding shows a growing research interest. To the best of our literature review, this chapter is the first pub-

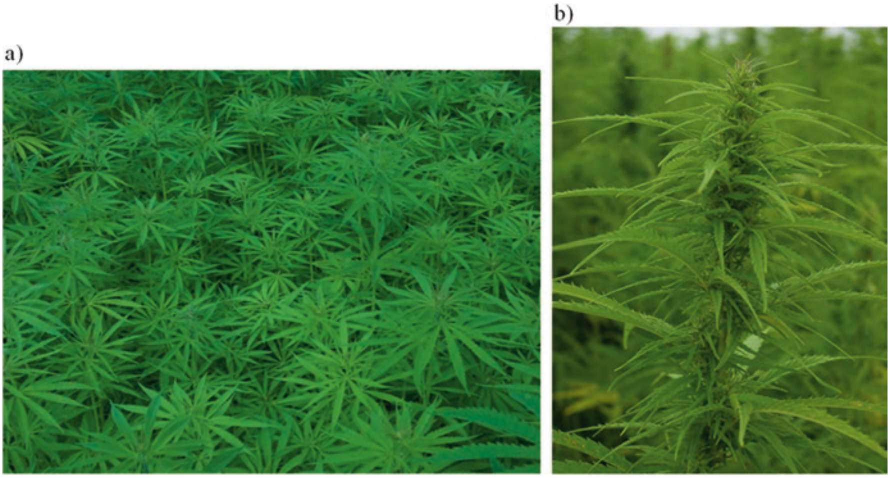

Fig. 1.1 Hemp field (**a**) and dioecious male plant (**b**)

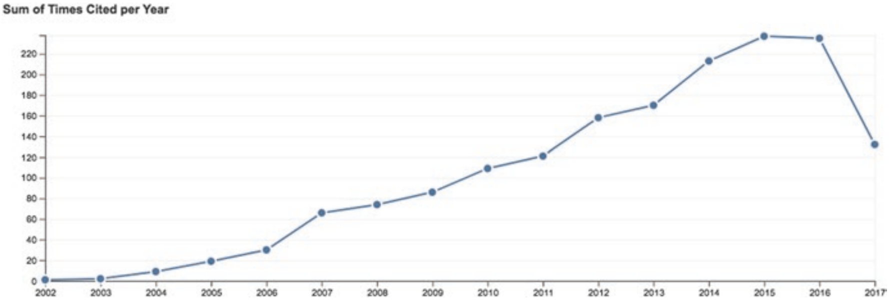

Fig. 1.2 Citations of the 104 publications on hemp and metal in the Web of Science Core Collection, published from 2002 to 2017 (the analysis was performed using the expression 'hemp AND metal' in the topic category, on July 4, 2017)

lished review on the potential use of hemp-based materials in water and wastewater treatment. After a brief description of hemp and its properties and applications, the chapter gives a general overview of liquid-solid biosorption processes for metal removal from aqueous solutions onto hemp-based materials. For this, an extensive list of hemp-based biosorbent literature has been compiled and discussed.

1.2 Hemp, an Interesting Raw Material

1.2.1 Production

Hemp is one of the oldest domesticated crops known to man. Hemp fibres were used for textiles and cordages, and the seeds as nutrition for thousands of years. Hemp originated from Asia and was already cultivated 4500 years ago in China (Ranalli

1999; Bouloc 2013). The first copies of the Bible were made of hemp paper (Ranalli and Venturi 2004). Hemp bast fibres were the principal natural fibres used for maritime ropes and sails for centuries. Oils from hemp seeds were also used for a wide range of purposes, from cooking to cosmetics. It is estimated that hemp was imported to Europe by nomads in the sixteenth century (Bouloc 2013). In the middle of nineteenth century, hemp cultivation decreased with disappearance of the sailing navy and competition from other natural fibres (cotton, jute…) for textile applications, and later due to intensive development of synthetic fibres (Milanovic et al. 2012). In the 1930s, cultivation was forbidden in the vast majority of Western countries due to the fact that hemp and marijuana come from the same genus and species plant (*Cannabis sativa* L.), and this introduced a lot of confusion and social and political controversies. In the last two decades, the increasing consideration of natural resources and energy conservation has renewed the interest on hemp as a "new" low-cost, ecological, biodegradable, sustainable, recyclable, and multipurpose biomaterial (Shahzad 2012; Bouloc 2013; Bono et al. 2015).

Hemp is a dicotyledonous plant from the order of Rosales, from the family of Cannabaceae, genus *Cannabis* (Bouloc 2013). Hemp – also called industrial hemp – refers to the non-psychoactive varieties of *Cannabis sativa* L. Industrial hemp is often incorrectly associated with hemp for narcotics due to the fact that the psychoactive ingredient, delta-9-tetrahydrocannabinol (THC), found in hashish, is present in all hemp varieties to some extent. European regulations limit THC content to 0.3% in industrial hemp. In Canada, the THC limit is 1%. Marijuana (called medical cannabis) contains about 10–30% of THC level (Bouloc 2013; Pacaphol and Aht-Ong 2017).

Hemp is an annual high yielding industrial crop grown for its fibres and seeds. This plant is being mainly cultivated in Europe, Canada and China (the largest supplier in the world). France is the top European producer of hemp with an area of cultivation around 12,000 ha. Other important producing countries are Romania, Italy, Poland and Hungary (Amaducci 2005; Bouloc 2013; Salentijn et al. 2015). Since hemp is one of the most efficient plants known for its ability to utilize sunlight and capture large quantities of CO_2 to photosynthesize, with an annual growth up to 5 m in height, production of hemp fiber is experiencing a renaissance again. Currently, hemp is the subject of a European Union subsidy for non-food agriculture, and a considerable initiative for its further development in Europe is underway (Ranalli and Venturi 2004; Faruk et al. 2012; Bouloc 2013).

Hemp is considered as an excellent crop for sustainable agriculture. Selection of a hemp cultivar and the manner of sowing depend on the purpose of the material produced (fibre or seed). Indeed, there are mainly two groups of Cannabis varieties being cultivated today: varieties primarily cultivated for their fibre (called industrial hemp) used for example for construction material, clothing or animal related purposes, and varieties grown for seed from which oil is extracted (breeding, or food); hemp can also be cultivated as dual-purpose crop that implies that both fibres and seeds can be processed (Bouloc 2013).

As a biodegradable plant which needs no irrigation or phytosanitary treatments, hemp is excellent as a crop rotation leader to alternate with crops such as beets or grains (Amaducci and Gusovious 2010). Furthermore, hemp can also be an excellent predecessor in crop rotation, in particular before winter cereals such as wheat. Hemp is more environmentally friendly than traditional crops. After sowing, cultivation is not difficult. The crop requires only rarely the use of plant protection products and hemp requires low fertilization. Easily adaptable to all types of soil and well-adapted to temperate climates such as in Europe, hemp is appreciated by organic growers not only for its ease of production but also for its rapid growth (120–150 days cropping cycle). Fibre hemp may yield up to 25 t above ground dry matter per ha (20 t stem dry matter per ha) which may contain maximum 12 t/ha of cellulose, depending on the genetics (e.g. varieties), cultivation practices, climate and environmental conditions (Bouloc 2013; Ingrao et al. 2015). Hemp also leaves an excellent quality, weed-free soil at the end of each season. Hemp detoxifies the soil and prevents soil erosion. Finally, hemp cultivation is a vector of development for local agricultural resources in emerging countries and an industrial output for crops in developed countries (Le Troëdec et al. 2011).

1.2.2 Types of Hemp-Based Products and Applications

Hemp is an interesting raw material for its very low-cost, abundancy, renewable character, particular chemical composition of its fibres including moisture content, macromolecular network with numerous hydroxyl groups capable of forming intra- and intermolecular bonds, and specific physical (low density), mechanical, thermal, acoustic and aseptic properties (Păduraru and Tofan 2008; Bouloc 2013; Amaducci et al. 2015). Hemp fibres are also classified as eco-friendly material and good candidates as a (partial) substitute for synthetic fibres such as glass, carbon or metallic fibres.

Cannabis sativa L. is the source of two types of natural fibres: bast fibres (fibrous form) and woody core fibres, called hurds or shives (granular form). Its cultivation also provides seeds for oil production. Hemp stem consists of approximately 20–40% of bast fibres and 60–80% of hurds (Stevulova et al. 2014). The outside of the stem is covered with bark (called epidermis). Inside the stems are bast fibres and the woody core. The separation of the bast fibre is carried out through defiberization or decortication (breaking the woody core of the stems into short pieces and separation of bast fibre from the hurds) using specialized machineries. The hemp fibres are situated in the bast of the hemp plant. The byproduct of the hemp stem obtained after the industrial defiberization process is called chenevotte (constituted from the xylem tissue of the stem, i.e. the shives).

Technical (multi-cellular) fibres, composed of elementary fiber bundles obtained by primary processing of stalks are characterized with heterogeneous chemical composition and fairly complicated structure. The main constituents are cellulose, hemicellulose and lignin (Table 1.2), while minor components such as pectin and waxes are regarded as surface impurities (Placet et al. 2014, 2017). As member of the bast fibre family, hemp contains over 75% of cellulose and less than 10 to 12% of lignin (compared with 60% and 30% respectively for wood). The bast fibres contain higher amounts of cellulose than the hurds (Table 1.2).

Table 1.2 Chemical composition of hemp fibres in wt % (Placet et al. 2017)

Component	Bast fibres	Hurds
Cellulose	57–77%	40–48%
Hemicellulose	9–14%	18–24%
Lignin	5–9%	21–24%

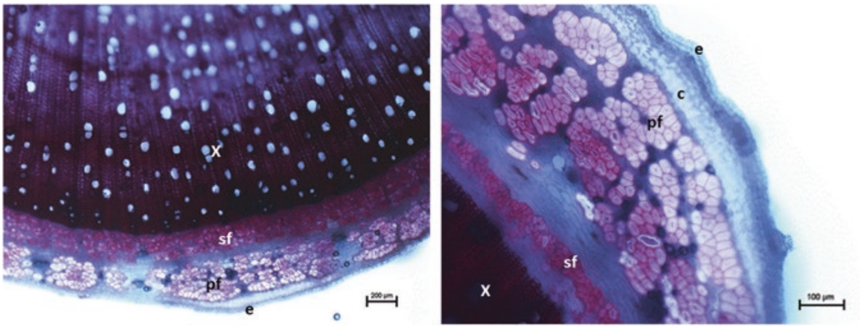

Fig. 1.3 Hemp (*Cannabis sativa*) stem cross sections – Microscopic observations of fresh transverse sections at two different magnifications after cytochemical staining using the Wiesner reagent (phloroglucinom-HCl) that gives a purple-red coloration to lignin (*X* xylem, *pf* primary fibres, *sf* secondary fibres, *c* collenchyma, *e* epidermis)

Their structure is complex. Indeed, hemp fibres are very heterogeneous and can be considered themselves as a composite material comprising three different parts (Le Troëdec et al. 2011). From the outer to the inner part, fibres consist of a middle lamella, a primary, a secondary and a tertiary cell wall, build up around an opening, the lumen. The bast fibres are joined together by the middle lamella, mainly composed of pectin (macromolecules of galacturonic acid) encrusted with lignin that hold fibres together into a bundle. Next to the middle lamella, the primary cell wall consists of disorganized arrangements of cellulose fibrils embedded in an organic matrix of hemicelluloses, lignin and proteins. The secondary cell wall consists of three layers of cellulose fibrils with different axial orientation that are bound by hemicelluloses. Each fibre bundle consists of single (elementary) fibres. There are two types of fibres with approximately the same diameter: (i) the useful primary fibres (5–55 mm long) and (ii) the short secondary fibres (2 mm long). However, the cell walls of the bast fibres are 5 to 10 times thicker than those of woody fibres. In contrast to the high quality of bast fibres, the hurds is the least valuable part of the plant, chemically close to wood (Stevulova et al. 2014). Figure 1.3 shows microscopic observations of fresh transverse hem stem sections at two different magnifications showing lignin component.

Above mentioned complex structure and heterogeneous chemical composition of hemp fibres are the crucial factors that affect their specific characteristics. On such way, the chemical composition and cell wall microstructure can help to determine properties and end uses of the fibres. For instance, higher cellulose content and low cellulose MFA (microfibrils angle) correlate to high strength and stiffness and is ideal for polymer reinforcement. From the other hand, polar and hydrophilic nature of cellulose fibres, mainly as a consequence of their chemical structure, is limiting factor for the extended use of these fibres in composites (Bismarck et al. 2005). In the same time, this hydrophilic character of the fibres positively affects their biosorption properties as it will be discussed.

In plant fibres, water can be held in the form of bound water and free water. Free water can be found as liquid, liquid-vapor mixture or vapor within the fibre lumen. Bound water interacts with the hydrophilic polymers of the fibre wall. It is absorbed into the cell wall by hydrogen bonds on the accessible polar hydroxyl groups, generally termed biosorption sites. The constitutive hydrophilic polymers are classically classed into three types: (i) cellulose, (ii) hemicelluloses and pectins and (iii) lignins.

Cellulose is made of linear chains of glucose aggregated into microfibrils, including highly crystalline parts surrounding by amorphous components (also called paracrystalline cellulose). Even though cellulose has a high hydroxyl group to carbon element (OH/C) ratio, most of them are inaccessible to water molecules, due to the crystalline organization, and water molecules can gain access only into amorphous cellulose. Hemicelluloses and pectins are predominantly amorphous polysaccharides with high (OH/C) ratio and highly accessible to water molecules. Lignin is third main type of hydrophilic polymeric constituent. It is an amorphous crosslinked polymer, composed of phenolic units, that occurs in plant fibres with more or less amounts, and which has relatively low OH/C ratio when compared to polysaccharides. So the water adsorption capacity in fibre wall is mainly determined by the amount and accessibility of hydroxyl groups.

The physical and chemical states of water in plant fibres depend on the surrounding environment. In ambient air, plant fibres are constantly exchanging moisture with atmosphere. Water molecules can be found in the form of bound water in the cell wall and water vapor within the fibre lumen. When fibres are exposed to liquid water (i.e. submerged in or in direct contact with liquid water), or when freshly cut, in addition to the bound water that is saturating the cell wall, liquid water can also fill the lumen by capillary suction. Water absorption in the cell wall is the result of a combination of complex mass transfer mechanisms as in all the open porous materials. It includes water vapor diffusion within the lumen and in the air surrounding the outer surface of the fibre, adsorption on the hydroxyl groups of hydrophilic polymers and diffusion of bound water in the wall.

When bast tissues or technical fibres are submerged in water, a separation of fibres is generally observed (see Fig. 1.4) due to the leaching and also to the degradation of the gummy substances (pectins mainly) surrounding the technical and individual fibres due to the action of enzymes produced by micro-organisms. This is the mechanism observed during water retting, one of the process employed to facilitate the separation of the fibres from the stem (Di Candilo et al. 2009).

Its versatility is also another important advantage, being useable in the form of fibres, felts, powders (byproducts, fragments, shives) and oils, due to the fact that the entire plant (seeds and plant stem) is recoverable. Indeed, all parts of the hemp plant can be used for myriad applications (Ranalli 1999; Bouloc 2013; Liberalato 2003; Ranalli and Venturi 2004; Amaducci et al. 2015). Figure 1.5 depicts a

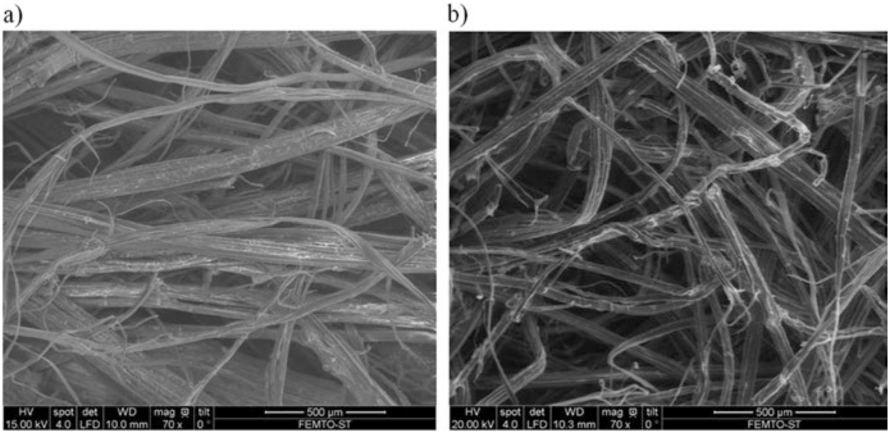

Fig. 1.4 Electron microscopy images of the fibre surface (**a**) before and (**b**) after washing by water

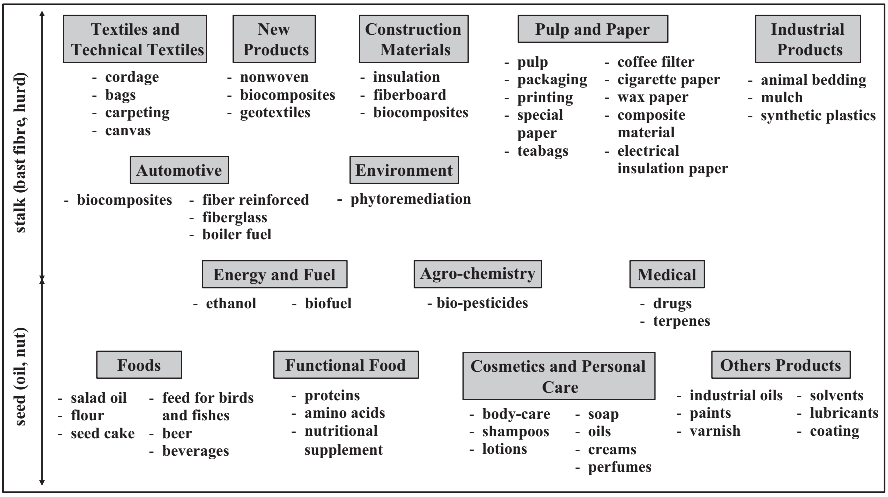

Fig. 1.5 Examples of multi-purpose hemp applications in domestic and industrial sectors

flowchart of multi-purpose hemp applications in domestic and industrial sectors. Hemp fibres and stalks are thus used for numerous applications such as in textiles (e.g. clothes, sport clothing, jeans, ropes, shoes, bags…) and pulp and paper industries (e.g. paper products, cardboard, packaging, filters), construction applications, biocomposites, agrochemistry, mulch and animal bedding. Textiles made from hemp are easy to produce, durable, versatile and biodegradable. Fibres are also more resistant to weather and ultraviolet rays than cotton and silk, and can be mixed with other materials to create clothing hybrids.

Oils are used for applications in cosmetics and body care products (e.g. soaps, shampoos, lotions, creams, perfumes…), pharmacy (e.g. to reduce acne breakouts and to improve skin conditions, interesting in dermatitis and eczema treatments), food-processing (e.g. health foods, nutraceutical products, protein isolates, beverages, animal food as feed for birds and fishes), agrochemistry, fuel (a by-product of its cultivation), paint, varnish, detergent, ink and lubricants. In cosmetology, hemp-based oils are interesting as additive due to their high concentration of fatty acids. In food chemistry, hemp is nutritious thanks to high levels of proteins, essential amino acids (rich in lanolin and linolenic acids), and other valuable elements (fibre, iron, potassium, zinc…). In China, hemp is widely used as a component for food and medicine.

Hemp can also be processed into different forms of felt, with various densities, used for example in automotive and construction applications (insulation materials) or as reinforcement in composite materials (plastic composites, biocomposites). Hemp provides all sorts of good building materials. They are durable, light weight, affordable to produce, and water-, fire- and rodent-proof. These materials are also ideal for resisting damage caused by earthquakes, floods or other natural disasters. Furthermore, the woody core part (shives) and short and entangled fibers obtained as by-product of hemp processing can be used in lower grade products such as insulation products, fiberboard and erosion control mats, while the fibrous core can be blended with lime to make strong, lightweight concrete (Ranalli and Venturi 2004; Shahzad 2012; Keijsers et al. 2013; Kostić et al. 2014).

Other innovative applications such as nanotechnology (e.g. nanomaterials with similar properties as graphene, supercapacitors and nanosheets), hemp plastic for 3D printing, biocomposites for airplanes, solar panels, bacteria-fighting fabric, bioactive metabolites such as cannabinoids, terpenoids and flavonoids, bio-pesticides, in cleaning up air and soil contamination, and biofuel production (with no sulfur emissions) opens new challenges (Citterio et al. 2003; Rehman et al. 2013). Indeed, one of the most interesting uses for hemp is in cleaning up soil contamination through phytoremediation process (Citterio et al. 2003). Hemp could be grown on soils contaminated with metals or radioactive elements. Hemp plants were shown to be effective in cleaning the soil around the site of Russia's Chernobyl nuclear disaster (Vandenhove and Van Hees 2003). Recently, they were considered for use near Fukushima. Hemp is also receiving more and more attention in water and wastewater treatment.

1.3 A Novel Application of Hemp-Based Material for Removal of Metals: A Review of the Literature

1.3.1 Biosorption, a Useful Decontamination Process for Contaminant Removal

Liquid/solid adsorption is one of the most frequently used techniques for the decontamination of aqueous media worldwide (Berefield et al. 1982; Volesky 1990; McKay 1996; Wase and Forster 1997; Cooney 1999; Crini and Badot 2010).

Adsorption is a physical-chemical method of separation in which substances present in a liquid become bound to the surface of a solid material (Yang 2003; Volesky 2004). It is a process of partition of the molecule to be eliminated, called the adsorbate, between the aqueous solution and the solid, named the adsorbent or biosorbent/sorbent, depending on the type of material used.

The technique most frequently used to study adsorption (biosorption/sorption) phenomena, not only in research laboratories but also in the industrial sector, is the static approach or batch process. This approach involves mixing a known volume of water with known concentrations of adsorbate to be processed with a given quantity of adsorbent, in previously established conditions of stirring rate, stirring duration, concentration, pH, ionic strength, and temperature. The mixture is stirred for a given contact time, then separated by a physical step involving centrifugation, sedimentation or filtration. By determining the concentrations in the supernatant and in the initial solution it is possible to calculate the efficiency of the solid material, i.e. its performance in terms of pollutant elimination (Crini and Badot 2010). This efficiency is generally compared to more conventional commercially available adsorbent systems, such as activated carbon, alumina or synthetic resins.

Batch methods are the most frequently used since they are simple, quick, and easy to set up (McKay 1996). In addition, they can be used to study the influence of a large number of parameters (e.g. pollutant concentration, pH, ionic strength, temperature…) on the efficiency of the biosorbent, while easily obtaining reproducible results. For instance, by varying the contact time, the quantity of biosorbent or the concentration of the pollutant(s), it becomes possible to experimentally determine various isotherms and biosorption/adsorption kinetics and to model the process.

Modeling based on equations with 2 or more unknowns (see in particular the reviews of McKay and Al Duri (1989) and Ho et al. (2002) and the books of Berefield et al. (1982), Treybal (1987), Tien (1994), Volesky (1990, 2004) and McKay (1996)) provide information on adsorption mechanisms and enables interpretation depending on the conditions used in the batch. In industrial applications, batch techniques are used for example to "neutralize" abnormal peaks in the pollutant load at the entry to the water treatment plant, to recover economically interesting substances, such as noble metals, or to facilitate the production of denser sludge (Crini and Badot 2010; Sharma 2015).

Recently, the development of hemp-based materials as biosorbents is an expanding field in the area of pollutant removal. This is an interesting challenge because the majority of commercial polymers are derived from petroleum-based raw materials using processing chemistry that is not always safe or environmental friendly. Today, there is growing interest in developing natural low-cost alternatives to synthetic polymers. Hemp could be a promising alternative. Commercial hemp-based products are usually offered as powders (byproducts), fibres, or felts (Fig. 1.6).

To characterize hemp-based materials, numerous techniques such as Fourier transform infra-red spectrophotometry (FT-IR), energy-disperse X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), solid-state nuclear magnetic spectroscopy (NMR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), contact angle measurement, and scanning electron microscopy

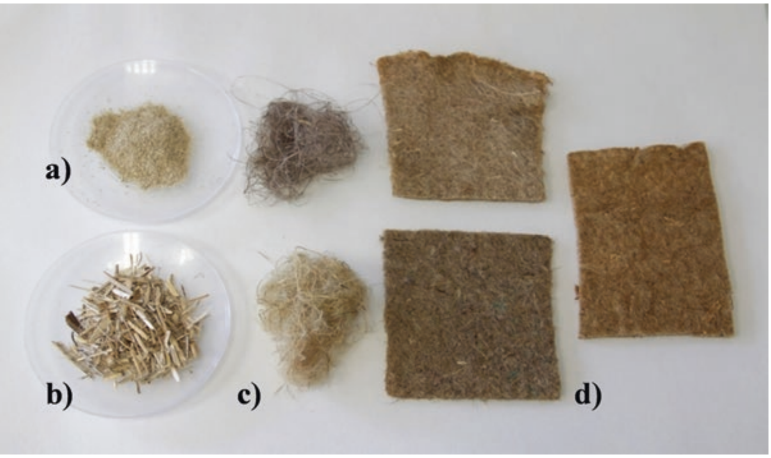

Fig. 1.6 Pictures of the hemp-based materials used as biosorbents: (**a**) sawdust, (**b**) hurds (shives), (**c**) fibres and (**d**) felt

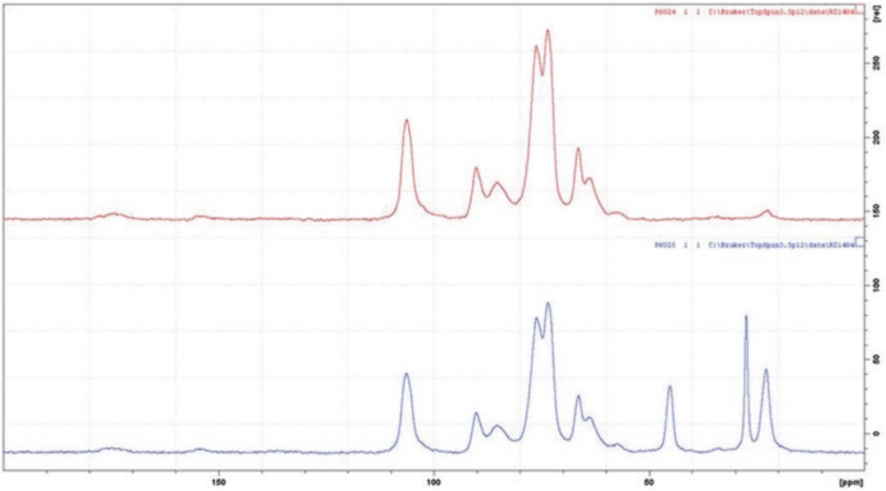

Fig. 1.7 Comparison of the ^{13}C NMR spectra of two felts containing hemp fibres without (in red) and with (in blue) the presence of an additive (10% of polypropylene)

(SEM) can be used. For example, NMR is a powerful tool for hemp characterization. In Fig. 1.7, the solid-state ^{13}C-NMR spectra show the peaks of disordered cellulose in the range 50 and 110 ppm. These broad signals are attributable to the glucopyranose unit of the cellulose structure of the raw fibres. The spectrum of felt containing 10% of polypropylene (PP, used as a matrix to reinforce fibres; typical applications on these composites include automotive interior substrates, furniture and other consumer products) clearly shows three additional peaks between 20 and 50 ppm due to PP.

1.3.2 Hemp-Based Materials as Biosorbents

Hemp-based biosorbents have been proposed for applications in water treatment, in particular for metal ion removal from aqueous synthetic solutions. Table 1.3 list some of the researchers whose results are discussed in this chapter and the pollutants they investigated.

The interaction between hemp and metal ions has been intensively investigated by Păduraru and co-workers using batch and fixed-bed column studies (Tofan and Păduraru 1999, 2000, 2004; Tofan et al. 2001a, b, 2009, 2010a, b, c, 2013, 2015, 2016a, b; Păduraru and Tofan 2002, 2008). These authors studied the capacity and mechanism of hemp fibres in removing different metals (i.e. Cd, Co, Cr, Cu, Pb, Ag and Zn) from aqueous monometallic solutions. Before use raw hemp fibres, wastes from the textile industry, were purified by boiling for 4 h in a solution containing soap and soda ash, followed by washing several times with water, and drying in an oven at 45 °C. Their investigations clearly indicated, for the first time, that hemp fibres had a high capacity for metals adsorption and were very useful for the treatment of wastewaters. Between 7.5 and 13.5 mg of metal can be eliminated per gram of fibre, depending on the type of metal. For example, the monolayer adsorption capacity for Cu(II) Cr(III), Cd(II) and Ag(I) was 9.0735, 4.0006, 2.5909, and 1.2253 mg/g, respectively. In all the experimental conditions tested, the order of affinity was the same: Cu > Cr > Cd > Ag (Păduraru and Tofan 2002). The results also reported that hemp waste materials were efficient in removing Co (II), Pb(II) and Zn(II) from diluted and concentrated aqueous solutions.

In another work, the authors evaluated the thermodynamic feasibility of Pb(II) biosorption process on hemp by calculating thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS). Evaluation of these parameters gives an insight into the possible mechanisms of adsorption. At all studied temperatures (between 277 and 333°K), the ΔG values were negative, showing the feasibility and spontaneous nature of Pb biosorption on fibres (Tofan et al. 2010b). ΔG was estimated from the equilibrium adsorption data under the assumption that the adsorption of a pollutant was reversible and that an equilibrium condition was established in the batch system. The positive values of ΔH indicated that Pb biosorption was an endothermic process, favored by temperature increase. The positive value of ΔS suggested an increased randomness at the interface of hemp-solution and high affinity of the hemp fibres for Pb ions. Kinetics were also rapid and could be described by a pseudo-first order model. The Langmuir model was found to be the most appropriate to describe the adsorption process in all the case of metals studied.

For Co removal, the authors showed that the biosorption capacity of the fibres used in column (15.44 mg/g) performed better than that of the batch system (13.58 mg/g) (Tofan et al. 2013). They explained this result by the fact that the gradient concentration decreased with time in batch experiments while it continuously increased in the interface of the biosorption zone in the column. The Langmuir model better described the Co(II) adsorption process on hemp fibres in comparison

Table 1.3 Authors of recent research on pollutant removal by hemp-based materials

Corresponding author	Country	Hemp form	Hemp material	Pollutant(s)	Experimental protocol	Reference(s)
Crini G.	France	Fibres, felt, shives	Raw	Al, Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, Zn	Batch, filtration	Loiacono et al. (2017a, b, c); Bugnet et al. (2017a, b)
Gryglewicz G.	Poland	Stem	Carbonized	Atrazine	Batch	Lupul et al. (2015a, b)
Holub M.	Slovakia	Shives	Raw	Cu	Batch	Balintova et al. (2014)
Kostić MM.	Serbia	Fibres	Raw, modified	Cd, Pb, Zn	Batch	Kostić et al. 2003, 2008, (2010); Pejić et al. 2008, 2009, 2011; Milanovic et al. (2012); Vukčević et al. (2014a);
Kyzas GZ.	Greece	Shives	Raw	Ni	Batch	Kyzas et al. (2015)
Mintova S.	France	Fibres	Composite	Benzene, toluene, chlorobenzene		Zou et al. (2012)
Păduraru C.	Romania	Fibres	Raw, modified, impregnated	Ag, Cd, Co, Pb, Zn	Batch, column	Tofan and Păduraru (1999), (2000), (2004); Păduraru and Tofan (2002), (2008); Tofan et al. (2001a, b), (2009), (2010a, b, c), (2013), (2015), (2016a, b)
Rezić I.	Croatia	Fibres	Raw	Al, Cr, Cu, Fe, Zn	Batch	Rezić 2013
Vukčević MM.	Serbia	Fibres	Carbonized	Pb, pesticides	Batch, solid-phase extraction	Vukčević et al. 2012, 2014b, 2015
Yang R.	China	Stem	Carbonized	CO_2		Yang et al. (2012)

with the Freundlich model. This finding complied with the results of fixed-bed studies which emphasized that the optimal solution for describing the behavior of the investigated hemp bed column was provided by the Thomas model.

The authors explained their results by the fact that the main mechanism was chemisorption of the metal ion via the formation of electrostatic interactions, complexation and ion-exchange. Indeed, strong bonding of metal ions by carboxylic (present in hemicelluloses, pectin and lignin), phenolic (lignin and extractives), carbonyl (lignin) and hydroxyl (polysaccharides) groups were responsible of the adsorption through chemisorption.

Practical use of hemp has been mainly confined to the unmodified forms using spiked metal solutions. Although raw hemp fibres were useful for treating contaminated solutions, it may be advantageous to chemically modify hemp, e.g. by grafting reactions on cellulose macromolecules. Indeed, from the polymer chemist's point of view, the chemical substitution of cellulose offers enormous challenges. This chemical modification is interesting because, in polysaccharide chemistry, it is well-known that the grafting of ligands can improve their adsorption properties (Crini 2005; George et al. 2015). Cellulose present an interesting reactivity due to the presence of numerous hydroxyl groups located on carbons 2,3 and 6 on each glucose residue of the cellulosic chains. In general, grafting of ligands resulted in fibres with reduce surface polarity and improved thermal and chelating properties. However, this chemical treatment can directly alter the surface and bulk chemical compositions of natural fibres. In addition, chemical treatment can also result in removal of significant amounts of components (cellulose, hemicellulose…), and therefore, it is important to characterize the modified fibres (Crini 2005; George et al. 2015).

In order to improve the performance of raw hemp fibres, Păduraru's group proposed a chemical treatment using β-mercaptopropionic acid as chelating agent. This functionalization permitted to introduce sulphydryl functional groups onto surface fibres (Tofan and Păduraru 2004). A systematic study on the Ag(I), Cd(II) and Pb(II) removal onto these raw and modified fibres was realized under similar experimental batch conditions. For raw and modified hemp, the adsorption capacities were 1.2253 and 10.75 mg/g for Ag(I) and 2.5909 and 14.05 for Cd(II), respectively. This clearly demonstrated the important role of sulphydryl chelating groups. However, for Pb(II), the adsorption capacity decreased, but no explanation was given.

Tofan et al. (2015) studied Cr(III) removal from aqueous solutions by adsorption in a fixed bed column filled with alizarin S impregnated hemp fibres. The breakthrough time and saturation time decreased from 110 to 80 min and from 300 to 160 min, respectively, with the increase in the initial concentration from 13.00 mg/L to 26.14 mg/L. The increase in the initial concentration from 13.00 to 26.14 mg/L increased the breakthrough adsorption capacity from 4.178 to 6.163 mg/g and decreased the percentage of Cr(III) removal from 73.57% to 62.64%. The breakthrough predictions by Thomas model were found to be very satisfactory. The hemp impregnated with alizarin S column removed >90% of Cr(III) from three samples of synthetic wastewaters containing different amounts of other heavy metal ions. All these findings were significant for the future development of hemp materials for metal removal from industrial effluents.

Polysaccharide-based biosorbents present considerable advantage including their high adsorption capacity and selectivity but also the facility of regeneration. The regeneration of saturated hemp biosorbent for non-covalent adsorption can be easily achieved by using an acid solution as the desorbing agent. In a recent work, batch studies on desorption and multiple adsorption-regeneration cycles for Zn removal by natural hemp fibres have been carried out by Tofan et al. (2016a). The best desorption results were performed in acidic medium, where the protons in solution replaced the Zn ions on the loaded hemp. The efficiency of Zn desorption with 0.1 M hydrochloric acid was higher than that achieved using sulfuric acid of the same concentration. The amount of Zn desorbed by 0.1 M HCl, 0.1 M H_2SO_4, and 5% NaCl increased sharply in the first 15–20 min of the process, attaining values that subsequently stay almost constant (for 0.1 M HCl) or slightly increase (for 0.1 M H_2SO_4 and 5% NaCl). The adsorptive potential of the tested hemp remained almost unchanged after three cycles of adsorption-desorption of Zn from solutions. This showed both the chemical stability of the biosorbents and reproducibility of the values. The results of this study were also important in order to demonstrate that regenerated hemp could be used for Zn metal removal from water sources without the threat of the adsorbent becoming another source of Zn pollution for the environment. From their numerous results, Păduraru's research group concluded that hemp and its derivatives may be a useful and promising biosorbent in water and wastewater treatment.

Kostić's group also published a series of papers on the ability of hemp to act as an effective biosorbent for the removal of metals from aqueous solutions (Pejić et al. 2009, 2011; Kostić et al. 2010, 2014; Vukčević et al. 2014a). Their results clearly demonstrated that hemp in fibre form had a high affinity for Cd, Zn and Pb, in accordance with the results published by Păduraru's group. In order to obtain better adsorption capacities, these authors also proposed to modify fibres by simple and inexpensive alkaline and oxidative treatments, causing gradual removal of either hemicelluloses or lignin and altering fibre structure. Observed increase in adsorption properties was ascribed not only to the decrease of lignin or hemicelluloses content, but also to the increased fibre fibrillation, surface peeling and roughness increase, which affects fibre specific surface area. Besides changes in fibre surface and structure, applied chemical treatments affects the amount and accessibility of functional groups incorporated in the fibre structure. Both chemical treatments used remove the accompanying components from the fibre surfaces, leading to the liberation of the functional groups, and increasing their amount. Since functional groups act as active sites for adsorption, chemical modification efficiently improve the adsorption properties of this biosorbent.

Similar materials and results were published by Kyzas's group for the removal of Ni from diluted and concentrated solutions (Kyzas et al. 2015). They noted that adsorption capacities between 160 and 206 mg of Ni per gram of material were achieved. The differences in the degree of performance were mainly attributed to the hemp form used (fibres or shives). After chemical modification (by sodium hydroxide or citric acid), the respective capacities were improved to 237 and 242 mg/g, respectively. A characterization study (FT-IR, XRD, SEM, EDX, crystallinity, and cellulose content) demonstrated the surface morphology of the modified hemp along with some possible biosorption interactions between them and Ni. At least ten sequential reuse cycles revealed the reuse potential of the modified hemp-based materials. The authors concluded that hemp fibres were a promising material for the removal of Ni from single ion solution mainly through chemical interactions.

Balintova et al. (2014) studied the removal of Cu onto raw hemp shives and treated hemp by NaOH. This treatment permitted to remove either hemicelluloses or lignin. However, no significant differences were obtained. The adsorption capacities for raw and treated hemp were 3.91 and 4.45 mg/g, respectively (conditions: dosage = 1 g/100 mL; initial Cu concentration = 50 mg/L, initial pH = 4, and contact time = 24 h). These performances were compared with those of commercial sorbents and similar adsorption capacities were obtained. The authors concluded that hemp was a useful non-conventional biosorbent for copper removal from acidic environment.

New hemp fibres derivatives in environmental, pharmaceutical and biomedical fields to reduce metal pollution and to prevent bacteria growth were proposed by Cassano et al. (2013). The materials were prepared *via* esterification of hemp with 2-benzyl-4-chlorophenol (a germicide agent), that was covalently coupled to cellulose backbone of fibres by a heterogeneous process. Carboxylated materials were also synthetized. FT-IR spectroscopy was used to obtain qualitative information on hemp fibres after derivatization. The materials were also characterized using differential scanning calorimetry. The new materials possessed an excellent *in vitro* antibacterial activity in inhibiting *Staphylococcus aureus* and *Pseudomonas aeruginosa* growth and also exhibited interesting adsorption capacities toward Cd present in aqueous solutions. However, the performances for Cd removal were dependent on pH solution. In addition, their results showed that carboxylated fibres had a higher chelating capacity than the esters derivatives.

All these studies demonstrated that hemp could be a viable biosorbent for environmental applications. However, these previously published works focused on the removal of only one or two metals at a time using hemp in fibre form. Recently, Crini's group proposed the use of a hemp-based material in felt form to treat polymetallic aqueous solutions, containing a mixture of six metals, namely Cd, Co, Cu, Mn, Ni and Zn (Bugnet et al. 2017a, b; Loiacono et al. 2017a, b, c). These six metals were studied due to their common presence in discharge waters from the metal industry. Adsorption experiments showed that this non-conventional biosorbent exhibited interesting adsorption capacities. In 10 min, 1 g of material was able to remove 7.4 mg of metals (total = 2.14 (Cu) + 1.69 (Cd) + 1.3 (Zn) + 0.93 (Ni) + 0.84 (Co) + 0.5 (Mn)) at a concentration of 25 mg/L for each metal present in 100 mL of solution. The results were also almost independent of pH between 4 and 6. The following order was obtained: Cu > > Cd > Zn > Ni ~ Co > Mn, while, in single solution, the order was Cd > Cu > Zn > Co ~ Ni > Mn. Figure 1.8 shows material before and after batch, indicating the coloring of the felt after metal removal. This was the

Fig. 1.8 Hemp felt before (*left*) and after adsorption (*right*) in a solution containing a mixture of six metals

first report on the removal of metals from polycontaminated aqueous solutions by hemp-based material in felt form (Loiacono et al. 2017a).

In another work, in order to ameliorate its adsorption properties towards the same six cationic metal species, the authors proposed to modify chemically the raw felt (Loiacono et al. 2017b). The felt was treated with a mixture of maltodextrin (MALTO), an oligosaccharide obtained from starch hydrolysis, and 1,2,3,4 butanetetracarboxylic acid (BTCA) used as cross-linking agent. This chemical treatment provided ion-exchange properties to the material by introducing carboxylic groups on hemp fibres. Potentiometric titration data revealed that the quantity of carboxylic groups was increased from 0 ± 0.09 meq/g for raw hemp to 0.67 ± 0.03 meq/g for modified hemp. A weight increase of 35% of modified felt confirmed that a cross-linking reaction occurred by esterification between BTCA carboxylic groups and MALTO hydroxyl groups on the one hand, and cellulose hydroxyl group of hemp fibres on the other hand. The modified material was also characterized using solid state NMR technique, SEM and EDX. For the total metal load, the adsorption capacity of modified hemp was determined to be twofold higher than that of non-modified felt in all conditions studied. The carboxylic groups present in BTCA were responsible for metal ion binding through chemisorption mechanism (e.g. complexation, electrostatic interactions, ion-exchange) and their presence in modified material positively influenced its performance. Nevertheless, in the multi-component system studied, strong competition prevails among metallic species for the binding sites. For modified hemp, the following order was obtained: Cu > Cd > Zn > Mn > Ni ~ Co, while, in single solution, the order was Cd > Cu ~ Zn ~Mn > Ni ~ Co. Interesting results were also obtained for real effluents containing the same six metals (Loiacono et al. 2017a). Crini's group concluded that raw and modified hemp-based materials in felt form can be utilized as an interesting tool for the purification of metal-containing wastewater because of their outstanding adsorption capacities and easy of use.

1.3.3 Composite Materials

Zou et al. (2012) proposed a hemp-zeolite composite material obtained by a simple procedure for the removal of aqueous aromatic organic pollutants (benzene, toluene and chlorobenzene). This new biosorbent, prepared *via in situ* crystallization of zeolite L nanocrystals on hemp fibres, exhibited a high removal degree (above 80%). The order obtained was: chlorobenzene > benzene > toluene. The composite also presented high flux of 19.9, 19.3 and 20.9 kg/m^2 h for chlorobenzene, benzene and toluene, respectively. The results showed that the removal of the composite was much higher in respect to only hemp fibres (48%). The better performance of the composite was explained by an improved absorption ability of the zeolite-hemp material coupled with higher dynamic separation efficiency. In addition, this new material possessed high mechanical and chemical stabilities before and after water purification, demonstrated by XRD and SEM experiments. The authors concluded that, both materials (zeolite L and hemp) used for preparation of the composite were environmentally friendly, and made the adsorbents particularly appropriate for water purification.

1.3.4 Activated Carbons from Hemp

Amongst all the commercial adsorbents materials proposed, activated carbon (AC) is the most popular adsorbent for the removal of pollutants from the wastewater (Ramakrishna and Viraraghavan 1997; Derbyshire et al. 2001; Babel and Kurniawan 2003). The world demand of AC is steadily increasing due to its high performance in many purification and separation processes. The most commonly used raw precursors are wood, coal, coconut shells and some commercial polymers. However, the use of carbons based on relatively expensive starting materials is unjustified for most pollution control applications (Streat et al. 1995). This had led many researchers to search for more economic carbon-based adsorbents from non-conventional resources. Indeed, certain waste products from various industrial by-products (wastes generated during lactic acid fermentation from garbage, waste carbon slurries…), city wastes (PET bottles, waste tires, waste newspaper…), and agricultural operations (bagasse, date pits, corn cob…), including lignocellulosic and wood by-products (pinewood, sawdust, lignin, sugarcane…), represent potentially economical alternative material to prepare activated carbon. These waste materials have little or no economic value and often present a disposal problem. Therefore, there is a need to valorize these low-cost by-products. So, their conversion into activated carbon would add its economic value, help reduce the cost of waste disposal, and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbons as reported by Oliveira and Franca (2008).

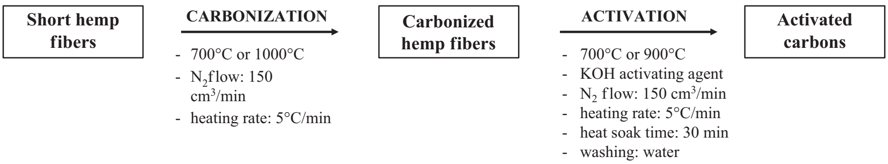

Fig. 1.9 Scheme of activated carbons production from hemp-based wastes. (Adapted from Vukčević et al. 2015)

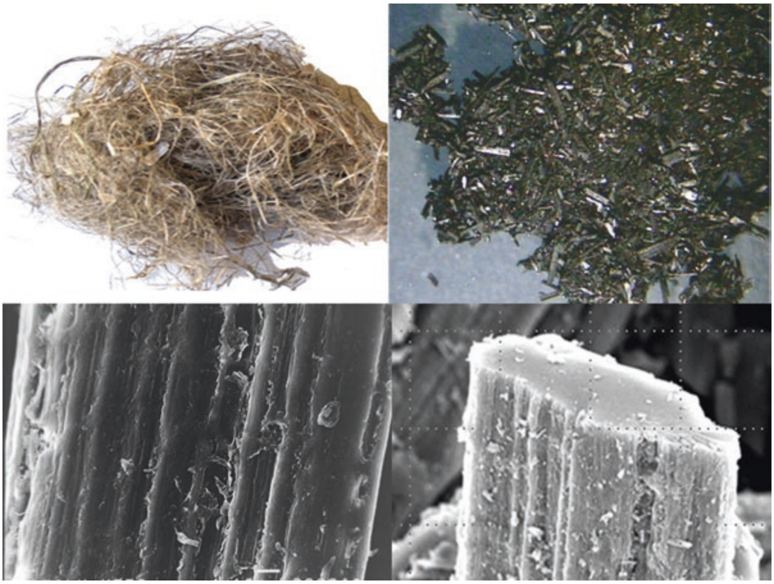

Fig. 1.10 Short hemp fibers before (left) and after (right) carbonization. (Adapted from Vukčević et al. 2015)

Although hemp has many practical applications, its transformation generates a high proportion of waste. Development of recycling processes of such biomass waste is generating great interest, and the production of activated carbon could be an appropriate solution. There are several reports on the production of activated carbon from hemp-based materials (Rosas et al. 2009; Vukčević et al. 2012, 2014b, 2015; Yang et al. 2011, 2012; Sun et al. 2013; Wang et al. 2015; Lupul et al. 2015a, b).

An important work on this topic was done by Vukčević and co-workers (Vukčević et al. 2012, 2014b, 2015). They proposed activated carbon from waste short hemp fibres as adsorbent for metal ions and pesticides removal. Activated carbon with high specific surface area (up to 2192 m^2/g) and microporous structure were prepared by carbonization of waste hemp fibres and activation with KOH. Figure 1.9 depicts the synthesis procedure used while Fig. 1.10 shows hemp fibers before and after carbonization. These non-conventional carbons exhibited high adsorption properties toward metals such as Pb and 15 pesticides including atrazine, simazine, malathion and linuron. Their results showed that the adsorption capacities of an activated carbon depend on the history of its preparation and treatment conditions such as pyrolysis temperature and activation time. The best efficiency was achieved with samples with the highest specific surface area and the amount of surface oxygen groups. Many other factors can also affect the adsorption capacity in the same adsorption conditions such as surface chemistry (heteroatom content), surface charge and pore structure (Vukčević et al. 2015). In general, specific surface area and pore size distribution are dominant factors of influence in the case of physical adsorption of nonpolar organic molecules, while adsorption of inorganic and polar organic compounds is also influenced by surface chemistry of carbon adsorbent.

The specific adsorption mechanisms by which the adsorption of pollutant takes place on these non-conventional carbons are still not clear. This is because of the fact that adsorption onto carbon adsorbent is usually complex process that may occur through the mechanism of physisorption (e.g. hydrophobic interactions, electrostatic attraction…), and chemisorption (e.g. surface complexation ion-exchange…). For example, metal ions adsorption on carbon surface can be considered as physisorption if it occurs through the mechanism of electrostatic attraction between metal ions and graphene layer's π electrons. Furthermore, oxygen groups present on the carbon surface might behave as ion-exchange sites for the retention of metal ions. From the other hand, surface functional groups can also act as active chemisorption sites, since oxygen in the surface functional groups possesses a pair of lone electrons (Lewis base) and therefore may coordinate with electron deficient metal ions (Lewis acid). In the case of organic molecules, the surface chemistry of the carbon has a great influence on adsorption, both in the case of electrostatic and non-electrostatic interactions. Electrostatic interactions, which can be either attractive or repulsive, strongly depend on the charge densities of both the carbon surface and the adsorbate molecule, as well as of the ionic strength of the solution. The non-electrostatic interactions, which are always attractive, include van der Waals forces, hydrophobic interactions and hydrogen bonding. Aromatic compounds can be physisorbed on carbon materials essentially by dispersion interactions between the π electrons of the aromatic ring and those of the graphene layers. The presence of aromatic rings, as well as a branched substituent on the aromatic ring, increased the level of organic compound adsorption. On the other hand, electron-acceptor surface groups, present on the carbon adsorbent surface, can withdraw π electrons from the graphene layers, decreasing the dispersive interactions and leading to reduced adsorption. On the base of obtained results, Vukčević and co-workers concluded that application of hemp wastes as new solid-phase extraction adsorbent was a procedure of choice for analysis of pesticides in water samples with recoveries comparable or even better than those obtained with commercial cartridges.

Similar interesting results were published by Lupul et al. (2015a, b). These authors proposed adsorption of atrazine on hemp stem-based activated carbon with different surface chemistry using potassium hydroxide as activating agent. The presence of oxygen and nitrogen functionalities on the carbon surface was found to be undesirable for atrazine adsorption. The superior adsorbent was obtained by heat treatment of activated carbon in an inert atmosphere at 700 °C, resulting in a very high adsorption capacity due to its enhanced hydrophobicity. Adsorption capacities were in the range 169–227 mg/g depending on the chemical treatment (Lupul et al. 2015a). The adsorption of atrazine on the studied carbons mainly involves π-π dispersive interactions between the atrazine π electron ring and the π electron of graphene layers of carbon. The Langmuir-Freundlich and Langmuir models gave a better fit for equilibrium isotherms compared with the Freundlich model. Modeling also showed that the atrazine adsorption process was controlled by an intraparticle diffusion mechanism into small micropores with a significant contribution from film diffusion.

Rosas et al. (2009) proposed hemp-based activated carbon fibres by chemical activation with phosphoric acid at different carbonization temperatures and impregnation rates. Surface properties of the fibres were significantly influenced by the activation temperature and the impregnation ratio. An increase of either of these parameters produced a high development of the porous structure of the fibres. Activated carbon fibres with apparent surface area of 1350 m^2/g and mesopore volume of 1.25 cm^3/g were obtained at 550 °C with an impregnation ratio of 3. The fibres presented a high oxidation resistance due to the presence of phosphorus compounds on the carbon surface. The oxidation resistance results suggested that C-O-PO_3 and mainly C-PO_3 and C-P groups act as a physical barrier, blocking the active carbon sites for the oxidation reaction. The authors concluded that the use of hemp residues to produce activated carbon was very feasible and presented the advantage of the potential revalorization of a residual material. Williams and Reed (2003, 2004), studying the preparation of activated carbon fibres by physical activation with steam and chemical activation with $ZnCl_2$ of hemp fibres, previously published a similar conclusion.

Yang and co-workers (Yang et al. 2011, 2012; Wang et al. 2015) also prepared activated carbon fibres using hemp bast and a simple method consisting in a phosphoric acid activation at different temperatures. These carbons were then used as sorbents for dye removal. The textural properties of the activated carbon fibres were found to be strongly dependent on the activation temperature. Activated carbon fibres exhibited narrow pore size distributions with maxima in the micropore and small mesopore regions. BET surface area, total pore volume, micropore volume and mesopore volume increased with the increase of activation temperature up to 450 °C and then decreased with further heating, and a sample with maximum surface area of 1142 m^2/g and total pore volume of 0.67 cm^3/g was obtained. Phosphoric acid facilitated the conservation of porous structure in the precursor fibres, led to the creation of tremendous porosity, and resulted in various phosphore-containing functional structures on the surface and in the bulk phase of the resultant samples. The adsorption of Acid Blue 9 as guest compound on the sample could be favorably described by Langmuir isotherm (q_{max} = 28.75 mg/g), and the adsorption kinetics was found to be well fitted by the intraparticle diffusion model. Yang et al. (2011) concluded that hemp bast was a suitable low-cost byproduct for use in the production of activated carbon for dye removal, thus contributing for the implementation of sustainable development in both the hemp production and environmental protection.

In another recent work, the same authors presented a new route for high-value-added utilization of hemicellulose extracted from hemp stem to prepare well-shaped carbon spheres (Wang et al. 2015). Activated carbon with high large surface area up to 2192 m^2/g were prepared by an improved low-temperature hydrothermal carbonization method and KOH activation. A pre-carbonization strategy before activation was also employed to keep activated carbon in perfectly spherical morphology even at a high KOH/carbon ratio 5/1. The characterization of activated carbon demonstrated that the surface area, micropore volume, mesopore volume and surface oxygen content all increases with increasing KOH/carbon ratio. Activated carbon exhibited excellent electrochemical performance due to abundant micropores and plentiful oxygen functionalities, and showed good adsorption capacities of CO_2 and CH_4 at ambient pressure and 0 °C. The authors concluded that activated carbon converted from inexpensive hemp stem could be potential materials for CO_2 and CH_4 storage (Wang et al. 2015).

Sun et al. (2013) prepared mesoporous activated carbon using hemp stem as precursors by air-phosphoric acid activation method. The crystallite size of carbon was small, and its pores was larger. The phosphoric acid solution concentration had a signification effect on pore structure and adsorption property of activated carbon. The mesopore activated carbon attained at phosphoric acid solution concentration of 50% exhibited a maximum BET specific surface area of 1351 m^2/g, total pore volume of 1.21 cm^3/g, mesopore pore volume of 0.90 cm^3/g and a mesopore fraction of 74.4%. The resulting carbon had smaller crystal size, developed pore structure, wider pore size distribution.

1.4 Conclusion

The past decade has seen an intense interest in hemp-based biosorbents for metal ion removal from aqueous synthetic solutions. Many biosorbents in raw, modified or carbon forms could be used for this purpose. Outstanding removal capacities for metals were reported. Table 1.4 presents a summary of some of the highest adsorption capacities reported (the q_{max} values are expressed in mg of pollutant per g of biosorbent). Which material is better? There is no direct answer to this question because the biosorption capacity depends on the residual concentration of the pollutant in the solution. The uptake by two materials must be then compared only at the same equilibrium concentration. In addition, the comparison of performance also depends on several other parameters related to the solution and analytical method used. Thus, a direct comparison of data obtained using different materials is not possible since experimental conditions are not systematically the same. However, the authors believe that hemp can compete with conventional adsorbents for wastewater treatment. Although interesting works at the stage of laboratory-scale study has been done, future research needs to look into some of the following: (i) it is necessary to continue to search for and select the most promising types of

Table 1.4 Adsorption capacities (q_{max} in mg/g) for various pollutants using hemp-based biosorbents

Metal	Type of biosorbent	Technique	Biosorbent dosage	pH	Contact time	q_{max}	Reference(s)
Ag(I)	Raw fibres	Batch		5		1.2253	Tofan and Păduraru (2000); Păduraru and Tofan (2002)
Ag(I)	Sulphydryl fibres	Batch	0.25 g/25 mL	5.1	24 h	10.75	Tofan and Păduraru (2004)
Al(III)	Raw felt	Batch	0.25 g/100 mL	5	1 h	6.38	Bugnet et al. (2017b)
Al(III)	Carboxylated felt	Batch	0.25 g/100 mL	5	1 h	10.15	Loiacono et al. (2017b)
Cd(II)	Raw fibres					2.5909	Tofan and Păduraru (2000); Păduraru and Tofan (2002)
Cd(II)	Sulphydryl fibres	Batch	0.25 g/25 mL	5.75	24 h	14.05	Tofan and Păduraru (2004); Tofan et al. (2009)
Cd(II)	Fibres treated with NaOH	Batch	0.5 g/200 mL	5.5	2 h	0.078[a]	Pejić et al. (2009)
Cd(II)	Fibres treated with $NaClO_2$	Batch	0.5 g/200 mL	5.5	2 h	0.039[a]	Pejić et al. (2011)
Cd(II)	Raw felt	Batch	0.25 g/100 mL	5	1 h	27.47	Loiacono et al. (2017a); Bugnet et al. (2017b)
Cd(II)	Carboxylated felt	Batch	0.25 g/100 mL	5	1 h	129.87	Loiacono et al. (2017b)
Co(II)	Raw fibres	Batch	0.25 g/50 mL	4.5–5	6 h	13.58	Tofan et al. (2013)
Co(II)	Raw fibres	Column		4.5–5		15.44	Tofan et al. (2013)
Co(II)	Raw felt	Batch	0.25 g/100 mL	5	1 h	7.99	Loiacono et al. (2017a); Bugnet et al. (2017b)
Co(II)	Carboxylated felt	Batch	0.25 g/100 mL	5	1 h	37.88	Loiacono et al. (2017b)
Cr(III)	Raw fibres	Batch				4.006	Tofan and Păduraru (2000); Păduraru and Tofan (2002)
Cr(III)	Fibres impregnated with Alizarine S	Batch				8.632	Tofan et al. (2001b)
Cr(III)	Fibres impregnated with Alizarine S	Column				6.163	Tofan et al. (2015)

(continued)

Table 1.4 (continued)

Metal	Type of biosorbent	Technique	Biosorbent dosage	pH	Contact time	q_{max}	Reference(s)
Cr(III)	Raw felt	Batch	0.25 g/100 mL	5	1 h	6.53	Loiacono et al. (2017a); Bugnet et al. (2017b)
Cr(III)	Carboxylated felt	Batch	0.25 g/100 mL	5	1 h	15.54	Loiacono et al. (2017b)
Cu(II)	Raw fibres	Batch				9.0735	Păduraru and Tofan (2002)
Cu(II)	Bleached fibres impregnated with α-benzoinoxime	Batch				8.0378	Tofan and Păduraru (1999); Tofan et al. (2001a)
Cu(II)	Fibres impregnated with α-benzoinoxime	Batch				13.8072	Tofan and Păduraru (1999); Tofan et al. (2001a)
Cu(II)	Shives	Batch	1 g/100 mL	4	24 h	3.91	Balintova et al. (2014)
Cu(II)	Treated shives with NaOH	Batch	1 g/100 mL	4	24 h	4.45	Balintova et al. (2014)
Cu(II)	Raw felt	Batch	0.25 g/100 mL	5	1 h	14.64	Loiacono et al. (2017a); Bugnet et al. (2017b)
Cu(II)	Carboxylated felt	Batch	0.25 g/100 mL	5	1 h	63.32	Loiacono et al. (2017b)
Fe(II)	Raw felt	Batch	0.25 g/100 mL	5	1 h	7.87	Loiacono et al. (2017a)
Fe(II)	Carboxylated felt	Batch	0.25 g/100 mL	5	1 h	23.93	Loiacono et al. (2017b)
Mn(II)	Raw felt	Batch	0.25 g/100 mL	5	1 h	4.55	Loiacono et al. (2017a); Bugnet et al. (2017a, b)
Mn(II)	Carboxylated felt	Batch	0.25 g/100 mL	5	1 h	44.25	Loiacono et al. (2017b)
Ni(II)	Treated hemp fibres	Batch	0.1 g/100 mL	5	24 h	242	Kyzas et al. (2015)
Ni(II)	Treated hemp shives	Batch	0.1 g/100 mL	5	24 h	237	Kyzas et al. (2015)
Ni(II)	Hemp fibres	Batch	0.1 g/100 mL	5	24 h	206	Kyzas et al. (2015)
Ni(II)	Hemp shives	Batch	0.1 g/100 mL	5	24 h	160	Kyzas et al. (2015)
Ni(II)	Raw felt	Batch	0.25 g/100 mL	5	1 h	7.85	Loiacono et al. (2017a); Bugnet et al. (2017a, b)

Ni(II)	Carboxylated felt	Batch	0.25 g/100 mL	5	1 h	40.98	Loiacono et al. (2017b)
Pb(II)	Fibres treated with NaOH	Batch	0.5 g/200 mL	5.5	2 h	0.078[a]	Pejić et al. (2009)
Pb(II)	Fibres treated with $NaClO_2$	Batch	0.5 g/200 mL	5.5	2 h	0.037[a]	Pejić et al. (2011)
Pb(II)	Raw fibres	Batch	0.25 g/50 mL	5	24 h	25.05	Tofan et al. (2010b, c)
Pb(II)	Sulphydryl fibres	Batch	0.25 g/25 mL	3.03	24 h	23	Tofan and Păduraru (2004)
Pb(II)	Carbonized fibres	SPE	0.2 g/50 mL		2 h	15.89–24.18	Vukčević et al. (2014b)
Zn(II)	Fibres treated with NaOH	Batch	0.5 g/200 mL	5.5	2 h	0.078[a]	Pejić et al. (2009)
Zn(II)	Fibres treated with $NaClO_2$	Batch	0.5 g/200 mL	5.5	2 h	0.038[a]	Pejić et al. (2011)
Zn(II)	Raw fibres	Batch	0.25 g/50 mL	5	24 h	21.047	Păduraru and Tofan (2008)
Zn(II)	Raw fibres	Batch	0.5 g/200 mL	5.5	2 h	8.3	Vukčević et al. (2014a)
Zn(II)	Raw felt	Batch	0.25 g/100 mL	5	1 h	10.59	Loiacono et al. (2017a); Bugnet et al. (2017b)
Zn(II)	Carboxylated felt	Batch	0.25 g/100 mL	5	1 h	68.5	Loiacono et al. (2017b)
CO_2	Carbonized fibres					5.62[a]	Wang et al. (2015)
Atrazine	Carbonized fibres treated N_2	Batch	50 mg/100 mL		1 h	263	Lupul et al. (2015a)
Atrazine	Carbonized fibres	Batch	50 mg/100 mL		1 h	227	Lupul et al. (2015a)
Atrazine	Carbonized fibres treated HNO_3	Batch	50 mg/100 mL		1 h	179	Lupul et al. (2015a)
Atrazine	Carbonized fibres treated NH_3	Batch	50 mg/100 mL		1 h	169	Lupul et al. (2015a)
Atrazine	Carbonized fibres	Batch	0.2 g/50 mL		3 h	14.5–15.5	Vukčević et al. (2015)
Nicosulfuron	Carbonized fibres	Batch	0.2 g/50 mL		3 h	11.6–19.5	Vukčević et al. (2015)
Dimethoate	Carbonized fibres	Batch	0.2 g/50 mL		3 h	11.8–14.7	Vukčević et al. (2015)

[a] in μmol/g

hemp-based material; (ii) the experimental conditions should be chosen to simulate real wastewater containing metals; (iii) much work is necessary to demonstrate the possibilities on an industrial scale using real wastewaters and discharge waters.

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Chapter 2
Biosorption of Metals and Metalloids

Leticia B. Escudero, Pamela Y. Quintas, Rodolfo G. Wuilloud, and Guilherme L. Dotto

Contents

Abstract Industrial activities such as mining operations, refining of ores and combustion of fuel oils play a relevant role in environmental pollution since their wastes contain high concentrations of toxic metals that can add significant contamination to natural water and other water sources if no decontamination is previously applied. As toxic metals and metalloids, including arsenic, cadmium, lead, mercury, thal-

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lium, vanadium, among others, are not biodegradable and tend to accumulate in living organisms, it is necessary to treat the contaminated industrial wastewaters prior to their discharge into the water bodies. There are different remediation techniques that have been developed to solve elemental pollution, but biosorption has arisen as a promising clean–up and low–cost biotechnology. Biosorption is one of the pillars of bioremediation and is governed by a variety of mechanisms, including chemical binding, ion exchange, physisorption, precipitation, and oxide-reduction. This involves operations (e.g. biosorbent reuse, immobilization, direct analysis of sample without destruction) that can be designed to minimize or avoid the use or generation of hazardous substances that have a negative impact on the environment and biota, thus following the concepts of "green chemistry" and promoting the environmental care. Furthermore, it has to be specially considered that the design of a biosorption process and the quality of a biosorbent are normally evaluated from the equilibrium, thermodynamic, and kinetic viewpoints. Therefore, a successful biosorption process can be only developed based on multidisciplinary knowledge that includes physical chemistry, biochemistry and technology, among other fields.

In this chapter, we explain in detail all the aforementioned aspects. State of the art applications of biosorbents for metals and metalloids removal are carefully revised based on a complete analysis of the literature. Thus, it is evidenced in this chapter that the main points to consider regarding biosorption are the type of biomaterial (e.g. bacteria, fungi, algae, plant–derivatives and agricultural wastes, chitin–chitosan based materials) and the presence of a broad set of functional groups on their surface that are effective for the removal of different toxic metals and metalloids. In fact, removal percentages as high as 70–100% can be found in most works reported in the literature, which is demonstrating the excellent performance obtained with biosorbents. Also, biosorbents have evolved with the help of nanotechnology to modern bio–nano–hybrids materials having superlative sorption properties due to their high surface area coming from the nano–materials structures and multifunctional capacity incorporated from the several types of chemical groups of biomaterials. These, as well as other important aspects linked to biosorption are fully covered in the present chapter.

2.1 Introduction

2.1.1 Metals and Metalloids in the Environment

Metals are a group of elements of the periodic table that include alkali metals, alkaline earth metals, transition metals, post–transition metals, lanthanides, and actinides. According to their physical properties, metals have been defined as a group of opaque elements that form alloys, conduct heat and electricity, and are usually malleable (Goyer 2004). Metalloids are those elements that show properties of both metals and non–metals, and are commonly represented by Boron (B), Silicon (Si), Arsenic (As), Antimony (Sb), and Tellurium (Te) (Goldsmith 1982). Both metals and metalloids manifest different effects in processes involved in living organisms. Elements such as Sodium (Na), Potassium (K), Calcium (Ca), Zinc (Zn), Iron (Fe), Cooper (Cu), Magnesium (Mg), Chromium (Cr), and Selenium (Se) are considered essential for normal biochemical and cellular processes. However, some of them (Cu, Cr, Se) can be toxic at high concentrations (Smith et al. 2015). Additionally, metals and metalloids including As, Mercury (Hg), Cadmium (Cd), Lead (Pb), Thallium (Tl), Vanadium (V), and Nickel (Ni) are extremely toxic for living organism, even at trace concentrations, which cause severe damages in the normal functions of the organism (Maestri et al. 2010).

The toxicity occurs when metal ions involved in biological processes are displaced by toxic metals, or via the formation of complexes (Bruins et al. 2000). Due to their high toxicity, As, Cd, Hg, Tl, Cr, and Pb have been listed by the U.S. Environmental Protection Agency among the priority metals that are of public health relevance (Goyer 2004). Most of these elements have been also classified by the International Agency for Research on Cancer as known human carcinogens (Goyer and Clarkson 2001). Table 2.1 shows the main effects of some elements and their compounds on human health, and the toxicity of different chemical species. It is important to highlight that the type of damage and the target organ are conditioned by the kind and route of exposure.

Metals can be introduced into the environment through natural and anthropogenic routes; however, the contribution of human activities is relevant to increase metal concentrations (Vijayaraghavan and Yun 2008). For example, in China, as result from fast economic development, the generation of industrial hazardous wastes has increased to 34.31 million tons in 2011 (Li et al. 2015). Likewise, from cement industry, approximately 3 million of tons per year of industrial wastes were

Table 2.1 Health effects caused by the exposure of metals and metalloids in humans

Element	Health effects	Chemical species/toxicity	References
Al	Hazardous effects on nerve cells and synaptic transmission, lungs (pulmonary fibrosis, chronic pneumonia), high correlation with Alzheimer disease	The chemical species of Al that appear to be toxic are Al^{3+} and the mononuclear hydroxides, $Al(OH)^{2+}$ and $Al(OH)^{2+}$	Meiri et al. (1993) and Nasiadek and Sapota (2004)
As	Heart, cerebrovascular, and respiratory diseases; skin, lung, liver, and kidney cancer	Arsines > Inorganic arsenates > Organic trivalent compounds > Inorganic arsenates > Organic pentavalent compounds > Arsonium compounds > Elemental As	Ratnaike (2003) and Cornelis et al. (2005)
Cd	Organ targets are kidney, bone, and lung, causing pulmonary edema, pleural effusions, hepatic necrosis, and hemorrhage	Many toxic effects seem to involve the divalent ion cadmium	Seiler et al. (1988)
Cr	Skin, respiratory tract, kidney, and lung damage	Inorganic hexavalent chromium > Inorganic trivalent chromium	Baruthio (1992) and Cornelis et al. (2005)
Cu	Hemolysis, headache, febrile reactions, gastrointestinal damage, liver toxicity	Water soluble and divalent copper salts > less or non soluble and divalent copper salts	Cornelis et al. (2005) and Zhang et al. (2016)
Hg	Harmful effects on the nervous, digestive and immune systems, lung and kidney	Organic species > Inorganic species	Seiler et al. (1988)
Ni	Respiratory tract, skin, kidney, and bone affections	Although organic nickel compounds are known, the inorganic nickel is toxic and dominant in the environment	Cornelis et al. (2005)
Pb	Negative effects in hematopoietic, nervous, kidney, and reproductive systems	Although organic lead compounds are known, the inorganic lead is toxic and dominant in the environment	Cornelis et al. (2005) and Abadin et al. (2007)
Sb	Cardiotoxicity, lung cancer, nervous system diseases, blood hemolysis, hepatic damage and necrosis	Inorganic antimonite > Inorganic antimonate > Organic antimony	Winship (1987) and Cornelis et al. (2005)
Se	Selenosis (nausea, dizziness, hair and nails loss, falling teeth, abnormalities in the central nervous system)	Selenite > Selenate (in aquatic environment) Selenate > Selenite (for terrestrial animals)	Eisler (2007), Somogyi et al. (2007) and Brodowska et al. (2016)
Tl	Harmful effects on the nervous system, lung, heart, liver, and kidney	Inorganic trivalent thallium > Inorganic monovalent thallium	Lan and Lin (2005)
V	Respiratory tract disorders, hematological and biochemical alterations, neurobehavioral injuries	Vanadate ion > Vanadyl ion	Ghosh et al. (2015)

produced in Argentina (Stafford et al. 2015). The rapid growth of communication equipment is also driving electronic wastes production (Luo et al. 2011). In fact, the United Nations University has indicated that 8.3–9.1 million tons of electronic wastes were produced across the 27 members of the European Union in 2005 (Oliveira et al. 2012). There are many published works regarding the contamination of the environment by the presence of metals due to human activities (Bermudez et al. 2010; Manzano et al. 2015d; Pandey et al. 2016; Cui et al. 2017). Thus, mining, refining of ores, combustion of fossil fuels, processed food industry, and other industrial processes play an important role in elemental contribution, as their wastes contain high concentrations of toxic metals that could be disposed to natural water and other water sources if no decontaminant treatment is previously applied (Ahmed and Ahmaruzzaman 2016). Since metals and metalloids are not degraded in the environment, they can be accumulated for a long time in ecosystems, and hence, they can be directly translated to food and drinking water available for population.

For the above-mentioned reasons, the concern of researchers regarding the environmental pollution is growing and intense work is being done to solve this problem. In this sense, several remediation techniques have been developed and applied to remove environmental contaminants, including biological treatment, reverse osmosis, coagulation/flocculation, electrochemical oxidation, and adsorption/biosorption (Yeung and Gu 2011; Dasgupta et al. 2015; Samer 2015). Regarding adsorption, activated carbon is the most common sorption material used for pollutant removal from wastewaters due to its outstanding properties, such as good pore structures and high specific surface area. However, the application of this adsorbent is not always feasible because of its high cost, being necessary the exploration of less expensive alternatives that can be also efficient for decontamination treatments. In this way, the concept of "biosorption" has been conceived as a promising clean–up, free of secondary pollution, and low–cost biotechnology, and researchers have therefore focused in the preparation of new bio–materials to remove environmental pollutants from contaminated matrices (Fomina and Gadd 2014).

2.1.2 Biosorption

Initially, it must be pointed out that the term "biosorption" represents only one particular process. The sorption includes both absorption and adsorption, which are usually confused. The absorption is the incorporation of a substance that is presented in a particular aggregation state into another with different aggregation state (Gadd 2009). For instance, liquids can be absorbed by a solid or gases can be absorbed by liquids. On the other hand, the adsorption is the physical adherence or bonding of ions and molecules onto the surface of a solid bio–material. In this case, the material accumulated at the interface is the adsorbate and the solid surface is the adsorbent (Gadd 2009).

Biosorption is one of the pillars of bioremediation, together with bioaccumulation and phytoremediation (Gavrilescu 2004). The concept of biosorption has been defined by one of pioneers in this field, Professor Bohumil Volesky, as the property of certain bio–molecules or biomasses to bind and concentrate selected ions or other molecules from aqueous solutions (Volesky 2007). Contrary to bioaccumulation processes, which involve an active metabolic transport, biosorption is based on the use of non–living biomasses or bio–molecules. Therefore, a passive remediation treatment is verified mainly, due to the affinity between the biosorbent and the adsorbate, which represent the solid surface from the bio–substrate and the chemical contaminant that is accumulated at the interface, respectively (Volesky 2007).

Although the potential of biological substrates for removal of metals and metalloids has been studied from eighteenth century, it is only during the last half century that biosorbents have been used for removal of metals and metalloids contaminants from aqueous solutions (Modak and Natarajan 1995). In the literature of the history of biosorption, it has been reported the first quantitative study on metal biosorption in 1902 (Muraleedharan et al. 1991). In that contribution, Hecked used spores of two strains of fungi for the uptake of Cu from aqueous solutions (McCallan and Miller 1956; Muraleedharan et al. 1991). In the following years, some studies using agricultural wastes (Kumar and Dara 1982; Suemitsu et al. 1986), isolated microorganisms (Tsezos and Volesky 1981; de Rome and Gadd 1987), and consortium of microorganisms (Steen and Karickhoff 1981) for metal removal were reported. Later on, biosorption field grew up and turned more complex because of a deep understanding of biosorption mechanisms, methods of characterization and quantification, equilibrium, thermodynamic, and kinetics studies were required. This facilitated the innovation of additional biosorption–based processes as efficient alternatives for the removal of pollutants from the environment.

In order to represent the worldwide development of biosorption research occurred during the last decades, the number of publications related with biosorption from 1980 to 2016 is exhibited in Fig. 2.1. Although a slight increase in the number of publications happened from 1980 to 2000, the highest growth has been observed from 2000 to 2016. This data reflects the interest of researchers and governments around the world to develop studies based on biosorption for the removal of pollutants from the environment.

Although the biosorption is highly used due to its low cost, it offers other advantages over classical remediation technologies, such as a high efficiency, the reduction of chemical or biological sludges, the possibility of biosorbent reuse, and the recovery of metal after the biosorption process. In fact, biosorption has been catalogued as a bioremediation method comparable to ion–exchange resin–based treatments to remediate metal ions (Volesky 2007). For this reason, the present book chapter will be focused on the state–of–the–art and know–how in biosorption science. The importance of biosorption for the encouragement of Green Chemistry will be detailed. Aspects including types of biosorbents, analytical techniques, and mechanisms involved in biosorption will be also commented and discussed. Finally, challenges, trends, and perspectives related biosorption of metals and metalloids will be exposed.

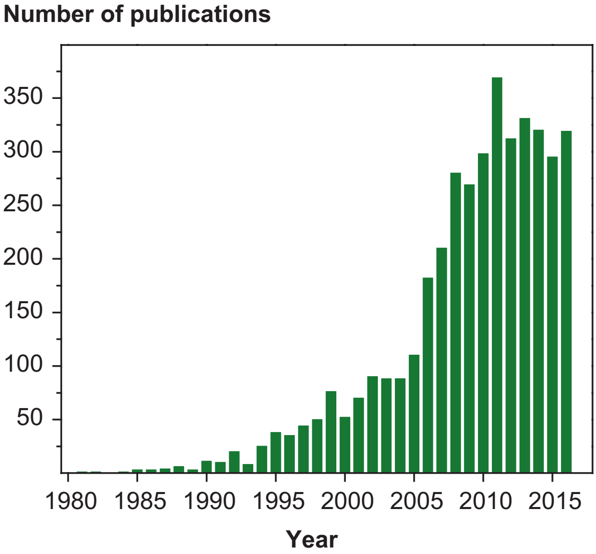

Fig. 2.1 Number of publications related to biosorption from 1980 to 2016. Data obtained from a Scopus search (http://www.scopus.com) performed with the term "biosorption" as a single search filter. A slight increase in the number of publications between 1980 and 2000 can be observed. However, the greatest growth in scientific contributions has been observed between 2000 and 2016. These data reflect a clear interest by researchers and governments around the world to develop studies based on biosorption for the elimination of pollutants from the environment

2.2 Biosorption for Green Chemistry Development

According to the Environmental Protection Agency of the United States, "green chemistry", "sustainable chemistry", and "environmental–friendly chemistry" are terms often used as synonyms and represent chemical products and processes designed to minimize or avoid the use or generation of substances that could be hazardous for the environment and, hence, for any type of life (EPA 2017). The literature establishes 12 principles related to "green chemistry": (1) design for energy efficiency, (2) less hazardous chemical synthesis, (3) use of renewable feedstocks, (4) atom economy, (5) safer chemistry, (6) safer solvents and auxiliaries, (7) designing safer chemicals, (8) use of selective catalyst, (9) reduced derivatives, (10) design for degradation, (11) prevention and (12) real–time analysis for pollution prevention (Srivastava and Goyal 2010a). It is a great challenge for scientists to develop safe and clean processes that can be framed in the concept of green chemistry and biosorbents represent an excellent tool to achieve that goal. Figure 2.2 shows a scheme of some factors that should be considered in the biosorption field to follow the concept of "green chemistry", specifically when biosorption is used as a tool for removal of metals and metalloids from environmental samples.

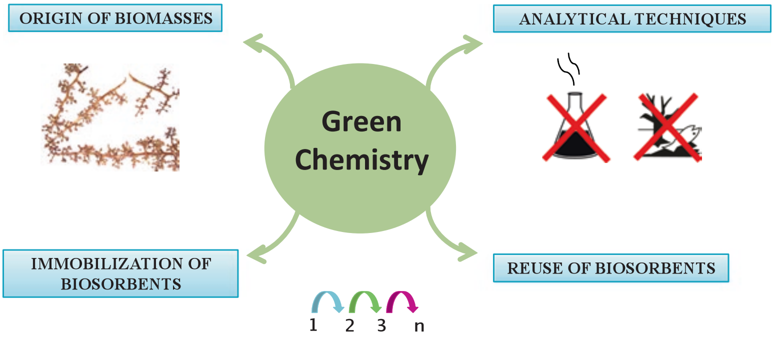

Fig. 2.2 Relevant aspects that encourage the "green chemistry" concept in the biosorption field for the removal of metals and metalloids from the environment. An ideal approach is based on the use of biodegradable biosorbents that can be immobilized and/or reutilized. These practices contribute with a decrease the amount of sorption material and also the generation of wastes. In addition, the use of analytical techniques that avoid or minimize the consumption of toxic reagents and the generation of additional wastes should be considered in pollutant removal technologies

The origin of the biomass used for removal of contaminants is an important factor to be considered in the frame of operations based on green chemistry. For instance, if the biomass consists on an agriculture/industry waste or an ubiquous and easily cultivated microorganism, the environmental and economic impact for obtaining the biosorbent is markedly minimized, which is in agreement with green chemistry goals. Several works have used wastes for removal of metals and metalloids from aqueous solutions (Habineza et al. 2017). Blázquez et al. studied the biosorption of Pb using olive stone and olive tree pruning, two industrial wastes of olive–iol production (Blázquez et al. 2015). Vishan et al. also studied the biosorption of Pb, but using a bacterial strain isolated from compost of green waste, which proved to be an efficient, robust, and low cost biosorbent (Vishan et al. 2017). Although one of the principles of green chemistry aims to state that it is better prevent than cure, when bio–wastes are used for purposes of environmental decontamination, it is a favorable practice to treat the waste created previously.

The reutilization of the biomass in biosorption operations is a good experimental practice as it decreases the amount of sorption material and also the generation of wastes. Generally, it is possible to use a biosorbent for some cycles of biosorption-desorption (2–10 cycles are usually possible), minimizing not only the economic cost of the process, but also the environmental damage.

For example, it has been reported the use of modified *Auricularia Auricular* matrix wastes for three biosorpion/desorption cycles of Cd(II) (Song et al. 2017). After the sorption experiment, the biosorbent was put in contact with 0.1 mol/L of HCl and the mixture was stirred at 150 rpm for an hour at 293 K. Afterwards, the biosorbent was washed with distilled water and dried until constant weight. The results of these experiments showed a reduction in the adsorption efficiency as the cycles were performed, observing the highest decrease between the first and the second cycle. Despite this variation, it was demonstrated that the biosorbent had a good potential reuse since it was useful to remove Cd(II) ions from aqueous solutions in all the assayed cycles. *Vigna Subterranean* Verdc hulls have been evaluated for four biosorpion/desorption cycles of Cr(VI) (Nharingo et al. 2016). Desorption proved to be efficient by using 0.14 mol/L H_2SO_4 and after four biosorption–desorption cycles, no significant loss of Cr(VI) biosorption-desorption capacity was observed. Some biosorbents can show some disadvantages for their reuse, including poor mechanical strength, small particle size, mass loss after a regeneration step, and difficulty in separation from the aqueous phase. However, it is important to evaluate the possible reutilization of the biosorbent in order to promote the sustainable chemistry.

The immobilization of biomass on a solid supporting material represents another advantage for biosorption since it could improve mechanical strength, rigidity, porosity, and hence the performance of the biosorption (Dodson et al. 2015). Immobilized biomass can be implemented in automated systems, which helps to minimize the times elapsed for operations (washing, conditioning, cycles of biosorption and desorption). A large variety of polymeric compounds have been used for immobilization of biomass, including polysulfone, polyurethane, polyacrylamide, polyethyleneimine, and alginates. The selection of the support material can also be in accordance with the concept of green chemistry, although several characteristic such as solubility, biodegradability, and stability should be firstly considered in order to be suitable for the removal of contaminants from wastewaters.

When biosorption involves the removal of metals and metalloids, the analytical chemistry starts to acquire an important role on the contribution for an environmental friendly chemistry. In fact, it has been evidenced that analytical chemistry can contribute for 11 principles of the green chemistry (de la Guardia and Garrigues 2011). The atom economy is the only principle that has no evident application in the analytical field. It has been reported six basic strategies for greening analytical methods, which include the analysis of samples without previous treatment, the use of less polluting sample treatment, the miniaturization/automation of methods, the online decontamination of wastes, the use of alternative reagents, and the reduction of energy consumption (de la Guardia and Garrigues 2011).

Fourier transform infrared spectroscopy (FTIR) is a vibrational spectrosopic technique usually used for the identification of functional groups present in biosorbents. Considering that it provides a high quality spectral information of spectra, a direct analysis of sample without destruction, and generally avoid the use of solvents or reagents, it seems to be an optimal green analytical technique to characterize the biosorbent. Moreover, the detection technique to determine the analyte concentration is another aspect to take into account. A very good alternative to reduce the amounts of acids, organic solvents, and wastes is the selection of an analytical technique that led the analysis in the solid sample, such as electrothermal atomic absorption spectrometry (ETAAS), induced plasma optical emission spectroscopy (ICP–OES), laser ablation (LA), laser–induced breakdown spectroscopy (LIBS) (de la Guardia and Garrigues 2011). On the other hand, if the supernatant (liquid phase) is analyzed, flame atomic absorption spectrometry (FAAS), ETAAS, and ICP–OES techniques can be used, avoiding or minimizing in each case the use of additional reagents.

2.3 Mechanisms Involved in Metal and Metalloids Biosorption

The mechanisms responsible for the metal binding differ according to the biomass type and the contaminant present in the environmental sample (Michalak et al. 2013). Due to the complexity of biomaterials, it is highly possible that several mechanisms can be present simultaneously (Fomina and Gadd 2014; Vijayaraghavan and Balasubramanian 2015). The removal of toxic metals and metalloids may involve both chemical and physical mechanisms (Vijayaraghavan and Yun 2008). Physisorption is associated with the presence of Van der Waals' attraction forces, whereas the chemisorption takes place as a result of relatively strong chemical bonding between adsorbates and biomass surface functional groups (Abdolali et al. 2014). Figure 2.3 shows different mechanisms involved in the removal of metals using biological substrates.

2.3.1 Chemical Binding

A brief description of the main mechanisms involved in chemical binding are presented next:

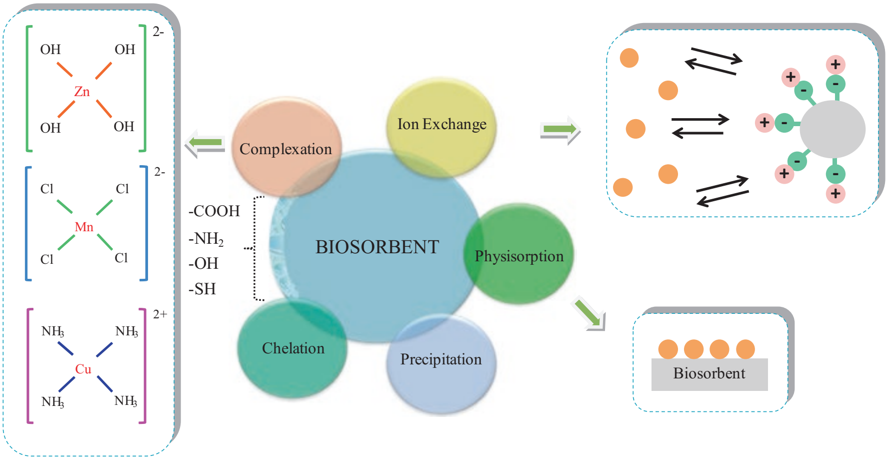

Fig. 2.3 Mechanisms associated with biosorption of metals and metalloids. Chemical binding (complexation, chelation), ion exchange, physisorption, microprecipitation and/or oxide–reduction can be simultaneously present in the biosorption of metals and metalloids. COOH, NH_2, OH, and SH are some functional groups often present in the surface of a biosorbent. Some examples of metal complexes that could be formed between a functional group of the biological substrate and a metal ion are showed. For instance, the ion tetrachloromanganese (II) can be formed between chloride groups present on the biosorbent surface and manganese present in an aqueous solution. (●) Metal ion

2.3.1.1 Complexation

The metal removal from solutions may take place by a complex formation on the cell surface after the interaction between the metal ion and the active groups on the cell wall. A complex compound is a poly–atomic molecule that takes place by association of one or several central atoms, which are metal cations, with a surrounding array of bound ligands. They are organic molecules or inorganic species (cations or anions) that contain free pair of electrons. Complex compounds can be neutral, positively or negatively charged, while bonding could be electrostatic, covalent or a combination of both (Volesky 2003a; Srivastava and Goyal 2010b). Figure 2.3 shows some examples of metal complexes that could be formed between a functional group of the biological substrate and a metal ion.

2.3.1.2 Coordination

Although this mechanism is not involved in metal biosorption, it is interesting to describe as complexation and coordination are usually considered as synonyms. However, the literature shows that there is a difference between both concepts (Volesky 2003b). The term coordination involves compounds that can also be formed by non metallic species. For instance, when trimethylamine is combined with phosphorous fluoride, a coordinate bond is formed by the overlapping of the lone pair orbital of nitrogen with the vacant sp. hybrid of phosphorous (Volesky 2003b). Therefore, complexation is one type of coordination reaction, but coordination has a broader meaning considering that they are not restricted to the presence of metal species with ligands.

2.3.1.3 Chelation

Chelation is a process in which chelate compounds are formed. If one ligand is attached to the central atom through two or more coordinating atoms, the complex is called chelate (Javanbakht et al. 2014). These compounds are more stable than complexes involving monodentate ligands. Different biomasses have been reported to contain ligands useful for metal chelation. For example, Jaafar et al. (2016) reported that the removal of Cd(II) and Pb(II) ions occurred through the formation of a chelate with carboxyl groups of bacterial biomass of *Deinococcus Radiodurans*. It was elucidated by comparison of the FTIR spectra between the biomass and biomass with metal, where some changes were observed in the region of the peak at 1387 cm^{-1} attributed to C–O bond, which was shifted to 1392 and 1390 cm^{-1} when biomass was exposed to Cd(II) and Pb(II) ions, respectively.

2.3.2 Ion Exchange

Ion exchange is known as a reversible interchange process that involves electrostatic interactions between cations present in the solution and the negatively charged groups of the cell wall or vice versa (Abdolali et al. 2014). The cell wall of biomass contains mainly polysaccharides as basic building blocks, and it is a well–established fact that bivalent metal ions are exchanged with counter ions of the polysaccharides (Veglio and Beolchini 1997; He and Chen 2014). Indeed, bio–materials have numerous functional groups able to offer ion exchange sites, including –OH, NH_2, –COOH, phosphate, sulfate, thiol or other groups (Escudero et al. 2016). It has been demonstrated that the biosorption of Cu(II) by *Cystoseira crinitophylla* biomass took place between the metal ions and the hydroxylic oxygens present in the polysaccharide chains of the brown algae (Christoforidis et al. 2015). The pH plays an important role in the ion exchange mechanism. In this work, it was verified that at low pH values, the biosorption capacity was dramatically reduced as result of the competition between metal ions and protons for the binding sites, while at basic pH values, there is risk of precipitation of Cu(II) as hydroxide.

2.3.3 Physisorption

As it was previously commented, physisorption is non–specific and involves weaker forces as compared to chemical mechanisms. The activation energy involved in physisorption processes are less than 1 Kcal/gmol (Volesky 2003b). Even though the interaction energy is very weak (~10–100 meV) (Oura et al. 2003), physisorption plays an important role in the field of decontamination.

Cid et al. (2015) reported that the biosorption of Cu(II) on the brown macroalgae *Durvillaea Antarctica* was due to a physisorption mechanism by forming an heterogeneous multilayer, followed by ion exchange mechanism. It is a good representation of the simultaneous mechanisms that can take place for the removal of toxic metals from aqueous solutions using biomass. Khan and colleagues have also proved that biosorption of Ni(II) and Cu(II) on different agricultural wastes occurred through a mechanism of physisorption that was notably affected by the pH of solutions (Khan et al. 2015). In fact, pH is a critical experimental parameter to be optimized as it can affect the functional groups present in the biomass and metal speciation.

2.3.4 Micro–Precipitation

The micro–precipitation mechanism ocurrs when the solubility of the sorbate reaches its limit. It is defined by the chemical interaction between the metal and the cell surface and is a process not depending on metabolism (Naja and Volesky 2011). Micro–precipitation is a good alternative mechanism used for the removal of metals from aqueous solutions. Liu and co–workers have demonstrated that watermelon rind was an effective biosorbent for the removal of Cu(II), Zn(II) and Pb(II), both ion exchange and micro–precipitation mechanisms were responsible by metal biosorption (Liu et al. 2012b). Moreover, it has been also studied the removal of Pb(II) using bacterial biomass through several mechanisms, including physisorption, micro–precipitation as well as ion exchange (Jin et al. 2016).

2.3.5 Oxide–Reduction

An oxide–reduction reaction can take place if there is one electrons donor element and another that accepts them. Oxide reduction has been used not only to remove toxic metals present in environmental samples, but also to recover precious metals (Das 2010). However, another mechanism is often needed to finally eliminate metals using biomass. For instance, tea waste and date pits were investigated for their potential to remove toxic Cr(VI) ions from aqueous solution (Albadarin et al. 2013). The authors proved that the biosorption processes occurred by the initial biosorption of Cr onto positively charged functional groups of the biomass and then, by a reduction of Cr(VI) to Cr(III) in an acidic medium. FTIR confirmed –COOH, $-NH_2$ and $O-CH_3$ groups were involved in the biosorption and reduction of metals.

An interesting research developed by Dittert et al. was developed on Cr(VI) biosorption using protonated *Laminaria digitata* macro–algae (Dittert et al. 2014). The process was mainly associated to a direct reduction mechanism, in which Cr(VI) was directly reduced to Cr(III) by contact with electron–donor groups of the biomass in an acidic medium, besides chemical binding of Cr(III) species to the negatively charged binding groups present in the cell wall (e.g. –COOH group). The mechanisms for biosorption of As(III) and As(V) on a chemically modified sugarcane bagasse with 2–mercaptoethanol has been also studied (Gupta et al. 2015a). The researchers postulated that after biosorption of As(V) by electrostatic interactions, a reduction occurred by the electron donation from the $-SH^+$ group to form As(III) thiolate complexes.

2.4 Biosorption Equilibrium, Thermodynamic, and Kinetics

The design of a biosorption process and the quality of a biosorbent are normally evaluated from the equilibrium, thermodynamic, and kinetic viewpoints.

The biosorption equilibrium is analyzed using isotherm curves. These curves represent the relation between the amount of metal biosorbed on the biosorbent (q_e, mg/g) and the amount of metal remaining in the liquid phase (C_e, mg/L), at a fixed temperature and under equilibrium conditions. The shape of these curves can give an idea about the biosorption mechanism. Moreover, from the isotherms, the maximum biosorption capacity of a determined biosorbent can be obtained.

From the thermodynamic viewpoint, biosorption is commonly evaluated by the standard values of Gibbs free energy change (ΔG^0, kJ/mol), enthalpy change (ΔH^0, kJ/mol), and entropy change (ΔS^0, kJ/mol K). The standard values of Gibbs free energy change (ΔG^0) are used to verify if the biosorption is spontaneous or favorable. The standard values of enthalpy change (ΔH^0) are used to verify the biosorption nature (exothermic or endothermic) and also provide an idea about the biosorbent–metal interactions. The standard entropy change (ΔS^0) is related with the randomness that occurs in the biosorbent surface during the biosorption process.

Evaluation of kinetic is also fundamental. For this purpose, curves of the amount of metal biosorbed on the biosorbent (q_t, mg/g) along with the time (t, min) are used. Concentration decay curves (C_t *versus* t) are also used. From the kinetic curves, it is possible to verify how fast the biosorption occurs and scrutinize about the biosorption mass transfer mechanism. The objective of this section is to present the main tools to be used in biosorption studies, such as conventional and statistical physics equilibrium models; estimation of thermodynamic parameters; biosorption kinetic models and mass transfer models.

2.4.1 Conventional Equilibrium Models

Several conventional models are used to interpret the biosorption isotherms, including Henry, Langmuir, BET, Freundlich, Sips, Redlich–Peterson and others. The most simple is the Henry's law. This model is normally applied for low concentrations where the relationship between the fluid phase concentration and the biosorbed phase equilibrium concentration is linear (Eq. 2.1), with a constant of proportionality, which is equal to the biosorption equilibrium constant, known as the Henry constant (KH, L/g) (Ruthven 1984):

$$q_e = K_H C_e \tag{2.1}$$

This model can be applied for physical biosorption on a uniform surface at sufficiently low concentration, where all molecules are isolated from their nearest neighbors.

For the Langmuir model (Langmuir 1918), biosorption occurs through monolayer coverage and each site can hold only one molecule. Also, biosorption sites are energetically equivalent and the surface is uniform. Equation (2.2) is the most common form of the Langmuir model.

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \tag{2.2}$$

where q_m (mg/g) is the maximum biosorption capacity and k_L is the Langmuir constant (L/g).

When biosorption occurs in multilayers, the most widely used model is the BET isotherm, as presented in Eq. (2.3) (Ebadi et al. 2009):

$$q_e = \frac{q_{BET} k_1 C_e}{\left(1 - k_2 C_e\right)\left(1 - k_2 C_e + k_1 C_e\right)} \tag{2.3}$$

where, q_{BET} is the monolayer biosorption capacity (mg/g), k_1 and k_2 are the BET constants (L/mg).

The Freundlich model Eq. (2.4) is also used in biosorption systems. This model assumes that the biosorption occurs on a heterogeneous surface, and the amount that is biosorbed increases infinitely with an increase in concentration (Freundlich 1906).

$$q_e = k_F C_e^{1/n_F} \tag{2.4}$$

where k_F is the Freundlich constant (mg/g)(mg/L)$^{-1/\mathrm{nF}}$ and $1/n_F$ is the heterogeneity factor.

The Sips model Eq. (2.5) is a combination of Langmuir and Freundlich models (Sips 1948). If the value of m_s (Sips exponent) is equal to 1, then this equation will become a Langmuir equation. Alternatively, as either C_e or k_s approaches 0, this isotherm reduces to the Freundlich isotherm.

$$q_e \frac{q_{mS} \left(k_s C_e\right)^{m_s}}{1 + \left(k_s C_e\right)^{m_s}} \tag{2.5}$$

where, q_{mS} is the maximum biosorption capacity (mg/g) and k_s is the Sips equilibrium constant (L/mg).

Redlich–Peterson model (Redlich and Peterson 1959) Eq. (2.6) also combines elements of Langmuir and Freundlich models. This model was developed as empirical isotherm to represent the equilibrium over a wide concentration range, and can be applied in either homogeneous or heterogeneous systems due to its versatility.

$$q_e = \frac{k_R C_e}{1 + a_R C_e^{\beta}} \tag{2.6}$$

where k_R and a_R are the R–P constants (L/g and L$^{\beta}$ mg$^{-\beta}$, respectively) and β is the exponent which is varied between 1 and 0.

For all the above mentioned models, the parameters can be used to interpret the biosorption system and compare the process under different experimental conditions. So, the parameters should be correctly estimated. Normally, it can be obtained the parameters by fitting the experimental data (q_e *versus* C_e) with an adequate function.

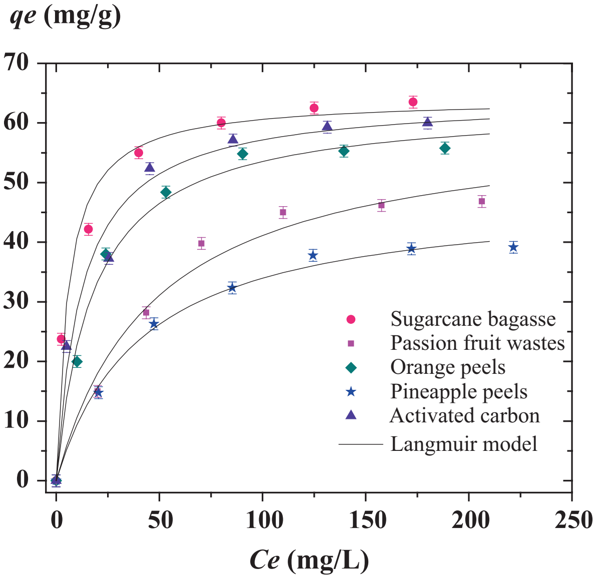

Fig. 2.4 Biosorption equilibrium isotherms of Ni(II) on agro–wastes and activated carbon. The curves show a typical behavior of an L2 type isotherm. It can be observed an initial inclined portion, which represents the affinity between Ni(II) and the biosorbents. Then, a plateau is observed, representing the maximum adsorption capacity. Due to the isotherms of sugarcane bagasse, orange peels, and activated carbon were more inclined than pineapple peels and passion fruit wastes, these biosorbents have more affinity and accessible sites for Ni(II). This means that sugarcane bagasse and orange peels can successfully compete with activated carbon to treat Ni containing effluents. On the other hand, Langmuir model was the most adequate to represent the experimental data. (Reproduced from Dotto et al. 2016, with permission from the copyright holders, IWA Publishing)

As an example, Dotto et al. compared four biosorbents (sugarcane bagasse, passion fruit wastes, orange peels, and pineapple peels) with activated carbon to remove Ni(II) from aqueous solutions (see isotherms in Fig. 2.4) (Dotto et al. 2016). The experimental isotherm data were fitted with Langmuir and Freundlich models. The equilibrium parameters were determined by fit of the models with the experimental data through nonlinear regression. The parameters were estimated minimizing the least squares function, using the Quasi–Newton estimation method. The fit quality was verified through determination coefficient (R^2), average relative error (ARE) and Akaike information criterion (AIC). Based on these statistical indicators, it was concluded that Langmuir model was the most adequate to represent the experimental data. Since the statistical indicators were accurate, the q_m parameter was used to interpret the results. The interpretation of q_m parameter revealed that mainly sugarcane bagasse and orange peels can compete with activated carbon in order to treat Ni containing effluents.

2.4.2 Statistical Physics Models

Statistical physics (sta–phy models) models are an alternative to fit and interpret the biosorption equilibrium isotherms. Some models based on statistical physics are used to fit and interpret the biosorption isotherms in liquid phase. These models are based on the canonical ensemble in statistical physics. The statistical physics models have physicochemical parameters, which are able to explain the biosorption from the macroscopic and microscopic viewpoints (Sellaoui et al. 2017). The usual statistical physics models are: monolayer model with one energy Eq. (2.7), monolayer model with two energies Eq. (2.8), double layer model with two energies Eq. (2.9) and multilayer model with saturation Eq. (2.10). Formulation details of sta–phy models can be found in Piccin et al. (2017).

$$Q = \frac{Q_0}{1+\left(\frac{c_{1/2}}{c}\right)^{n}} \tag{2.7}$$

$$Q = \frac{n_1 N_{1M}}{1+\left(\frac{c_1}{c}\right)^{n1}} + \frac{n_2 N_{2M}}{1+\left(\frac{c_2}{c}\right)^{n2}} \tag{2.8}$$

$$Q = nN_M \frac{\left(\frac{c}{c_1}\right)^{n} + 2\left(\frac{c}{c_2}\right)^{2n}}{1+\left(\frac{c}{c_1}\right)^{n} + \left(\frac{c}{c_2}\right)^{2n}} \tag{2.9}$$

$$Q = nN_M \frac{\left[F_1(c)+F_2(c)+F_3(c)+F_4(c)\right]}{\left[G(c)\right]} \tag{2.10}$$

Sta–phy models contain a series of physicochemical parameters that allow the microscopic interpretation of the biosorption systems, including, Q_0 (adsorbed quantity at saturation), $c_{1/2}$ (concentration at half saturation), n (number of ions per site), n_1 (number of ions per site in the first formed layer), n_2 (number of ions per site in the second formed layer), N_M, N_{1M}, N_{2M} (density of receptor sites), ε_1 and ε_2 (biosorption energies) (Sellaoui et al. 2017).

2.4.3 Thermodynamic Parameters

The biosorption thermodynamics is studied by the estimation of standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) (Liu 2009; Anastopoulos and Kyzas 2016). From these parameters, it is possible to verify if the biosorption is favorable, spontaneous, endothermic or exothermic. Moreover, it is possible to obtain information regarding the disorder in the solid–liquid interface during the biosorption. Furthermore, it is possible to infer about the biosorption nature i.e. physisorption or chemisorption and, verify if the operation is controlled by enthalpy or entropy (Ruthven 1984). It is accepted that the estimation of ΔG^0 can be made by Eq. (2.11):

$$\Delta G^0 = -RT\ln\left(K_e\right) \tag{2.11}$$

where, R is the universal gas constant, T is the temperature and K_e is the equilibrium thermodynamic constant. The K_e value (which should be dimensionless) is normally obtained from the experimental biosorption isotherms for each temperature (Piccin et al. 2017; Tran et al. 2017).

Standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) can be found by the plot of ln(Ke) versus (1/T), known as the Van't Hoff plot, according to Eq. (2.12).

$$\ln\left(K_e\right) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{2.12}$$

Since,

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{2.13}$$

The correct calculation of the thermodynamic parameters allows obtaining important information regarding the biosorption system. For example, negative values of ΔG^0 indicate spontaneous and favorable process. Negative values of ΔH^0 indicate an exothermic process, while positive values of ΔH^0 show an endothermic process. The magnitude of ΔH^0 can be related with the biosorption energies. Physisorption energies are from 5 to 80 kJ/mol. Chemisorption energies are from 80 to 450 kJ/mol. In relation to the ΔS^0, negative values show that the randomness decreases at the solid solution interface during the biosorption, while positive values suggest the possibility of some structural changes or readjustments in the adsorbate–biosorbent complex (Bergmann and Machado 2015).

2.4.4 Reaction Kinetic Models

From the kinetic viewpoint, the biosorption curves can be interpreted by the reaction kinetic models (Qiu et al. 2009). These models are based on chemical reaction kinetics and consider biosorption as a single phenomenon. The more applied models are the pseudo–first order, pseudo–second order, and the Elovich equation (Largitte and Pasquier 2016).

Pseudo–first order model is based on the solids capacity to adsorb and is given by Eq. (2.14) (Lagergren 1898):

$$q_t = q_e\left(1 - \exp\left(k_1 t\right)\right) \tag{2.14}$$

where q_e and q_t (mg/g) are the biosorption capacities at equilibrium and time t (min), respectively, and k_1 (min^{-1}) is the pseudo–first order rate constant. This model is used when the biosorption operation is fast, attaining the equilibrium within 20–30 min.

Pseudo–second order model was developed by Ho and McKay (2000), and is used to represent the entire biosorption period. This model is presented in Eqs. (2.15 and 2.16):

$$q_t = \frac{t}{\left(\frac{1}{h_0}\right) + \left(\frac{t}{q_e}\right)} \tag{2.15}$$

$$h_0 = k_2 q_e^2 \tag{2.16}$$

where h_0 (mg/g min) is the initial biosorption rate and k_2 (g/mg min) is the pseudo–second order rate constant.

The Elovich equation (Eq. 2.17) was developed by Zeldowitsch (1934) and can be used when the biosorption decrease exponentially with an increase of the metal biosorbed.

$$q_t = \left(\frac{1}{a}\right)\ln\left(1 + a\beta t\right) \tag{2.17}$$

where a (g/mg) is the desorption constant, and β the initial biosorption rate (mg/g min).

For all the above mentioned models, the parameters can be used to interpret the biosorption system and compare the process under different experimental conditions, in the same way that the equilibrium models. The parameters are estimated by the fit of the experimental data (q_t *versus* t) minimizing an adequate function. Zazycki et al. studied the biosorption of Au(II), Cu(II) and Ni(II) on chitin and chitosan (Zazycki et al. 2017). Pseudo–first order, pseudo–second order and Elovich equation were used to fit the kinetic data. It was found that the Elovich equation was the most suitable to represent the experimental data. According to these authors, for Au and Ni, the parameter of the Elovich model showed that these metals were adsorbed faster by chitin. Also, lower values of b parameter showed that chitosan has more biosorption capacity.

2.4.5 Diffusional Mass Transfer Models

Diffusional mass transfer models are the most realistic way to interpret the biosorption decay curves. These models are based on three consecutive steps of mass transfer: external mass transfer, intraparticle diffusion and biosorption on active sites (Ruthven 1984). PVSDM (pore volume and surface diffusion model) (Eqs. 2.18, 2.19, 2.20, 2.21, 2.22, and 2.23) is one of the most complete diffusional models and is based on the following assumptions: biosorption occurs at constant temperature; the biosorbent particles are spherical; the mass transport by convection within the pores is negligible; the intraparticle diffusion can occur by pore volume diffusion and surface diffusion or both; the values of effective pore volume diffusion coefficient (Dp) and effective surface diffusion coefficient (Ds) are constant; and the biosorption rate on an active site is instantaneous (Leyva-Ramos and Geankoplis 1985).

$$V\frac{dC_t}{dt} = -mSk_F\left(C_t - C_{S(t)}\big|_{r=R}\right) \tag{2.18}$$

$$t = 0, C_t = C_0 \tag{2.19}$$

$$\varepsilon_p\frac{\partial C_r}{\partial t} + \rho_p\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{r^2}\left[r^2\left(D_p\frac{\partial C_r}{\partial r} + \rho_p D_s\frac{\partial q}{\partial r}\right)\right] \tag{2.20}$$

$$t = 0, 0 \le r \le R, C_r = 0 \tag{2.21}$$

$$\left.\frac{\partial C_r}{\partial r}\right|_{r=0} = 0 \tag{2.22}$$

$$D_p\left.\frac{\partial C_r}{\partial r}\right|_{r=R} + \rho_p D_s\left.\frac{\partial q}{\partial r}\right|_{r=R} = k_F\left(C_t - C_{s(t)}\big|_{r=R}\right) \tag{2.23}$$

In PVSDM Eqs., V is the volume of solution, m is the amount of biosorbent, ε_p is the void fraction of the biosorbent, ρ_p is the apparent density of the biosorbent, S is the external surface area per mass of the biosorbent, C_0 is the initial metal concentration in the bulk solution, C_r is the metal concentration varying with the position and time and, q is the mass of metal per mass of biosorbent varying with the position and time. The PVSDM model can be simplified by considering that the sole intraparticle diffusion mechanism may be either pore volume diffusion (PVDM) ($D_p \neq 0$, $D_s = 0$) or surface diffusion (SDM) ($D_p = 0$, $D_s \neq 0$).

The mathematical solution of PVSDM model is not simple. Generally, the numerical method of lines is used. This method utilizes ordinary differential equations for the time derivative and finite differences on the spatial derivatives. PVSDM has no analytical solution, but can be solved numerically (Souza et al. 2017).

2.5 Biosorbents Used for Heavy Metal Removal

The following sub–sections describe and discuss the most important groups of biosorbents used during the last years for metals and metalloids removal.

2.5.1 *Bacteria*

According to the composition of their cell wall, bacteria are classified into Gram–positive and Gram–negative. Gram–positive bacteria are prokaryotic microorganisms characterized by the absence of outer membrane. Instead of this, they are surrounded by several layers of peptidoglycan, which is often densely functionalized with long anionic polymers, called teichoic acids (Young 2010). In contrast, Gram–negative bacteria show a thin layer of peptidoglycan cross–linked by short chains of amino acids, and an outer membrane rich in lipopolysaccharides (Young 2010). The composition of the cell wall plays a relevant role in metals and metalloids biosorption. In fact, it has been reported that functional groups including peptidoglycan, teichoic acids, phospholipids, lipopolysaccharides, and proteins are involved in elemental biosorption (Vijayaraghavan and Yun 2008). Figure 2.5 shows

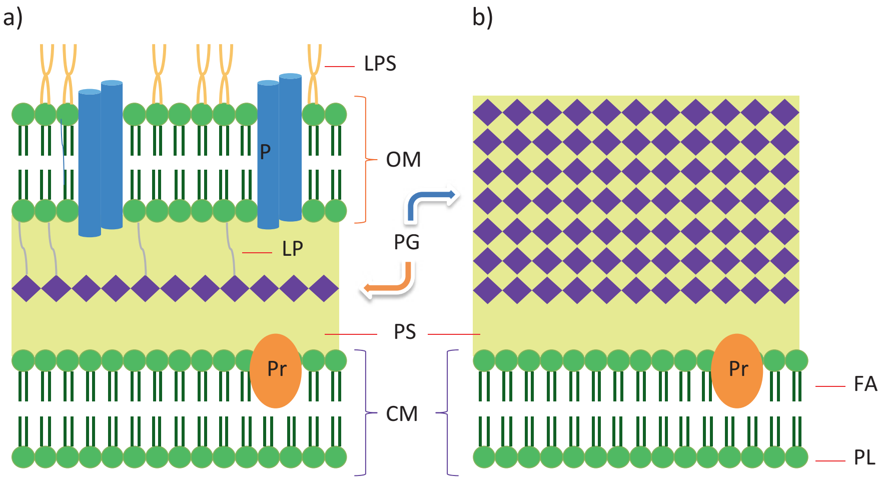

Fig. 2.5 Scheme of the structure and chemical composition of Gram–negative (**a**) and Gram–positive (**b**) bacteria. The group of Gram–positive bacteria is characterized by the absence of outer membrane and the presence of numerous layers of peptidoglycan, which is usually functionalized with long anionic polymers, named teichoic acids. Contrarily, Gram–negative bacteria show a thin layer of peptidoglycan cross–linked by short chains of amino acids, and an outer membrane rich in lipopolysaccharides. *CM* cytoplasmic membrane, *FA* fatty acid, *LP* lipoprotein, *LPS* lipopolysaccharide, *P* porin, *PG* peptidoglycan, *PL* phospholipid, *PS* periplasmic space, *Pr* protein, *OM* outer membrane

a scheme of the main structural and chemical composition differences between both Gram–positive and Gram–negative bacteria.

Within Gram–positive bacteria, *Bacillus* genus has been widely employed as biosorbent for removal of toxic metals, due to it is easy to be obtained, safety to humans, and environmental friendly. Table 2.2 shows a comparison on biosorption capacities of different micro and macro–organisms used as biosorbents for toxic metal removal. Ahmad et al. studied the biosorption potential of *Bacillus subtilis* immobilized on calcium alginate gel beads for the removal of Cd from aqueous solutions (Ahmad et al. 2014). Batch biosorption experiments were developed in order to optimize experimental variables, including pH, initial concentration of Cd, contact time, and biosorbent dose. In agreement with previous works, the optimal pH value to reach the highest biosorption capacity was around 5.92. At this pH, interactions between the negatively charged surface of the biosorbent and the positive ions of Cd can occurred. The biosorbent showed a biosorption equilibrium capacity of 251.91 mg/g at 45 °C, which is fourfolds higher than that obtained for the removal of Cd using a blank composed by calcium alginate beads, thus exhibiting the advantages of immobilizing the bacterial biomass.

Bacillus thuringiensis strains have been applied for removal of europium (Eu) from aquatic ecosystems (Pan et al. 2017). The biosorbent showed to be efficient in terms of biosorption capacity (160 mg/g), besides exhibiting good regeneration and reusability. *Bacillus genus* has been also studied to remove Pb(II) from aqueous solutions (Ren et al. 2015). The results obtained from FTIR and EDS analysis suggest that Pb(II) could be covalently bind with C–, O–, N– and P–containing functional groups present in the cell wall (carboxylate, hydroxyl, amino, and phosphate). The equilibrium data were well fitted with the Langmuir model, which manifests a monolayer biosorption process.

It is usual to chemically modify the surface of the biomass in order to improve the performance of the biosorbent. Kirova et al. studied the biosorption of Pb(II) ions from aqueous solutions by waste biomass of *Streptomyces fradiae* (Kirova et al. 2015). The biomass was a waste obtained as a result of the biotechnological production of antibiotic tylosin in the pharmaceutical industry. FTIR spectra of *S. fradiae* treated with NaOH showed several bands corresponding to functional groups able to bind Pb(II). Despite the chemical modification of the biomass, the biosorption capacity of this material was moderate (around 38 mg/g). Although the removal of Pb was affected by the presence of concomitant ions, the biomass resulted to be effective for biosorption purposes, due to the simplicity to be obtained and low cost.

Within Gram–negative bacteria, *Pseudomonas* genus has been one of the most used in biosorption studies. A recent work has investigated the Pb(II) biosorption by a psychrotrophic strain of *Pseudomonas sp.* (Li et al. 2017a, b). With the aim of evaluating the effect of using Pb–resistant bacteria on the biosorption and removal of this element, living and non–living Pb–resistant *Pseudomonas* strains were compared. It was observed that living strains showed higher biosorption capacity for

Table 2.2 Biosorption capacities of different micro and macro–organisms used as biosorbents for toxic metals removal

Biosorbent	Metal	Experimental conditions	Biosorption capacity (mg/g)	Reference
Bacteria				
Bacillus cereus	Zn(II)	303 K, pH = 6, C_0 = 50, X = 1.0	37	Joo et al. (2010)
Bacillus megaterium	Au(I)	298 K, pH = 3, C_0 = 10, X = 0.15	13.2[a]	Tsuruta (2004)
	Au(III)	298 K, pH = 3, C_0 = 10, X = 0.15	235[a]	
Bacillus sp.	Pb(II)	288 K, pH = 5, C_0 = 400, X = 40	9.3	Ren et al. (2015)
Bacillus subtilis	Cd(II)	318 K, pH = 5.9, C_0 = 496, X = 1.0	251	Ahmad et al. (2014)
Bacillus thuringiensis	Eu(III)	298 K, pH = 7, C_0 = 40, X = 0.5	160	Pan et al. (2017)
Burkholderia cepacia	Cd(II)	298 K, pH = 2, C_0 = 400, X = 0.75	37	Oyetibo et al. (2014)
Corynebacterium kutscheri	Cd(II)	298 K, pH = 2, C_0 = 400, X = 0.75	70	Oyetibo et al. (2014)
Pseudomonas aeruginosa	Zn(II)	303 K, pH = 6, C_0 = 50, X = 1.0	44	Joo et al. (2010)
Pseudomonas aeruginosa	Cd(II)	298 K, pH = 2, C_0 = 400, X = 0.75	80	Oyetibo et al. (2014)
Pseudomonas aeruginosa	Au(I)	298 K, pH = 3, C_0 = 10, X = 0.15	32.7[a]	Tsuruta (2004)
	Au(III)	298 K, pH = 3, C_0 = 10, X = 0.15	314[a]	
Pseudomonas maltophilia	Au(I)	298 K, pH = 3, C_0 = 10, X = 0.15	37.6[a]	Tsuruta (2004)
	Au(III)	298 K, pH = 3, C_0 = 10, X = 0.15	337[a]	
Pseudomonas sp.	Pb(II)	288 K, pH = 5, C_0 = 50, X = 0.5	43	Li et al. (2017a, b)
Rhodococcus sp.	Cd(II)	298 K, pH = 2, C_0 = 400, X = 0.75	55	Oyetibo et al. (2014)
Streptomyces fradiae	Pb(II)	298 K, pH = 5, C_0 = 100, X = 1.0	38	Kirova et al. (2015)
Fungi				
Activated carbon –Fe_3O_4– *Saccharomyces cerevisiae*	Hg(I)	298 K, pH = 7, C_0 = 0.1[d], X = 0.25[c]	720[a]	Mahmoud et al. (2015b)
Aspergillus niger	Zn(II)	301 K, pH = 5, C_0 = 50, X = 20	3.83[b]	Vale et al. (2016)
	Cr(VI)	301 K, pH = 2.5, C_0 = 50, X = 10	4.99[b]	

(continued)

Table 2.2 (continued)

Biosorbent	Metal	Experimental conditions	Biosorption capacity (mg/g)	Reference
Aspergillus ustus on SiO_2	Cr(III)	298 K, pH = 7, C_0 = 500, X = 5.0	2466[a]	Mahmoud et al. (2015a)
	Cr(VI)	298 K, pH = 2, C_0 = 500, X = 5.0	6466[a]	
Auricularia auricula – CTAB immobilized on sodium alginate	Cr(VI)	298 K, pH = 6, C_0 = 50, X = 500[c]	5.5	Zang et al. (2017)
Fusarium verticillioides on SiO_2	Cr(III)	298 K, pH = 7, C_0 = 500, X = 5.0	2666[a]	Mahmoud et al. (2015a)
	Cr(VI)	298 K, pH = 2, C_0 = 500, X = 5.0	6400[a]	
Lepiota hystrix	Cu(II)	298 K, pH = 4.5, C_0 = 50, X = 38	8.9	Kariuki et al. (2017)
	Pb(II)	298 K, pH = 6, C_0 = 50, X = 38	3.9	
Pencillium funiculosum on SiO_2	Cr(III)	298 K, pH = 7, C_0 = 500, X = 5.0	1866[a]	Mahmoud et al. (2015a)
	Cr(VI)	298 K, pH = 2, C_0 = 500, X = 5.0	3800[a]	
Saccharomyces cerevisiae	Ag(I)	288 K, pH = 3, C_0 = 100, X = 3.3	31	Zhao et al. (2015)
Algae				
Chlamydomonas reinhardtii	Tl(I)	298 K, pH = 6, C_0 = 100, X = 0.25	300	Birungi and Chirwa (2015)
Chlorella vulgaris	Tl(I)	298 K, pH = 6, C_0 = 100, X = 0.25	298	Birungi and Chirwa (2015)
Fucus vesiculosus	Zn(II)	298 K, pH = 5, C_0 = 400, X = 1.0	17.7	Castro et al. (2017)
Oedogonium sp.	Se(VI)	298 K, pH = 5, C_0 = 200, X = 10	14.9	Johansson et al. (2016)
	As(V)	298 K, pH = 5, C_0 = 200, X = 10	62.5	
	Mo(VI)	298 K, pH = 5, C_0 = 200, X = 10	67.4	
Pre–treated 2–*Hypnea valentiae*	Co(II)	303 K, pH = 6, C_0 = 0.7, X = 2.0	16.6	Vafajoo et al. (2018)
Scenedesmus acuminutus	Tl(I)	298 K, pH = 6, C_0 = 100, X = 0.25	295	Birungi and Chirwa (2015)
Scenedesmus dimorphus	Co(II)	293 K, pH = 5, C_0 = 0.001[d], X = 0.1	0.08	Bordoloi et al. (2017)
Undaria pinnatifida	Cu(II)	293 K, pH = 5.5, C_0 = 10, X = 10	98	Cho et al. (2013)

(continued)

Table 2.2 (continued)

Biosorbent	Metal	Experimental conditions	Biosorption capacity (mg/g)	Reference
Plant derivatives and agricultural wastes				
Barbula lambarenensis	Pb(II)	323 K, pH = 5, $C_0 = 700$, X = 25	70.6 (raw)	Okoli et al. (2016)
	Cd(II)	323 K, pH = 6, $C_0 = 400$, X = 25	124.6 (PPB)	
			86.2 (EGP)	
			45.1 (raw)	
			54.7 (PPB)	
			58.4 (EPG)	
H_3PO_4–activated carbon from fig sawdust	Pb(II)	298 K, pH = 4, $C_0 = 50$, X = 1	54.7	Ghasemi et al. (2014)
Jatropha curcas fruit coat	Cd(II)	303 K, pH = 6, $C_0 = 250$, X = 15	14.0	Jain et al. (2015)
J. curcas seed coat		303 K, pH = 6, $C_0 = 250$, X = 15	17.0	
KOH–activated carbon from banana peel	Cu(II)	298 K, pH = 7.4, $C_0 = 50$, X = 2.5	9.8	Van Thuan et al. (2017)
	Ni(II)	298 K, pH = 4.0, $C_0 = 90$, X = 5	18.2	
	Pb(II)	298 K, pH = 6.1, $C_0 = 75$, X = 2.5	27.8	
Magnetic Litchi chinensis peel	Pb(II)	298 K, pH = 6, $C_0 = 50$, X = 5	9.39	Jiang et al. (2015)
Magnetic walnut fruit shells	Pb(II)	298 K, pH = 5, $C_0 = 50$, X = 2	18.5	Safinejad et al. (2017)
Okra leaves	Cr(III)	308 K, pH = 4, $C_0 = 5$, X = 5.0	221.1[b]	Khaskheli et al. (2016)
	Cr(VI)	303 K, pH = 2, $C_0 = 5$, X = 5.0	81.9[b]	
Tomato wastes pre–treated with 3% (v/v) HCl	Cu(II)	293 K, pH = 8, $C_0 = 50$, X = 4	9.87	Yargıç et al. (2015)

C_0 = initial metal concentration (mg/L); X = biosorbent dosage (g/L)

[a] Biosorption capacity expressed as µmol/g

[b] Maximum biosorption capacity calculated by isotherms models

[c] Mass of biosorbent expressed as gram

[d] Concentration expressed as mol/L

PPB: sodium tripolylphosphate

EGP: ethylene glycol

Pb(II) than non–living bacteria (51 and 43 mg/g, respectively). Biosorption of Pb(II) by living and non–living biomass was well described by the PSO model, showing that the chemical interactions between Pb(II) and functional groups present in the bacterial wall cell govern the rate control step. Both biosorbents demonstrated to be good alternatives to remediate Pb–contaminated aqueous matrices.

Due to the differences in the cell wall that divide bacteria into Gram–positive and Gram–negative groups, it would be interesting to answer if one group of bacteria is better than the other for biosorption of metals and metalloids. Some contributions can be useful to clarify this point. It has been reported that functional groups present in Gram–negative bacteria are most exposed and available to remove toxic elements, contrarily to Gram–positive bacteria, which show low levels of surface available because of the densely cross–linked peptidoglycan layer (Joo et al. 2010). This statement arises from a study that compares *Bacillus cereus* and *Pseudomonas aeruginosa* strains for the biosorption and removal of Zn(II) from aqueous solutions (Joo et al. 2010). Although both bacterial groups were effective and low cost biosorbents, the Gram–negative bacterium showed a higher biosorption capacity, which could be due to the different structure of the cell wall. Tsuruta et al. have previously studied the performance of Gram–negative bacteria, such as *Bacillus megaterium*, *P. aeruginosa*, *P. maltophilia*, concluding that all of them are better materials to biosorb gold (Au) from aqueous solutions compared to Gram–positive bacteria (Tsuruta 2004).

More recently, Oyetivo et al. developed equilibrium studies of Cd biosorption by bacterial strains isolated from polluted sites (Oyetibo et al. 2014). Four strains were evaluated, two Gram–negative (*Pseudomonas aeruginosa*, *Burkholderia cepacia*) and two Gram–positive bacteria (*Corynebacterium kutscheri*, *Rhodococcus* sp.). In this case, the experimental biosorption capacity was higher for *Pseudomonas aeruginosa* in comparison with the values obtained by Gram–positive bacteria. Nevertheless, *Burkholderia cepacia* showed less biosorption capacity than *Corynebacterium* and *Rhodococcus* genres. Therefore, although the wall cell structure of Gram–negative strains could facilitate the biosorption of some contaminants, this behavior is not always observed and depends on each system. In fact, it has been demonstrated that Gram–positive bacteria can be also useful to remove elemental pollutants from contaminated environments (Aryal and Liakopoulou-Kyriakides 2015).

2.5.2 Fungi

Fungal biomasses have received great attention as biosorbent materials to remove toxic elements mainly because they are easy to grow and are available as industrial waste products (Fomina and Gadd 2014). The elemental biosorption by fungi takes place in the cell wall. Fungal cell walls are complex macromolecular structures consisting mainly on polysaccharides (80–90%) and proteins, lipids, and pigments as minority compounds (Fomina and Gadd 2014). Chitin is also a common constituent of fungal cell walls. This variety of structural components ensures many different functional groups able to bind metal ions of toxicological interest.

Although fungi are a large group of eukaryotic microorganisms, three types have major importance in the field of biosorption: molds, mushrooms, and yeasts (Wang and Chen 2009).

2.5.2.1 Molds

Molds, also known as filamentous fungi, are composed of long and branched threads called hyphae, which form a tangled mass named mycelium (Pokethitiyook and Poolpak 2016). Vale and co–workers have evaluated the capacity of *Aspergillus niger* to adsorb and remove Cr(VI) and Zn(II) from wastewaters (Vale et al. 2016). Comparing infrared spectra before and after biosorption of the metals, the authors demonstrated that hydroxyl groups were mainly responsible for the removal of Zn(II), while amine groups were involved in the biosorption of Cr(VI). A very low biosorption capacity was reported for both metals (3.8 and 4.9 mg/g for Zn(II) and Cr(VI), respectively), which could be countered by the fact of being an economical and easily obtainable biosorbent.

Some works have proposed that the implementation of metal oxides nanoparticles as solid supports can improve the biosorption capacity, the physical and chemical stability, and the lifetime of biosorbents (Bakircioglu et al. 2010; Mahmoud et al. 2011). Mahmoud et al. have reported the immobilization of three fungal biomass, *Aspergillus ustus*, *Fusarium verticillioides*, and *Pencillium funiculosum*, on SiO_2 nanoparticles for the selective biosorption of Cr(III) and Cr(VI) from aqueous solutions (Mahmoud et al. 2015c). In this study, the researchers reported that only by monitoring and controlling the pH value of the solution, the biosorbents were selective for speciation and extraction of Cr species. Thus, maximum biosorption efficiency of Cr(III) was detected at pH 7, while for Cr(VI) it was found at pH 2.0. The time to reach the equilibrium biosorption was very short (15 min) and the experimental data was in accordance by both Langmuir and Freundlich models. Within the Freundlich isotherm parameters, the biosorption intensity constant was higher than unit, which means that the biosorption process was favorable. By the comparison of the three biosorbents, *F. verticiloides* immobilized on nanoparticles show the higher intensity of biosorption. Seawater and industrial wastewater samples were analyzed, reporting a removal percentage between 83.9 and 98.2% for Cr(III), and 80.6–99.8% for Cr(VI) species.

2.5.2.2 Mushrooms

Mushrooms are macro–fungi big enough to be observed by the naked eye and to be picked up handly (Maurya et al. 2006). This class of fungi has been extensively applied in biosorption studies.

Recently, Kariuki and co–authors have proposed the use of *Lepiota hystrix* for biosorption of Cu(II) and Pb(II) ions from aqueous solutions (Kariuki et al. 2017). The efficiency of biosorption was evaluated in batch experiments and the optimized procedure was applied in river water samples. The analysis of the FTIR spectrum indicated that an interaction between metal ions and fungi biomass occurs through hydroxyl, carboxyl, amine, and amide groups. In the desorption study, the percentages of recovery obtained with 0.1 mol/L HCl were around 70% and 50% for Cu(II) and Pb(II), respectively. The researchers suggested that it was because some extra

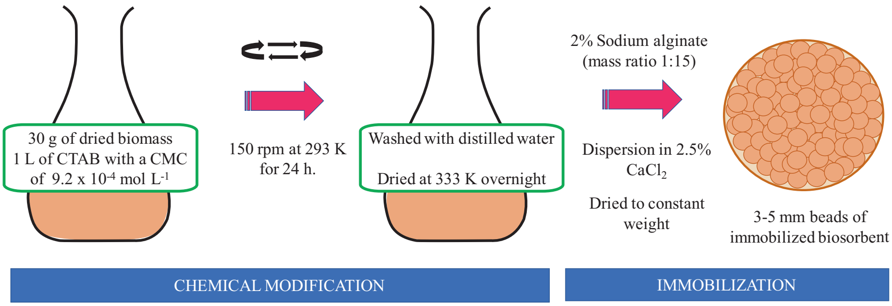

Fig. 2.6 Representation of the chemical modification of *Auricularia auricula* and its immobilization onto a solid support. The dried biomass was chemically modified using cetyltrimethyl ammonium bromide (CTAB), stirring at 150 rpm and 293 K during 24 h. Subsequently, the modified biomass was washed with distilled water and dried at 333 K overnight. Then, the modified biomass was immobilized onto sodium alginate beads using sodium alginate and calcium chloride at concentrations showed in the figure to finally obtain 3–5 mm beads of immobilized biosorbent

mechanisms, besides ion exchange, could be involved in the biosorption of metal ions. In real samples, the percentage of adsorption was lower for both metals. This behavior could be attributed to high levels of competing cations and ligands present in natural waters. However, although the matrix effect played a negative role in terms of reducing the removal of the contaminants, the biosorption by mushrooms is still efficient to be applied in real contaminated matrices.

In other recent work, the removal of Cr(VI) from industrial wastewater samples was evaluated using a fixed–bed column modified by immobilization of *Auricularia auricula* substrate (Zang et al. 2017). The biosorbent was chemically modified using cetyltrimethyl ammonium bromide (CTBA) and immobilized onto sodium alginate. The procedure to obtain the modified and immobilized biosorbent is detailed in Fig. 2.6. The biosorption capacity of this mushroom was significantly higher ($p < 0.05$) than that obtained using the unmodified substrate of fungi, at different Cr(VI) concentrations. This could be due to a reduction of the surface tension by CTAB molecules or to an increase in the number of positive charges on the fungal surface, thus leading to an enhanced biosorption of the anionic species of Cr(VI). Furthermore, a study on the regeneration and reuse of the biosorbent was developed, obtaining a removal of around 50% after three biosorption–desorption cycles.

2.5.2.3 Yeast

Saccharomyces cerevisiae is a worldwide known unicellular fungus, and it is one of the most used for a variety of large–scale industrial fermentation processes, including the production of beer, wine, mead, bread, and antibiotics (Pokethitiyook and Poolpak 2016). These fungi have received increasing attention in the field of biosorption due to its capacity for metal biosorption. Zhao and co–workers used

S. cerevisiae to remove Ag(I) ions from low concentration aqueous solutions (Zhao et al. 2015). In this study, the authors highlighted the use of yeast without any modification and proved that, in comparison with other biosorbents, Ag(I) could be fastly adsorbed onto the biomass (60 min). Furthermore, the equilibrium was reached within 60 min and a removal percentage of 93% was achieved when the initial concentration of Ag(I) was lower than 100 mg/L. Thermodynamically, the biosorption process was spontaneous and exothermic. Different techniques, including TEM, XRD and XPS, suggested that Ag(0) were deposited on the surface of yeast and the FTIR spectrum confirmed that functional groups of the biosorbent were responsible of the reduction of Ag(I) to Ag(0).

Additionally, Mahmoud et al. obtained excellent extraction of Hg(II) in different real water samples (92.0–100.0 ± 1.0–3.0%) (Mahmoud et al. 2015). In this study, a magnetic solid–phase extraction (MSPE) procedure was developed using a composite made of activated carbon–immobilized nanoFe_3O_4–impregnated *Saccharomyces cerevisiae* was employed. The concentration of Hg(II) was determined using a UV–visible spectrophotometer at $\lambda = 488$ nm. The researchers showed that at pH values between 1 and 3, the highest removal of Hg(II) was achieved when activated carbon–immobilized–nano–Fe_3O_4 was used. However, at higher pH values, the biosorption of Hg(II) was 20% more efficient when *S. cerevisiae* was immobilized on the magnetic surface. This behavior could be attributed to the marked increase in the surface area resulting from the presence of magnetic nanoparticles within the structure of the yeast.

2.5.3 Algae

Algae represent another class of biomaterials applied for biosorption and removal of toxic elements from contaminated matrices. Their cell wall is composed of polysaccharides, glycoproteins, and sometimes chitin as an external thin layer (Wurdack 1923). The functional groups present in the algae cell wall (e.g. –COOH, $–NH_2$ groups) can be responsible of metal binding. These biological substrates have often an opportunistic life and can be easily cultivated under different laboratory conditions, thus generating biomasses with different functional groups that might be useful for the removal of various contaminants.

The biosorption of Tl(I) using green micro–algae from eutrophic water sources have been investigated by Birungi and Chirwa (2015). Algal samples were collected, washed and grown for 7 days in a bacteriological agar. The identification of the species was performed using 18S ribosomal RNA gene and the species identified through BLAST search. Three species were identified and evaluated for biosorption of Tl, including *Scenedesmus acuminutus*, *Chlorella vulgaris*, and *Chlamydomonas reinhardtii*. Each species was separately inoculated into AF–6 media and cultured in the laboratory under controlled temperature and light. At the optimal conditions, all biosorbents show outstanding biosorption capacities (please, see Table 2.2), which demonstrates the potential of these biomaterials to treat toxic elements from the aqueous media. In order to reuse the biosorbent, Tl desorption was also studied and HNO_3 was found to be best desorption reagent in all cases.

Some pre–treatments are commonly used to enhance the biosorption capacity of algal biomasses. Although raw algae can efficiently remove metals from aqueous media, secondary pollution caused by the release of organic compounds from the algae has to be mentioned. It has been recently compared the use of raw and pre–treated 2–*Hypnea Valentiae* algae for the removal of Co(II) from aqueous solutions (Vafajoo et al. 2018). The pre–treatment of the raw biomass consisted on mixing 10 g of sieved algae with 1 L of 10% formaldehyde (FA) during 1 h at room temperature. Afterwards, the biomass was separated from the aqueous media by filtration, washed with deionized water, and dried overnight at 60 °C. The authors suggested that this surface modification could not only prevent leaching of components from the algae, but also improve the stability of the biosorbent during the biosorption process. This was in agreement with the results of the study, which showed an improvement of the biosorption capacity using the pre–treated biomass in comparison with the raw algae (16.6 vs. 10.9 mg/g).

The char derived from the pyrolysis of algal biomass has been also explored in the biosorption field. Cho et al. (2013) proved that the char derived from *Undaria pinnatifida* macroalgae was efficient for the removal of Cu(II) from aqueous solutions. It was observed that physical activation of the biochar enhanced by 25% the biosorption of Cu(II) in comparison with the char without activation. This is probably because the activation process could have increased the surface area of the biosorbent, meaning that a high number of new pores were generated and this caused an increase of exchangeable cations on the surface. An optimum pH value of 5.5 was chosen to remove Cu(II) ions from aqueous solutions considering both the effect that pH causes on the surface of the biochar and the speciation of Cu(II). Regarding equilibrium studies, although Langmuir model was the best to represent the experimental data, the determination coefficient was not high enough to explain the biosorption of the metal on the biosorbent. Analyzing the type of isotherms obtained, it could be possible that the biosorbent was a bi–porous material, with macro and micropores involved in the biosorption process (Lee and Ruthven 1979).

More recently, *Scenedesmus dimorphushas* microalgae biochar has been studied for biosorption of Co(II) from aqueous solutions (Bordoloi et al. 2017). This process was faster in the initial stages and kept constant after reaching the equilibrium, which suggest that the more available sites of the surface of the biosorbent were saturated and the vacant binding sites still available on the biochar were of difficult access for Co(II) ions. Biosorption isotherms were in concordance with Freundlich, Temkin, and Dubinin–Radushkevich isotherms, showing in this last case a value of sorption mean free energy of 707.10 KJ/mol.

Simultaneous biosorption of Se, As, and Mo using a modified algal–based biochar was studied by Johansson et al. (2016). Initially, biomass of *Oedogonium* sp. was exposed to $FeCl_3$ solutions for 24 h at 20 °C on a shaker plate. Then, the Fe–treated biomass was converted to biochar by a slow pyrolysis stage. Three temperatures of pyrolysis and four concentrations of $FeCl_3$ solutions were assayed to synthesize the biochar derived from Fe–modified algae, being 300 °C and 12.5% (w/v) the most suitable values to obtain the highest removal of metals (around 100%) and biosorption capacity (17 mg/g). The biosorption process was successfully applied in Tarong Ash Water for the removal of Se, As, and Mo, despite the competitive oxoanions (e.g. SO_4^{-2}) present in the real samples.

Despite the efforts made in the biosorption field over the last years, advances have been mainly focused in laboratory–scale studies (Park et al. 2010). Most biosorption systems have shown limited industrial applications because industrial effluents are complex matrices and the presence of concomitants in these samples could deteriorate the performance of the biosorption. However, some contributions are taking the biosorption a step forward. For instance, the biosorption of Zn(II) from industrial effluents using the brown seaweed *Fucus vesiculosus* and sugar beet pulp was evaluated from laboratory tests to a pilot approach (Castro et al. 2017). Pilot experiments were made using a high feed rate to implement a reactor on an industrial–scale and large glass columns were built to evaluate the applicability of the biosorption for the treatment of wastewaters at this scale. Taking into account that sugar beet pulp is a biosorbent less expensive than brown algae, a combination of both biomasses at different ratios of pulp/algae was evaluated to reduce the cost of the process (1:2, 1:1, and 2:1). It was observed that the columns percolated suitably in all cases and results showed that the most cost effective option to treat Zn(II) ions would be the column packed with 1:1 pulp/algae biosorbent. The demonstrated ability of the pilot–scale biosorption for the efficient removal of Zn(II) ions from real wastewaters turns the biosorption into a very adequate process for large–scale applications. Moreover, by comparing the use of single and serial columns with reverse fed using both biomasses, it was concluded that the capacity of the treatment plant could be improved by the use of multiple columns in parallel or series.

2.5.4 Plant–Derivatives and Agricultural Wastes

Both plant–derivatives and agricultural wastes have been widely used as potential biosorbents for the removal of metals and metalloids (Jain et al. 2016). This kind of biosorbents presents a wide variety of functional groups that allows a broad range of possibilities for metal ions biosorption. Their cell wall consists on cellulose as the main polysaccharide, and other components such as proteins, hemicellulose, and lipids (Nguyen et al. 2013). These biosorbents are one of the more economic options to remove contaminants and it can be considered as environmental friendly due to their fast biodegradation. Furthermore, they are renewable, available in abundance, non–toxic and some of them can be regenerated and reused throughout several biosorption-desorption cycles (Dhir 2014).

Jain et al. (2015) have used *Jatropha curcas* seed coat and fruit coat for Cd(II) biosorption, prior to its determination in the aqueous phase by AAS. The air–dried fruit coat and seed coat were washed, dried in an oven at 60 °C, powdered and sieved using 40 mesh sieves. The results of FTIR indicated that Cd(II) binding was mainly due to the functional groups –OH, –NH, –COOH, and –CO present on the biosorbent surface. It was observed an increase in metal ion biosorption when increasing the biosorbent dose, which could be related with a major number of binding sites and surface area. However, at higher biosorbent doses, less biosorption capacities were obtained, which might be due to electrostatic interactions between cells and interference between the binding sites at high biosorbent dose. At the optimal experimental conditions, biosorption capacities around 14 ad 17 mg/g were obtained for fruit coat and seed, respectively. The adsorbents could be used efficiently up to three biosorption–desorption cycles of Cd(II).

A chemical pre–treatment has been proposed in tomato wastes using 3% (v/v) HCl for Cu(II) removal from aqueous solutions (Yargıç et al. 2015). The results showed that the highest removal of metal ions was obtained at pH 8 (around 92%). Furthermore, the evaluated kinetic models reflected that pseudo–second order kinetic model was the most suitable, indicating that the rate controlling mechanism for the biosorption was chemisorption.

The pseudo–second–order kinetics has also described adequately the biosorption of Pb(II) and Cd(II) onto the surfaces of untreated *Barbula lambarenensis* (RBL) and modified with sodium tripolyphosphate (PPB) and ethylene glycol (EGB) (Okoli et al. 2016). The authors reported that the use of sodium tripolyphosphate increased the specific surface area of the raw biosorbent in approximately 10 times, which was reflected in the biosorption capacities reported in Table 2.2. The tripolylphosphate group is a common chelating agent, and its use for the pre–treatment of the raw biosorbent generated extra tripolylphosphate groups on the surface of the biosorbent, causing an increase in the biosorption capacities. From the FTIR results, it was observed that the EGB biosorbent showed additional hydroxyl groups from ethylene glycol in comparison with the raw material, which resulted useful to adsorb metal ions. For Cd(II) biosorption, EGB biosorbent showed the highest biosorption capacity, while the highest biosorption capacity for Pb(II) was obtained with PPB biosorbent exhibited, which could be attributed to the smaller hydration radius of Pb(II), the greater affinity of Pb(II) for most functional groups and its higher electronegativity.

Jiang et al. (2015) proposed the synthesis of a magnetic biosorbent using *Litchi chinensis* peels for the removal of Pb(II) from aqueous solutions. Initially, Fe_3O_4 magnetic nanoparticles were prepared by coprecipitating Fe^{2+} and Fe^{3+} ions in an ammonia solution under ultrasonic agitation. Then, dry *Litchi chinensis* peels were pulverized and homogenized using deionized water. Finally, the biosorbent was synthesized by adding Fe_3O_4 magnetic nanoparticles powder, followed by the addition of sodium triphosphate. Under optimal experimental conditions, the biosorbent showed a biosorption capacity of 3.39 mg/g, using an initial metal concentration of 50 mg/L and adsorbent dosage of 5 g/L. The thermodynamic study suggested that Pb(II) biosorption was spontaneous and exothermic process. One of the major advantages of this work is that the biosorbent containing the metal can be rapidly and easily separated from the solutions using an external magnetic field, avoiding time consuming steps such as centrifugations or filtrations.

Recently, Safinejad and co–workers have also been used a magnetic biosorbent prepared by adhering Fe_3O_4 on the surface of an agricultural waste for biosorption Pb(II) from aqueous solutions (Safinejad et al. 2017). In this case, shells of walnut fruit were chosen as biosorbent. The magnetic biosorbent showed a remarkable capacity of regeneration. The authors stated that after 10 biosorption–desorption cycles, the biosorbent preserved its characteristics without losing its magnetic properties. Besides, real waste samples were analyzed and about 98% of Pb(II) ions was removed during to the first 10 min of the biosorption. The metal biosorption was quite fast and could be completed in the first minutes of the process due to the absence of an internal diffusion resistance.

The removal of pollutants using activated carbons prepared from agricultural waste material has been reported by several researchers (Sayɟili et al. 2015; Gupta et al. 2015b). Under controlled conditions, the wastes can be converted into activated carbon through pyrolysis with or without chemical activating agents. Biosorption using these types of biosorbents have been found to be renewable and at the same time shows high efficiency, ease of operation and low costs (Okman et al. 2014). Van Thuan et al. have proposed the use of KOH–activated carbon from banana peel for the biosorption of Cu(II), Ni(II) and Pb(II) ions (Van Thuan et al. 2017). The authors used the response surface methodology (RSM) to optimize the experimental variables, including initial concentration of metal ions, dose of biosorbent, and pH of solution. The biosorption model resulting from the quadratic equations proved to be statistically significant and the predictive potential of the model was also successful. The biosorption isotherms of Cu(II) and Ni(II) were in agreement with the Langmuir biosorption model.

In other work, Ghasemi and co–workers have studied the use of fig sawdust as a precursor for the production of activated carbon by chemical activation with H_3PO_4 for the removal of Pb(II) from drain water samples (Ghasemi et al. 2014). The authors proposed the formation of Cπ–Pb(II) complex and ion exchange reactions as the main mechanisms responsible for the biosorption of the metal by activated carbon. The biosorption of Pb(II) onto the biomaterial demonstrated to be spontaneous and thermodynamically favorable. In addition, the biosorbent could be used up to 5 biosorption-desorption cycles with no changes in the removal percentage of Pb(II), thus making this biosorption process more economic.

An appealing study based on the removal of Cr species from water samples has been recently proposed by Khaskheli et al. (2016). In this work, agricultural wastes of Okra leaves were evaluated for the biosorption of Cr(III) and Cr(VI). The leaves were ground, sieved to obtain small particle sizes and finally treated with HCl. The researchers found that the highest removal capacity of Cr(III) was 221.17 mg/g at pH 4.0 and it was 81.94 mg/g at pH 2.0 for Cr(VI). Thermodynamically, the positive values of enthalpy change and negative values of Gibbs free energy showed the endothermic and spontaneous nature of the biosorption process. Under optimal conditions, the biosorbent was able to remove around 90% of Cr from spiked real water samples.

2.5.5 Chitin–Chitosan Based Materials

Chitin is a linear biopolymer composed by 2–acetamido–2–deoxy–D–glucopyranose (GlcNAc) and 2–amino–2–deoxy–D–glucopyranose (GlcN) units (Fig. 2.8). This biopolymer is the second most naturally abundant polysaccharide after cellulose (Roberts 1992). The main sources of chitin are crustaceans, insects, mollusks, and fungi (Fiamingo et al. 2017). Chitin is normally obtained from shrimp and crab shells, which are wastes from the seafood industries, by sequential steps of demineralization, deproteinization, deodorization and drying (Moura et al. 2015). Chitosan, in turn, is the product of alkaline deacetylation of chitin (Fig. 2.7). During

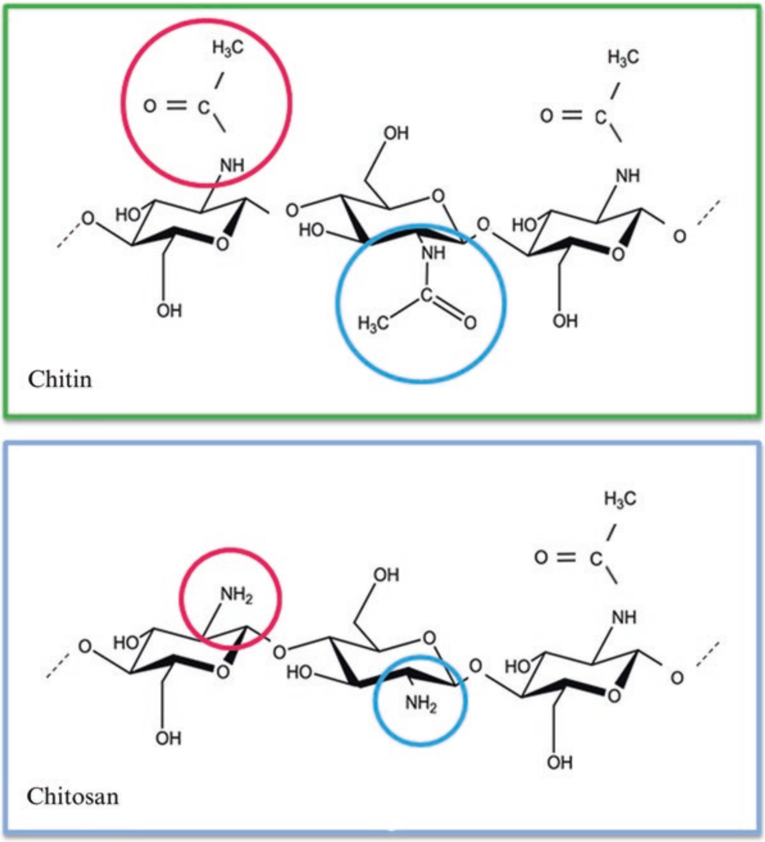

Fig. 2.7 Simplified chemical structure of chitin and chitosan biopolymers. Chitin: linear biopolymer of 2–acetamido–2–deoxy–D–glucopyranose (GlcNAc) and 2–amino–2–deoxy–D–glucopyranose (GlcN) units. Chitosan: product of the chitin alkaline deacetylation. During the deacetylation reaction, the chitin acetamido groups are converted into amino groups. If the acetylated units are higher than 60% of the biopolymer chain, we have chitin. On the other hand, if the de–acetylated units are higher than 60% of the biopolymer chain, we have chitosan

the deacetylation reaction, the chitin acetamido groups are converted into amino groups. If the acetylated units are higher than 60% of the biopolymer chain, we have chitin. On the other hand, if the de–acetylated units are higher than 60% of the biopolymer chain, we have chitosan (Fiamingo et al. 2017). Chitin and chitosan present a series of interesting physicochemical characteristics, which are responsible for their unlimited potential of application (Dotto and Pinto 2017). One of the most common applications for chitin and chitosan is the biosorption of metals and metalloids (Cadaval et al. 2017).

According to the literature (Guibal 2004; Mack et al. 2007; Crini and Badot 2008; Fu and Wang 2011; Dotto and Pinto 2017; Kanmani et al. 2017), the use of chitin and chitosan as biosorbents to remove/recovery metals and metalloids from aqueous media by biosorption is justified by the following issues:

- Chitin and chitosan are obtained from wastes: seafood industries generate large amounts of shrimp and crab wastes, which cannot be simply discarded, since can cause environmental impacts. Some industries need to pay for the correct management of these solid wastes. Chitin and chitosan can be obtained from these wastes, solving an environmental problem and reducing the industrial processing costs. For this reason, chitin and chitosan are considered low cost and eco–friendly biosorbents;
- Chitin and chitosan are abundant, renewable, biodegradable and no toxic: chitin is the second most naturally abundant polysaccharide and can be obtained from renewable sources. Consequently, chitosan is also abundant and renewable. Both, chitin and chitosan are not toxic for live organisms and are easy biodegradable;
- Chitin and chitosan are interesting functional groups to bind metals: chitin contains OH, CH_2OH, COC and acetamido groups, while chitosan contains OH, CH_2OH, COC and amino groups. These groups are able to bind metallic ions in solution through different types of interactions;
- Chitin and chitosan can be chemically or physically modified to improve its biosorption potential: these biopolymers can be physically modified to form membranes, sponges, hydrogels, nanoparticles, nanofibers, scaffolds, nanowhiskers, films and other based materials. Also, they can be chemically modified by several agents through grafting or crosslinking reactions. These chemical or physical modifications are normally employed to increase the biosorption capacity, avoid solubility and facilitate the phase separation.

The biosorption of metals and metalloids on chitin or chitosan is normally studied in batch systems and is dependent of some factors (Cadaval et al. 2017). The most important factors are the solution pH, deacetylation degree and metal speciation (Guibal 2004). Generally, the interactions of metals with chitin/chitosan based materials can be occurs by (I) complexation on nitrogen (free electronic doublet), (II) formation of ternary complexes and (III) ion exchange/electrostatic attraction (Guibal 2004). At pH lower than 6.7, the amino groups are susceptible to be protonated, turning chitosan into a polycationic material able to interact with negatively charged metals, like Cr (Cadaval et al. 2013), V (Cadaval et al. 2016) or As (Boddu et al. 2008), by electrostatic attraction or ion exchange. It is evident that higher deacetylation degrees contribute for these interactions. On the other hand, when pH is higher than 6.7, the amino groups are non–ionized and they possess a free electronic doublet on N atom able to interact with metal cations, like Ag (Zhang et al. 2015), Cd (Hu et al. 2017), Co (Dotto et al. 2015), Cu (Hu et al. 2017), Hg (Kyzas and Deliyanni 2013), Ni (Monier et al. 2010) and Pb (Hu et al. 2017). Regarding OH groups, it is accepted that they essentially contribute to stabilizing metal binding on amine groups (Guibal 2004).

Table 2.3 shows the biosorption capacities of different chitin–chitosan based materials for different metals and metalloids. Some interesting conclusions can be obtained from Table 2.3: (i) It is corroborated that chitin/chitosan based materials can be used as alternative biosorbents to remove a series of metals from aqueous media, (ii) It is demonstrated that several types of chemical and physical modifications can be performed in these biopolymers in order to improve its biosorption potential, (iii) The biosorption of metals and metalloids on chitin/chitosan-based materials is normally investigated from 293 to 333 K, (iv) For all investigated elements, the biosorption was favored under neutral or acid conditions and (v) The biosorption capacities vary in a wide range and are extremely dependent of the experimental conditions.

Despite many papers have been already published in this field, studies about biosorption of metals and metalloids on chitin/chitosan based materials continues to be relevant. The main trends to be explored are new or alternative modifications on chitin and chitosan; low cost and eco–friendly methods for modifications; development of selective chitin/chitosan based biosorbents; applications for pre–concentration, recovery and removal of toxic/precious metals; investigation of the mass transfer mechanisms involved in the biosorption process; development and design of fixed bed operations using chitosan based materials as biosorbents; development and design of fluidized bed operations using chitosan based materials as biosorbents; development and design of continuous stirred tank reactors (CSTR) using chitosan based materials as biosorbents.

2.6 Bio–Nano–Hybrids Materials

Bio–nano–hybrids materials are formed by the assembly of molecular species of biological origin and inorganic nano–substrates (Ruiz-Hitzky et al. 2008). These emerging materials are used in several fields, such as tissues engineering and new materials with enhanced functional and structural properties (Dujardin and Mann 2002b; Ruiz-Hitzky 2006; Darder et al. 2007c).

Nanotechnology is being introduced in the environmental field, particularly as it relates to the combination of biological substrates with nano–materials, for the development of new hybrid bio–nano–materials with high retention capacity of metals (Khanra et al. 2012; Mahmoud et al. 2013). Within the bio–nano–hybrids materials that are being synthesized and evaluated to remove pollutants from the

Table 2.3 Biosorption capacities of different chitin–chitosan based materials for several toxic metals and metalloids

Chitin/chitosan based material	Metal	Experimental conditions	Biosorption capacity (mg/g)	Reference
Chitin powder	Ag	303 K, pH = 2.2, $C_0 = 20$, X = 20	4.37	Songkroah et al. (2004)
Chitin flakes		303 K, pH = 2.2, $C_0 = 20$, X = 20	3.61	Songkroah et al. (2004)
Chitosan gel beads		298 K, pH = 5, $C_0 = 352$, X = 1	89.20	Zhang et al. (2015)
Chitosan/triethanolamine composite		298 K, pH = 5, $C_0 = 12000$, X = 2	510	Zhang et al. (2012)
Chitin nanofibers	As	298 K, pH = 6, $C_0 = 50$, X = 5	56	Yang et al. (2015)
Thiol–functionalized chitin nanofibers		298 K, pH = 7, $C_0 = 50$, X = 5	149	Yang et al. (2015)
Chitosan coated biosorbent		298 K, pH = 4, $C_0 = 500$, X = 2.1	93.46	Boddu et al. (2008)
Fly ash coated by chitosan		293 K, pH = 6, $C_0 = 2400$, X = 10	19.10	Adamczuk and Kołodyńska (2015)
Chitin	Au	298 K, pH = 1, $C_0 = 202$, X = 20	35	Côrtes et al. (2015)
Chemically modified chitosan		303 K, pH = 2, $C_0 = 3940$, X = 2	675.6	Donia et al. (2007)
Chitosan derivative		298 K, pH = 4, $C_0 = 4294$, X = 1	1650	Wang et al. (2012)
Glycine crosslinked chitosan resin		303 K, pH = 2, $C_0 = 500$, X = 3.33	169.98	Ramesh et al. (2008)
Chitosan saturated montmorillonite	Cd	298 K, pH = 5, $C_0 = 87.2$, X = 0.33	23.03	Hu et al. (2017)
Chitosan microspheres		298 K, pH = 5, $C_0 = 500$, X = 1.00	14.5	Yu et al. (2017)
Polymaleic acid–chitosan microspheres		298 K, pH = 5, $C_0 = 500$, X = 1.00	39.2	Yu et al. (2017)
Thiocarbohydrazide–chitosan gel		298 K, pH = 6.98, $C_0 = 500$, X = 2	81.26	Li et al. (2017a, b)
Raw chitin	Co	318 K, pH = 6, $C_0 = 100$, X = 1.00	50.03	Dotto et al. (2015)
Surface modified chitin		318 K, pH = 6, $C_0 = 100$, X = 1.00	83.94	Dotto et al. (2015)
Chitosan polymethacrylate nanoparticles		293 K, pH = 5.0, $C_0 = 200$, X = 0.5	220	Shaker (2015)
Modified chitosan resin		301 K, pH = 5.0, $C_0 = 400$, X = 1.5	53.51	Monier et al. (2010)

(continued)

Table 2.3 (continued)

Chitin/chitosan based material	Metal	Experimental conditions	Biosorption capacity (mg/g)	Reference
Chitosan powder	Cr	298 K, pH = 3.0, $C_0 = 400$, X = 0.2	97.4	Cadaval et al. (2013)
Chitosan–coated fly ash		288 K, pH = 5, $C_0 = 100$, X = 0.67	33.27	Wen et al. (2011)
Zirconium chitosan composite		308 K, pH = 5, $C_0 = 100$, X = 0.20	175	Zhang et al. (2013)
Thiocarbohydrazide–chitosan gel		298 K, pH = 4.26, $C_0 = 500$, X = 2	144.68	Li et al. (2017a, b)
Chitosan saturated montmorillonite	Cu	298 K, pH = 5, $C_0 = 87.2$, X = 0.33	34.90	Hu et al. (2017)
Chitosan polymethacrylate nanoparticles		293 K, pH = 6.0, $C_0 = 200$, X = 0.5	195	Shaker (2015)
Modified chitosan resin		301 K, pH = 5.0, $C_0 = 400$, X = 1.5	103.16	Monier et al. (2010)
Modified chitosan/$CoFe_2O_4$ particles		303 K, pH = 5.0, $C_0 = 800$, X = 0.5	168.07	Fan et al. (2017)
Chitosan	Hg	298 K, pH = 5.0, $C_0 = 500$, X = 1.0	145	Kyzas and Deliyanni (2013)
Magnetic chitosan		298 K, pH = 5.0, $C_0 = 500$, X = 1.0	152	Kyzas and Deliyanni (2013)
Coarse chitin		298 K, pH = 7, $C_0 = 1000$, X = 2.5	70	Barriada et al. (2008)
Fine chitin		298 K, pH = 7, $C_0 = 1000$, X = 2.5	66	Barriada et al. (2008)
Chitosan polymethacrylate nanoparticles	Ni	293 K, pH = 4.0, $C_0 = 200$, X = 0.5	340	Shaker (2015)
Modified chitosan resin		301 K, pH = 5.0, $C_0 = 400$, X = 1.5	40.15	Monier et al. (2010)
Crosslinked chitosan beads with histidine		298 K, pH = 6.0, $C_0 = 250$, X = 2.0	104.2	Nguyen and Juang (2015)
Poly(chitosan–acrylamide)		298 K, pH = 7, $C_0 = 4000$, X = 6.0	63.15	Saleh et al. (2017)
Chitosan saturated montmorillonite	Pb	298 K, pH = 5, $C_0 = 87.2$, X = 0.33	71.92	Hu et al. (2017)
Modified chitosan/$CoFe_2O_4$ particles		303 K, pH = 5.0, $C_0 = 800$, X = 0.5	228.3	Fan et al. (2017)
Thiosemicarbazide modified chitosan		298 K, pH = 4.3, $C_0 = 200$, X = 1.6	325.2	Li et al. (2016)
Magnetic chitosan/clinoptilolite/magnetite		333 K, pH = 6, $C_0 = 90$, X = 1	137	Javanbakht et al. (2016)

(continued)

Table 2.3 (continued)

Chitin/chitosan based material	Metal	Experimental conditions	Biosorption capacity (mg/g)	Reference
Chitin networks	U	298 K, pH = 6.0, $C_0 = 80$, $X = 0.21$	288	Schleuter et al. (2013)
Amidoximated chitosan– polyacrylonitrile		298 K, pH = 7.0, $C_0 = 80$, $X = 0.05$	312	Xu et al. (2015)
Chitosan/bentonite composite		303 K, pH = 5.5, $C_0 = 500$, $X = 2$	117.2	Anirudhan and Rijith (2012)
Magnetic chitosan resin		298 K, pH = 5.0, $C_0 = 420$, $X = 1$	187.26	Zhou et al. (2012)
Chitosan films	V	298 K, pH = 6, $C_0 = 200$, $X = 0.30$	251.4	Cadaval et al. (2016)
Ti–doped chitosan bead		303 K, pH = 4, $C_0 = 100$, $X = 0.20$	210	Liu and Zhang (2015)
Protonated chitosan flakes		298 K, pH = 6, $C_0 = 0.5$, $X = 5$	12.22	Padilla-Rodríguez et al. (2015)
N–citryl chitosan		303 K, pH = 3, $C_0 = 150$, $X = 0.5$	171.82	Abdul Mujeeb et al. (2014)

C_0 = initial metal concentration (mg/L); X = biosorbent dosage (g/L)

environment, it can be found those formed resulting from the combination of polysaccharides with nanomaterials. For instance, bio–nano–hybrid materials of nano–hydroxyapatite chitin (n–HApC) and nano–hydroxyapatite chitosan (n–HApCs) have been synthesized and applied for the removal of Fe(III) from aqueous solutions (Kousalya et al. 2010). The materials were prepared following the precipitation method, mixing a solution of ammonium dihydrogen phosphate with a mixture of $Ca(NO_3)_2$ solution and chitin or chitosan in the ratio 3:2. The obtained precipitate was rinsed with water up to reach a neutral pH, and dried at 150 °C. It has to be mentioned that the synthesized bio–nano–hybrid materials showed higher biosorption capacities than nano–hydroxyapatite only.

A relevant fraction within nano–materials is represented by those made of carbon structures. In recent years, its application in the removal of toxic metals has been extensively investigated, with the use of diamonds, fullerenes, carbon nanotubes (CNTs), graphene, carbon nanofibers, nanocouples and nanotrompets (Ihsanullah et al. 2016; Liu et al. 2017c; Zhao et al. 2017d; Pirveysian and Ghiaci 2018). CNTs are an allotropic form of carbon, such as diamond or graphite, and are made up of curved and closed carbon hexagonal networks forming nanosized carbon tubes. Depending on the formed graphite layers, CNTs can be classified as single wall (SWCNT), multiwall (MWCNT) and carbon nanofibers, which represents a more disordered form of MWCNT, but keeping the tubular structure (Tasis et al. 2006). Due to their mechanical and chemical properties, especially the large surface area, CNTs are nano–materials that have undoubtedly become a very promising alternative to be used as supports functionalized with microorganisms. Several studies on the combination of microorganisms with CNTs have been developed for technological applications such as contaminant removal, bio–battery production and electronic devices (Li 2016; Fu et al. 2017; Xue et al. 2017).

On the other hand, graphene is considered the fundamental structure of all forms of graphite, including nanotubes, graphite and fullerenes. Graphene consists of a single layer (monolayer) of carbon atoms arranged in a two–dimensional honeycomb network (Zhong et al. 2017b). It has a high surface area, which makes of this material an exceptional candidate to be used as support for biomolecules or microorganisms (Mohanty and Berry 2008; Wahid et al. 2013). For example, a bio–nano–hybrid material made of sulfur–graphene oxide nanosheets was synthesized and applied for the removal of Pb(II), Cd(II), Ni(II), and Zn(II) ions from aqueous solutions (Pirveysian and Ghiaci 2018). The presence of sulfur in the hybrid material was demonstrated by EDS and XPS techniques. In order to improve the efficiency of the sorbent, the hybrid material was coated with a mesoporous shell of TiO_2 or SiO_2. Although the hybrid material proved to be useful for the removal of metal ions from aqueous solutions, coating of GO–SO_xR with TiO_2 seems effectively improve the biosorption capacity for all metals under study, which could be associated with the higher surface area of the coated biosorbent.

In addition, the use of nanoparticles (NPs), and particularly magnetic nanoparticles (MNPs), is of great interest for the development of remediation processes that are based on the use of microorganisms as biosorbents. Among the outstanding properties that these NPs, they have ability to give magnetization to living cells of microorganisms (Tian et al. 2010). Figure 2.8a shows a schematic representation of a microbial cell before and after the magnetization process. The material resulting from the interaction of microorganisms–MNPs not only shows the advantage of acquire super–paramagnetic character of MNPs, but also exhibit good biosorption capacity, towards both metals and towards organic compounds (Ji et al. 2010; Tian et al. 2010). Thus, they also become excellent alternatives for the removal of contaminants from aqueous matrices. An additional advantage of magnetized cells is

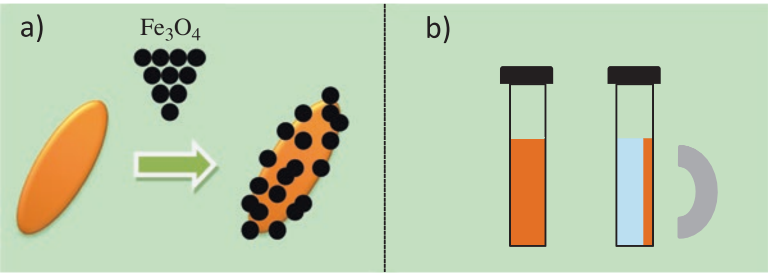

Fig. 2.8 (**a**) Schematic representation of a microbial cell before and after to interact with MNPs of Fe_3O_4 to produce a bio–nano–hybrid material with super–paramagnetic character and promising biosorption capacity towards metals and organic compounds. (**b**) As part of the use of the bio–nano–material for the removal of contaminants, an easy separation of the magnetic bio–nano–material from the aqueous solution by the application of a magnetic field can be carried out, avoiding time-consuming steps such as centrifugation

that, upon acquiring magnetic properties, they can be easily removed from the aqueous phase by application of a magnetic field (Fig. 2.8b).

Different procedures have been proposed for the magnetization of microbial cells, either by treatment with magnetic fluids, covalent immobilization on magnetic transporters, specific interaction with immunomagnetic particles, cell cross–linking in the presence of magnetic particles, among others (Pospiskova et al. 2013). For instance, Rao et al. synthetized a hybrid material using Fe NPs to confer magnetic properties to yeast cells of *Yarrowia lipolytica*. The cells modified with phyto–inspired Fe^0/Fe_3O_4 nanoparticles were applied to the removal of Cr(VI) ions from aqueous solutions (Rao et al. 2013). Alternatively, Safarik et al. synthesized *Kluyveromyces fragilis* cells magnetized with a magnetic ferrofluid. The ferrofluid was composed of magnetic iron oxides nanoparticles with diameters ranging between 10 and 20 nm. A volume of 1 mL of ferrofluid was added to 3 mL of the yeast cells suspension in diluted acetic acid and the resulting suspension was mixed during 1 h at room temperature. The excess of ferrofluid was removed by sequential washes with acetic acid and water, until the supernatant was clear. The magnetized yeasts were then captured using a magnet and stored in water at 4 °C until its use.

2.7 Conclusions, Trends, and Perspectives

At present, a wide variety of biosorbents have been successfully applied for the removal of metal and metalloids pollutants from the environment, offering generally good removal percentages of contaminants and biosorption capacities. Typical materials that are used in decontamination processes, such as microorganisms, agricultural wastes, and plant derivatives will continue to be used as biosorbents because of the great advantages they have shown, i.e. low cost of material, biodegradability, reutilization for several biosorption-desorption cycles and the possibility of developing environmental friendly processes. However, the fast introduction of nanotechnology in several science areas is quickly offering new nanomaterials and nanoparticles that have special physical chemistry properties. This opens the possibility of preparing novel biosorption materials resulting from the combination of nanomaterials with biomass (microorganisms, bacteria, fungi, etc.) or by functionalization of their surface with selected biomolecules, which could provide higher retention capacity, physical and chemical stability, and add remarkable advantages (e.g. magnetic separation) for more efficient and straightforward application of these novel bio–nanohybrids materials in future large–scale processes. These notorious advantages could lead, in a near future, to a partial replacement of conventional biosorption materials by bio–nanohybrids materials. Furthermore, one of the main disadvantages of classical biosorbents is related to the lack of selectivity towards a specific metal, and even worse, towards a particular chemical species of an element. For this reason, there is a trend towards the development of new bio–materials that are capable to improve these negative aspects. In addition to nanotechnology, genetic engineering will continue to acquire a protagonist role in the decontamination field based on biosorption processes, as manipulated cells could speed up the removal of pollutants, show increased biosorption capacity and enhance the selectivity of the biosorbents towards specific metal and metalloids. Therefore, as time will go on, it is expected that new and better biosorption materials will progressively appeared in the literature.

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Chapter 3
Leaf Biosorbents for the Removal of Heavy Metals

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Abstract The presence of heavy metals in waters is a global concern. Among various remediation technologies, biosorption is an attractive and promising process since in many cases, it is fast, selective, and highly efficient. Other advantages, such as applicability for various types of pollutants, simplicity, low cost, ease of operation, and the potential reusability of the adsorbents, make it beneficial. Nowadays, more and more green materials, raw or modified, are inclined to be explored instead of conventional adsorbents, within concept of Green Chemistry. This review focuses on the use of leaves-based biosorbents in raw or modified forms to sequestrate heavy metals from waters and wastewaters.

One of the main points is that chemical agents such as acidic (e.g. HCl, HNO_3, H_2SO_4, and H_3PO_4), alkaline (e.g. NaOH and $NaHCO_3$), oxidative (like $KMnO_4$), metal salt (e.g. NaCl, $CaCl_2$, and $MgCl_2$), and organic (e.g. formaldehyde, monosodium glutamate, and anionic surfactant) agents are satisfactorily used in order to improve the adsorption capacity of leaf based adsorbents. The maximum monolayer adsorption capacity, at different initial experimental conditions, obtained from Langmuir isotherm for the studied heavy metals ranges between 3.9–300 mg/g and 7.8–345 mg/g for raw and modified leaf biosorbents, respectively. In most cases, the Langmuir and pseudo-second-order kinetic model give the best fit.

Thermodynamic studies show that the adsorption in all studied cases was spontaneous and mainly endothermic with increased randomness at the solid-liquid interface during the adsorption process. Moreover, an enthalpy-entropy compensation revealed the necessity to re-examine the way that the thermodynamic parameters are estimated. Column studies, the mechanism of adsorption, multiple biosorption/desorption cycles and the study of biosorption of multiple pollutant systems are some crucial issues that have been addressed in this work. There is a lack of knowledge on the application of the leaf biosorbents in more realistic conditions, such as in real wastewaters, for understanding their behavior in order to be applied for pilot scale and full scale systems.

3.1 Introduction

The continuous industrialization and urbanization during the last two centuries brought about one of the saddest and most dangerous realities that the world is facing in the modern history, environmental pollution. The uncontrolled contamination of the water with various pollutants was, is, and will be one of the most challenging environmental problems, since it has many direct and indirect negative impacts and implications on the flora and fauna. Disposal of heavy metals, such as Pb, Cr, Zn, Ni, Cd, and Cu, can be considered as one of the greatest global concern, due to their toxicity, persistence, and bioaccumulation tendencies (Arcibar-Orozco et al. 2014; Edokpayi et al. 2015; Kaprara et al. 2016).

The chemical treatment methods, such as ion exchange, precipitation, electrochemical processes, membrane filtration, or adsorption onto activated carbon, are even nowadays the conventional wastewater treatment processes for the removal of the heavy metals in large scaled applications (Deliyanni and Bandosz 2011; Li et al. 2013; Dimiropoulos et al. 2015; Gröhlich et al. 2017). However, these methods are expensive and, additionally, can lead to a further pollution load. During the last years, the attention of the research community has been being oriented to more advantageous, economically feasible, and environmental friendly technologies for the removal of the heavy metal from the wastewaters. Adsorption has been proven to be one of the most promising candidate, since it can reach high level of effectiveness, with a lower cost and simpler operational design of the procedure compared to the chemical methods (Przepiórski 2006). Moreover, the side effects on the environmental balance can be limited by the use of suitable materials and treatment processes.

Various plain or advanced materials have been extensively studied as potential adsorbents for removal of heavy metals from aqueous solutions (Kyzas and Kostoglou 2014; Gallios et al. 2017; Wen et al. 2017). However, in the last decades, the focus has been shifted towards designing and synthesizing environmentally-friendly adsorbents, in order to apply them on green remediation techniques. The most fundamental and characteristic properties concerning the selection of the most proper industrial-scale used adsorbents are: (i) natural availability and low cost of the precursors, (ii) simple and inexpensive production in a large scale without environmental impacts like the use of toxic compounds, (iii) reusability/regeneration, and (iv) biodegradability (natural disposal). Algae, fungal, agricultural wastes and residues, and bacterial stains are among the examined biosorbents which satisfactorily have been applied to decontaminate waters and wastewater polluted with heavy metals (Mudhoo et al. 2012; Okenicová et al. 2016).

A strategy that allows the harmonization with all the above conditions is the development of adsorbents/biomasses derived from abundant natural sources and agricultural or industrial wastes. According to EU Directive 2003/30/EC, biomass is referred to “the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste” (Deliyanni et al. 2015). Among the numerous investigated sources (Ogata et al. 2013; Anastopoulos and Kyzas 2014; Joshi and Sahu 2014; Arampatzidou and Deliyanni 2016; Kyzas et al. 2016; Spagnoli et al. 2017), leaves-based adsorbents have attracted an extensive research attention, since they have been found to have efficient and feasible biosorption performances against heavy metals. The leaves that do not have generally a potential for alternative applications except as natural fertilizers, can be converted to valuable biomass powders by simple and non-costly physical treatment.

A comprehensive screening in literature reveals that biomasses derived from different varieties of leaves possess satisfactory capability for the biosorption of heavy metals from aqueous solutions. Moreover, the chemical pretreatment of the biomass has been reported to play a crucial role on the removal capability. But, up to now and to the best of our knowledge, no review article exists in the literature focused on the remediation of heavy metals from wastewater using leaves derived biomass. The aim of the present work is to gather published data about using leaves-based biosorbents, along with evaluating and comparing the biosorption performances of various leaves-derived materials towards different heavy metal ions. An extensive discussion in terms of biosorption capacity, reusability/regeneration, characterizations and effect of biosorption parameters (like contact time, pH, temperature or the co-existence of other ions), biosorption mechanisms, and thermodynamic aspects will bring more light to the factors that play the most crucial role on the biosorption (Fig. 3.1).

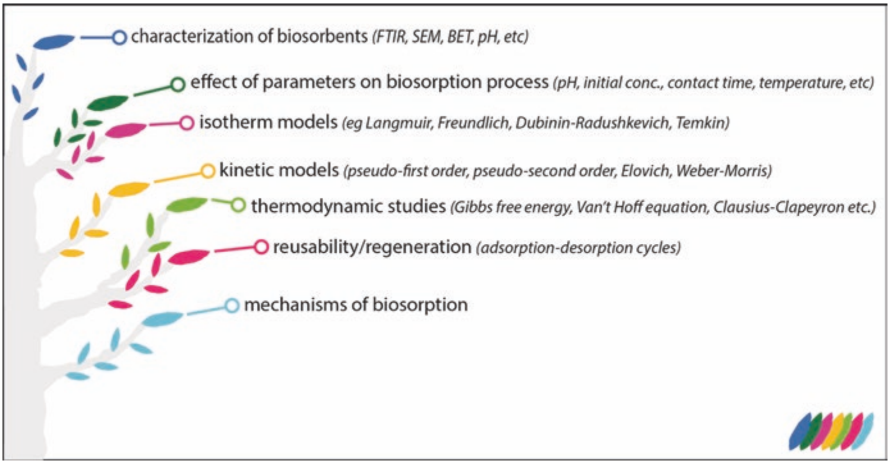


Fig. 3.1 A schematic representation of the included data and results in this work

3.2 Raw leaves as Biosorbents

3.2.1 General Comments for Raw Leaves as Biosorbents for Heavy Metal Removal

Leaf adsorbents (Table 3.1) are among the most studied biosorbents for the removal of metal ions, because leaves are considered as abundant, cheap and environmentally-friendly materials with a high sorption capacity (Chen et al. 2010; Edokpayi et al. 2015). However, these properties also apply to other biosorbent groups and, therefore, the preference of the studied leaf biosorbents must be justified by other arguments. For example, it has been often ignored that low mechanical strength could be an issue in full scale systems, as leaf particles can break down easily. In addition, the used methodology in most of the studies, especially in the last years, follow the same standard pattern and the given conclusions are trivial and without any insight into challenges or future directions. Therefore, the focus in this review is on researches where authors have applied less often used approaches and have taken steps to help to close the gap between the laboratory scale experiments and the application of biosorbents in full scale systems.

Surprisingly most of the studies have not included the comprehensive characterization data of the studied leaf biosorbents, as well as not thoroughly including of the process (also called system) parameters, such as pH and temperature of the solution. However, physicochemical properties of the biosorbent (e.g., specific surface area, ion exchange capacity, content of functional groups and the pH of the point of zero charge) can influence the sorption behavior and determines the maximum sorption capacity (Jorgetto et al. 2015). It should be also pointed out that high maximum sorption capacity and sorption behavior in general are not the only parameters determining suitability of a biosorbent for its utilization in full scale treatment systems. Concentration of heavy metals, availability of the biosorbent, hydraulic conductivity, mechanical strength and other parameters should be taken into consideration as well.

3.2.2 Characterization of Raw Leaf Biosorbents

The identification of functional groups can help researchers to explain the sorption capacity and sorption mechanism of the biosorbent (Kumar et al. 2006a). Kamar and co-authors (2017) concluded that carboxyl, amine, and hydroxyl groups are the major groups responsible for the biosorption process, when cabbage leave powder was used to remove Pb^{2+}, Cu^{2+} and Cd^{2+} ions in single and ternary systems. Besides the previously mentioned groups, amide and methyl groups have been mentioned as significantly important doers for metal ion binding (Mishra et al. 2010). Sawalha and co-workers (2007) suggested that biosorption system of saltbush leaves biomass could have more than one functional group, which is responsible for the metal binding.

Table 3.1 Comparison of maximum sorption capacity of raw leaf biosorbents and some process parameters

Adsorbent	Metal ion	Amount of adsorbent/volume of solution; initial metal concentration	Agitation speed; temperature	Maximum biosorption capacity; mg/g	Dominant isotherm/ kinetic model	Reference
Guava (*Psidium guajava*) leaves	Cd^{2+}	0.25 g/50 mL; 20–100 mg/L	250 rpm; 30–70°C	~ 12(exp.[a])	n/a/pseudo second-order	Abdelwahab et al. (2015)
Fig leaves	Cd^{2+}	0.1 g/50 mL; 5–1000 mg/L	n/a; 25°C	103.09(exp.)	Langmuir/pseudo second-order	Benaïssa (2006)
Sesame waste (leaf and stem parts)	Cd^{2+}	3.33 g dm^{-3}/30 mL; 2–1000 mg/L	240 rpm; 25 °C	84.74 (Langmuir) 22.88 (column studies)	Langmuir/pseudo second-order and pseudo second-order	Cheraghi et al. (2015)
Ficus religiosa leaves	Cd^{2+}	0.25 g/50 mL; 50–500 mg/L	n/a; 30°C	27.14 (Langmuir)	Langmuir/pseudo second-order	Rao et al. (2011)
Tobacco leaves	Cu^{2+}	~0.1–~0.9 g/100 mL; 5–50 mg/L	100–300 rpm; 20–50°C	10.66(exp.) 17.182 (Langmuir)	Langmuir/pseudo second-order	Çekim et al. (2015)
Tectona grandis L.f. leaves	Cu^{2+}	0.1 g/30 mL; 20–100 mg/L	180 rpm; room temperature	~ 10 mg/g (exp.) 15.43 (Langmuir)	Langmuir/pseudo second-order	Kumar et al. (2006b)
Ricinus communis leaves	Cu^{2+}	0.2 g/50 mL; 50–200 mg/L	120 rpm; room temperature	127.27(exp.)	Langmuir/pseudo second-order	Makeswari and Santhi (2014)
Melaleuca diosmifolia leaves	Cr^{6+}	0.1 g/20 mL; 100–500 mg/L	n/a; 24 °C	49.38 (exp.) 62.5 (Langmuir)	Langmuir/pseudo second-order	Kuppusamy et al. (2016)
Rubber leaves	Cr^{6+}	2 g/L/100 mL; 5–50 mg/L	120–130 rpm; 30–50 °C	21.45(exp.)	Langmuir/pseudo second-order	Nag et al. (2015)
Colocasia esculenta leaves	Cr^{6+}	0.08 g/50 mL; 20–100 mg/L	100 rpm; 303 K	43.61(exp.l)	Freundlich, Halsey/ pseudo second-order	Nakkeeran et al. (2016)
Ficus auriculata leaves	Cr^{6+}	0.5 g/50 mL; 20–100 mg/L	120 rpm; 303 K	6.80 (Langmuir)	Sips/pseudo second-order	Rangabhashiyam et al. (2015)
Castor tree (*Ricinus communis* L.) leaves	Hg^{2+}	0.25 g/100 mL; 5–100 mg/L	n/a; room temperature	37.2(exp.)	Langmuir/n/a	Al-Rmalli et al. (2008)

Bamboo leaves	Hg^{2+}	200 mg/100 mL; 100–250 mg/L	500 rpm; 300 K	27.11(exp.)	Freundlich and Temkin/pseudo second-order	Mondal et al. (2013)
Tomato (*Lycopersicum esculent*) leaves	Ni^{2+}	n/a/50 mL; 30–90 mg/L	180 rpm; 303 K	58.82 (Langmuir)	Langmuir/pseudo second-order	Gutha et al. (2015)
Syzygium cumini L leaves	Pb^{2+}	0.1 g/30 mL; 20–100 mg/L	180 rpm; 30 °C	32.47 mg/g (Langmuir)	Langmuir/pseudo second-order	King et al. (2007)
Phoenix tree leaves	Pb^{2+}	200 mg/40 mL; 0–1000 mg/L	150 rpm; 30 °C	71.0 (Langmuir)	Langmuir–Freundlich/ intraparticle diffusion	Liang et al. (2016)
Black tea leaves	Pb^{2+}	1 g/100 mL; 1–50 mg/L	200 rpm; 20 °C	19.7(exp.)	Freundlich/pseudo second-order	Mohammed et al. (2016)
Ficus religiosa leaves	Pb^{2+}	0.5 g/100 mL; 10–1000 mg/L	200 rpm; 25 °C	37.45 (Langmuir)	Langmuir/pseudo second-order	Qaiser et al. (2009)
Solanum melongena leaves	Pb^{2+}	0.4 g/L/n/a; 30–90 mg/L	180 rpm; 303–323 K	71.42 (Langmuir)	Langmuir/pseudo second-order	Yuvaraja et al. (2014)
Neem (*Azadirachta indica*) leaves	Pb^{2+}	0.8 g/L/50 mL; 50–150 mg/L	n/a; 300 K	300 (Langmuir)	Langmuir/pseudo second-order	Bhattacharyya and Sharma (2004)
Bael (*Aegle marmelos*) leaves	Pb^{2+}	0.2 g/50 mL; 8.7–180.2 mg/L	120 rpm; 303 K	104(exp.)	Langmuir/pseudo second-order	Chakravarty et al. (2010)
Cinnamomum camphora leaves	Pb^{2+}	0.05 g/25 mL; 50–400 mg/L	120 rpm; 333.2 K	75.82(exp.)	Langmuir/pseudo second-order	Chen et al. (2010)
Diceriocaryum eriocarpum leaves	Pb^{2+}	1.0 g/n/a; 1–50 mg/L	250 rpm; 298 K	41.9 (Langmuir)	Langmuir/pseudo second-order	Edokpayi et al. (2015)
Brazilian Orchid Tree (*Pata-de-vaca*) leaves	Cu^{2+} Cd^{2+}	20 mg/1.80 mL; 1–400 mg/L	n/a; 25 °C	0.238 mmol/g (exp.) 0.113 mmol/g (exp.)	Langmuir/pseudo second-order	Jorgetto et al. (2015)

(continued)

Table 3.1 (continued)

Adsorbent	Metal ion	Amount of adsorbent/volume of solution; initial metal concentration	Agitation speed; temperature	Maximum biosorption capacity; mg/g	Dominant isotherm/kinetic model	Reference
Cabbage leaves	Pb^{2+} Cu^{2+} Cd^{2+}	0.5 g/50 mL; 0–100 mg/L	200 rpm; 25 °C	6.081 mg/g (exp.) 5.493 mg/g (exp.) 4.843 mg/g (exp.)	Langmuir/pseudo second-order	Kamar et al. (2017)
Oak leaves (in mixture with fern bark and rice husks)	Cu^{2+} Ni^{2+} Mn^{2+} Zn^{2+} Cr^{6+}	1 g/150 mL; 6–400 mg/L	150 rpm; 25 °C	32.52 (Langmuir) 3.90 (Langmuir) 4.68 (Langmuir) 6.82 (Langmuir) 23.80 (Langmuir)	Langmuir/pseudo first-order	Rosales et al. (2015)
Arborvitae leaves	Pb^{2+} Cu^{2+} Co^{2+}	0.1 g/50 mL; 5–30 mg/L	150; 303 K	35.84 (Langmuir) 7.94(Langmuir) 6.78 (Langmuir)	Langmuir/n/a	Shi et al. (2016)
Mistletoe leaves	Pb^{2+} Cd^{2+}	0.1 g/50 mL; 10–210 mg/L	250 rpm; 318 K	68.53 (Langmuir) 50.07 (Langmuir)	Langmuir/pseudo second-order	Suc and Son (2014)
Teak (*Tectona grandis*) leaves	Ni^{2+} Co^{2+}	0.6 g/100 mL; 25–200 mg/L	150 rpm; 303–323 K	18.112 (Langmuir) 27.215 (Langmuir)	Langmuir/pseudo second-order	Vilvanathan and Shanthakumar, (2016)

The biosorption of the examined heavy metals onto raw leaf biosorbents at different experimental conditions followed in most cases the Langmuir isotherm. The biosorption kinetics was best described by the pseudo second-order. The maximum monolayer adsorption capacity obtained from the Langmuir isotherm for the studied heavy metals ranged from 3.9 to 300 mg/g

n/a not available

[a] Experimental

Specific surface area is another important parameter which determines the maximum sorption capacity – with the increase of the specific surface area, the increase in the sorption capacity is observed (Kumar et al. 2006a; Shi et al. 2016). Some of the reported specific surface areas (S_{BET}) (BET: Brunauer, Emmett and Teller) are: 0.96 m^2/g for teak leaves (Vilvanathan and Shanthakumar 2016), 3.33 m^2/g for taro leaves (Nakkeeran et al. 2016), 6.14 m^2/g for sacred fig leaves (Qaiser et al. 2009) and 29.52 m^2/g for arborvitae leaves (Shi et al. 2016).

The pH of the point of zero charge (pH_{PZC}) is the main property that specifies the electrical neutrality of the biosorbent at a particular value of pH (Cheraghi et al. 2015) and can help researchers to explain the effect of pH of the solution (Mondal et al. 2013; Zolgharnein et al. 2016) and obtain more information about surface characteristics (Jorgetto et al. 2015; Rosales et al. 2015). In addition to the above-mentioned parameters, other properties have been also investigated, such as the morphology of the particles, their size distribution, porosity and the composition of the adsorbent, which have been investigated through different techniques such as scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), surface area measurements, infrared spectroscopy and elemental analysis of C, H, N and S (Jorgetto et al. 2015).

3.2.3 Effect of Contact Time, pH and Temperature on Heavy Metal Removal by Raw Leaf Biosorbents

When tested material is being evaluated as a potential sorbent in a fixed bed or any other type of flow through system, kinetic performance is the most important data to be considered (Qiu et al. 2009). We have found that the minimum time to reach sorption equilibrium has been 10 min (King et al. 2007), when teak leaves were used for the removal of Cu^{2+} ions, but the maximum – 20 h (Liang et al. 2016), when the biosorption of Pb^{2+} by oriental arborvitae leaves was studied. Edokpayi and co-workers (2015) reported that the biosorption equilibrium has been reached in 60 min, when the removal efficiency reached 98.36%, however in the first 5 min already 97% of Pb^{2+} were adsorbed. Equilibrium time of 180 min have been reported by several authors (Kumar et al. 2006a; Nag et al. 2015), as well as 240 min (Benaïssa 2006).

The pH of the aqueous media has been also regarded as the most important variable governing metal adsorption by adsorbents (Makeswari and Santhi 2014). The pH can affect the form and the quantity of metal ions in water and the form and quantity of an adsorbent's surface sites (Chen et al. 2010). In general, results from leaf biosorption studies, where removal of metal cations has been studied, are in good agreement with the well-known explanation of competition between H^+ ions and metal ions in the solution. At lower pH values H^+ ions compete with metal ions for adsorption sites in the sorbent. When the pH of the solution is increased, the hydronium ion concentration in the solution decreases and, as a result, an increase of metal uptake is observed. For example: (1) adsorption efficiency of Pb^{2+} increased from 11.16 to 89.28% with the pH increase from 1.79 to 4.80 (Shi et al. 2016; (2) with the increase in initial pH from 2.0 to 5.0, the % Cd^{2+} adsorption increased from 1.38 to 77.4% (Rao et al. 2011; (3) the percentage removal of Pb^{2+} increased from 8.89 to 96.06% with an increase of pH from 2 to 5 (Yuvaraja et al. 2014). Some results seemingly reveal slight effect of the pH which is due to the fact that high removal efficiency was observed already at lower pH values. For example, Edokpayi and co-workers (2015) observed in their studies that the removal efficiency at pH 2 was 98.22%, but at pH 6 the removal efficiency was 98.69%. Beyond a certain pH value, precipitation reactions instead of adsorption can start to take place, as most heavy metals precipitate as hydroxides, therefore metal species at the given conditions must be identified.

Controversial results have been obtained regarding the effect of temperature on the sorption capacity. Most of the authors have concluded that the maximum adsorbent capacity increased with the increase in temperature (Chakravarty et al. 2010; Chen et al. 2010; Gutha et al. 2015; Rangabhashiyam et al. 2015; Yuvaraja et al. 2014). According to the reference (Suc and Son 2014) this phenomenon has the following explanation: "*this is due to the increase in the number of available active sites on the adsorbent and the decrease in boundary layer thickness surrounding the adsorbent leading to reduction in the mass transfer resistance of adsorbate in the boundary layer*". However, opposite results (i.e., the decrease of the sorption capacity with the increase of temperature) also have been observed (Bhattacharyya and Sharma 2004; Qaiser et al. 2009; Abdelwahab et al. 2015). Slight, but not significant, increase in Cr^{6+} removal by Green honey-myrtle leaves with increasing temperature was observed by Kuppusamy and co-workers (2016) (i.e., removal was independent of the temperature). Similar effect was observed also by other researchers (Mondal et al. 2013; Çekim et al. 2015). Interesting results were observed by Hymavathi and Prabhakar (2017) – the sorption capacity increased when the temperature was changed from 9.85 to 29.85 °C, however the further increase of the temperature did not result in the increase of the sorption capacity, which was linked to the structural deformations of the *Cocos nucifera* leaves. Mohammed et al. (2016) reported that their research team and several other groups of workers have observed similar results.

3.2.4 Mechanism of Biosorption of Heavy Metals onto Raw Leaf Biosorbents

Biosorption mechanisms have been identified in relatively few studies, and it seems that most of these studies have concluded that ion exchange is the main mechanism involved in the removal of metal ions from aqueous solutions. It has been justified by the release of Ca^{2+}, Mg^{2+} and Na^{1+} ions during the biosorption process (Qaiser et al. 2009; Liang et al. 2016) or by the fact that the use of acidic solutions has been effective for the desorption of adsorbed metal ions (Rosales et al. 2015). It is worth reminding that ion exchange process can be regarded as a subtype of chemisorption (Michalak et al. 2013), but not as a stand-alone process, therefore researchers should always specify what is meant by the term *"chemisorption"*. For example, Zolgharnein and co-workers (2015) stated the following: "*… it could be concluded that about 78 % of biosorption mechanism of Pb(II) by C. speciosa tree leave is handled by chemisorption (ion exchange)*". Some authors have concluded that physisorption is the main mechanism responsible for the removal of metal ions by leaf biosorbents, such as arborvitae leaves (Shi et al. 2016). Chemisorption (including complexation) has been also reported as the responsible mechanism (Mahmoud et al. 2016). It must be taken into consideration that several mechanisms can take place in parallel in different combinations, like ion exchange and chemisorption (Bhattacharyya and Sharma 2004), that the proportion of the involved mechanisms can change when process parameters (such as temperature or initial metal concentration) are changed (Chen et al. 2010). Also it should be mentioned that relatively few studies have investigated the biosorption mechanisms, and a correct identification of the biosorption mechanisms in leaf biosorbents is still a challenge and further investigation is needed.

3.2.5 Effect of Co-existing Ions on Heavy Metal Removal by Leaf Biosorbents

Wastewater contains different ions (such as, Mg^{2+}, Ca^{2+}, and Fe^{2+}) which may decrease the sorption effectiveness of the adsorbents, as these ions compete for the sorption sites with the metal ions present in the wastewater. Therefore, studies must also include the use of real wastewater (or other polluted aqueous media) in addition to synthetic solutions. However relatively few studies have used this approach. Yakout and co-workers (2016) observed that the removal efficiency of Co^{2+} and Ni^{2+} ions by mango (*Mangifera indica* L.) leaves from the industrial wastewater sample was lower than the other water samples due to the possibility of high contamination of the industrial sample with other competitive interfering ions. Edokpayi and co-workers (2015) observed that, when effluent from waste stabilization ponds was used, the removal efficiency was almost as high as when simulated aqueous samples were used. The removal efficiency in the first situation was in the range of 95.8% and 96.4%, but for the simulated aqueous samples it was 95–98.9%. Studies by Kuppusamy and co-authors (2016) showed almost complete removal of Cr^{6+} from real environmental samples.

3.2.6 Heavy Metal Removal by Leaf Biosorbents Using Column Studies

To test the suitability of biosorbents for using in full scale systems, column studies are one of the first steps to be taken (Table 3.2). Results from these studies are usually described by a breakthrough curve, which shows the history of the effluent concentration. This allows to estimate the sorption capacity and to optimize the process and design parameters. For example, it has been reported that the sorption capacity was 35.5 mg/g, which was very close to that obtained from batch equilibrium experiments (37.2 mg/g), when leaves of castor tree was used for the removal of Hg^{2+} ions (Al-Rmalli et al. 2008). In general, breakthrough curves are affected by the flow rate, bed height, and initial metal ion concentration. For example, it has been reported that the column breakthrough time was reduced from 39 to 6 h with the increase in flow rate from 5 to 20 mL/min (Qaiser et al. 2009). Mondal and his co-workers (2013) observed that the breakthrough increased from around 15 to 21 h, when the bed depth was increased from 5 to 8 cm, using the same flow rate of 0.2 L/h. In addition, column breakthrough data can be analysed using different models, such as the Bed depth service time (BDST) and the Thomas models (Qaiser et al. 2009).

Table 3.2 Effect of some parameters for biosorption of heavy metals by raw leaf biosorbents using column studies

Metal	Adsorbent	Amount of adsorbent; g	Height/diameter of column; cm	Initial metal concentration; mg/L	Flow rate; mL/min	Reference
Cu^{2+}	Boston fern (*Nephrolepis exaltata* Schott *cv. Bostoniensis*) leaves	0.2	n/a/0.6	50	1	Rao and Khan (2017)
	Maple tree (*Acer saccharum*) leaves	40	27/3.42	15–110	5–30	Amirnia et al. (2016)
Cd^{2+}	Sesame leaves and stems	4.0	30/2.2	60	2.5	Cheraghi et al. (2015)
Cr^{6+}	Rubber tree (*Hevea brasiliensis*) leaves	2.5	50/1.5	10	5–20	Nag et al. (2015)
Pb^{2+}	Sacred fig (*Ficus religiosa*) leaves	118	50[a]/5	100	5–20	Qaiser et al. (2009)
Hg^{2+}	Castor tree (*Ricinus communis* L.) leaves	1.0	30/1.0	100	2	Al-Rmalli et al. (2008)

n/a not available

[a] Bed height

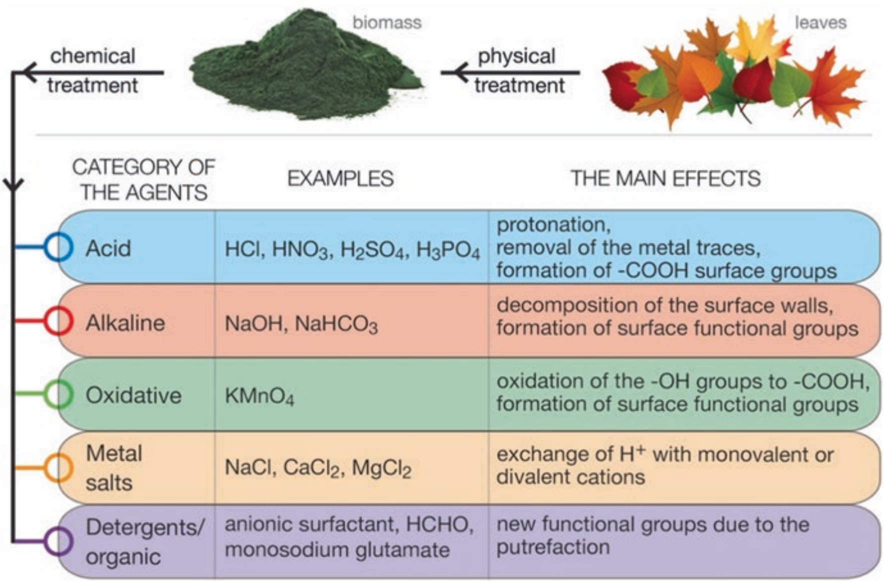
3.3 Modified Leaf Biomass as Heavy Metal Biosorbents

3.3.1 Methods of Leaf Biomass Pretreatment

The pretreatment of the leaf biomass has an ultimate goal to improve the biosorption efficiency. The most valuable and widely studied pretreatment of leaf biomass is the chemical modification, due to the low cost and the procedure easiness, and is a one-step process in the most of the cases. The most used reagents/solutions which have been frequently applied in one-stage pretreatment processes, can be categorized to the following groups: (1) acids (HCl, HNO_3, H_2SO_4, H_3PO_4), (2) bases (NaOH, $NaHCO_3$), (3) oxidizing agents ($KMnO_4$), (4) inorganic salts (NaCl, $CaCl_2$, $MgCl_2$), and (5) organic agents/detergents (anionic surfactants, formaldehyde, monosodium glutamate). The use of each pretreatment process aims to a specific effect like to improve the chemical surface heterogeneity, enhance the number and dispersion of the functional groups available for binding with the metal and/or alter the surface morphology; thus the useful pretreatment method should be chosen according to the targeted metal ion. Moreover, in addition to changes in the sorption properties resulted from pretreatment or modification techniques, chemical modification of the biomass can improve its stability and prevent the leaching of organic compounds when applied in real biosorption conditions. In this part, we tried to gather and compare the effect of the above mentioned categories of the chemical reagents on the biosorption performance. The main chemical pretreatment categories, along with some examples of the used agents, and their most vital effects on the biomass can be seen in Fig. 3.2.

3.3.1.1 Acid Pretreatment

Pretreatment of the raw obtained powder with various acids has been found to be the most widely applied modification method. The formation of free carboxyl groups is the most reported result, responsible for the enhancement of the biosorption performance. Treatment of the leaves of marine plant *Posidonia oceanica* with HCl resulted in an increase of the maximum biosorption capacity of Cd^{2+} to 1.1 mmol/g, compared to 0.69 mmol/g for the untreated natural biomass. This was linked to the resulted protonation, but it led to a significant weight loss of ca. 50% (Meseguer et al. 2016). Biosorption of Cu^{2+} onto *Marrubium globosumsubsp. globosum* (MGSG) leaves was also significantly enhanced after modification with 0.5 M H_2SO_4 and HNO_3 by 11.8% and 10.2%, respectively and compared to the capacity of the raw biomass (8.54 mg/g), while pretreatment with formic acid did not stimulate the biosorption capacity (Yazıcı et al. 2008). It is worthy to point out that the weight loss after the pretreatment of MGSG leaves with H_2SO_4, HNO_3, or HCOOH was in the range between 24% to 27%. The treatment of *Imperata cylindrica* leaf powder with H_2SO_4 or H_3PO_4 showed also very high biosorption performance against Ni^{2+}, with biosorption capacities around 19.2 mg/g (Li et al. 2013).



CATEGORY OF THE AGENTS	EXAMPLES	THE MAIN EFFECTS
Acid	HCl, HNO_3, H_2SO_4, H_3PO_4	protonation, removal of the metal traces, formation of -COOH surface groups
Alkaline	NaOH, $NaHCO_3$	decomposition of the surface walls, formation of surface functional groups
Oxidative	$KMnO_4$	oxidation of the -OH groups to -COOH, formation of surface functional groups
Metal salts	NaCl, $CaCl_2$, $MgCl_2$	exchange of H^+ with monovalent or divalent cations
Detergents/ organic	anionic surfactant, HCHO, monosodium glutamate	new functional groups due to the putrefaction

Fig. 3.2 A collective representation of the main chemical pretreatment categories, along with some examples of the used agents, and their most vital effects on the biomass

In another study, citric acid ($C_6H_8O_7$) was used as modification agent to attach additional free carboxyl groups on the hydroxyl groups of polysaccharide matrix of cellulosic waste biomass of *Moringa oleifera* (Reddy et al. 2012). It is well known that carboxyl-rich biosorbents exhibit a higher capacity for heavy metals because of the additional carboxyl groups after pretreatment which enhance complexation with metals ions. The received biomass prepared from acid modified *Moringa oleifera* leaves presented high experimental biosorption capacities against Cd^{2+} (20.9 mg/g), Cu^{2+} (16.0 mg/g), and Ni^{2+} (14.1 mg/g).

Interestingly, the pretreatment with a strong acid reported to have in some cases a negatively effect on the biosorption performance (Dabbagh et al. 2016). Specifically, the pretreatment of *Ficus carica* leaves (FCLs) with HCl led to a significantly removal decrement of Co^{2+} ions of about 32% in pH 7, compared to the biosorption capacity of raw powder obtained from the FCLs (17.5 mg/g). This was linked to a decline in the electronegativity of biomass surface.

3.3.1.2 Alkaline Pretreatment

Biosorption of Cu^{2+} onto *Marrubium globosum subsp. globosum* leaves was also studied after pretreatment with alkali solutions such as NaOH and $NaHCO_3$ (Yazıcı et al. 2008). Compared to the pretreatment with acidic solution, the use of base had a more enhanced impact on the capacities. After the modification with NaOH, the sorption capacity reached 12.45 mg/g that is 45.8% higher than the raw material, while modification with $NaHCO_3$ led to an increase of 43.9%. The main drawback was the biomass loss by 48% after the modification with the strong base while the use of $NaHCO_3$ led to a smaller biomass loss (30%).

According to Reddy et al. (2012), the darker color after treatment of *Moringa oleifera* leaves with NaOH and citric acid was indicative of degradation of cellulose, hemicellulose and lignin (Reddy et al. 2012). Modification with NaOH of biomass derived from *Desmostachya bipinnata* (kush grass) leaves (MDBL) and *Bambusa arundinacea* (bamboo) leaves (MBAL) had also a positive effect on the biosorption of Cd^{2+} (Pandey et al. 2015). The q_{max} calculated based on the Langmuir model was found to be 15.2 mg/g for MDBL and 19.7 mg/g for MBAL at room temperature. Alkaline treatment (NaOH) of the biomass derived from *Michelia Champaca* leaves also found to have a positive impact on the removal of Cr^{6+}, but lower than that of the acid treatment (HCl) (Jayaraman 2015).

3.3.1.3 Pretreatment with Oxidizing Agent

The most commonly used oxidizing agent applied on the chemical modification of the leaves derived biomass was potassium permanganate. An increased ion exchange capacity for Pb^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+} was found for $KMnO_4$ and phosphorylation (incorporation of phosphate groups) treated banana leaves (El-Gendy et al. 2013). The derived biomass of banana leaves treated with 0.8 M $KMnO_4$ exhibited higher removal efficiencies than that of the raw biomass in the order of $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$ (% values are not available in text, but they could be estimated approximately in Figures). The higher biosorption of Pb^{2+} was attributed to the higher atomic number of Pb^{2+} ion (207) than that of Cu^{2+} (63).

It was also observed that the biosorption of the same metals by phosphorylated banana leaves treated with $KMnO_4$ was higher than the phosphorylated untreated leaves following the same order of $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$. On the other hand, phosphorylated banana leaves adsorbed the metal ions more effectively than the biomass treated only with $KMnO_4$ (El-Gendy et al. 2013). The authors linked the biosorption performance to the presence of two functional groups, phosphate and carboxyl. The simultaneous presence of these two groups had a more positive impact rather than the existence of each of them alone.

The formation of carboxylic groups on the active surface was also reported when the powder derived from rubber leaves was treated with $KMnO_4$, due to the oxidation of the primary alcohol groups (Kamal et al. 2010). Further treatment with Na_2CO_3 led to the conversion of the carboxylic acid (-RCOOH), ester (-RCOOR′) and unreacted hydroxyl (-R-OH) groups to $–COO\text{-}Na^+$ and $–RO\text{-}Na^+$. The latter groups were acted as the biosorption sites of Pb^{2+}, via chemical adsorption and/or ion exchange mechanisms. The rubber leaves biomass pretreated with $KMnO_4$ and Na_2CO_3 presented a much higher maximum theoretical adsorption capacity (95.3 mg/g) for lead, based on Langmuir model, compared to all the other reported mineral and biomass adsorbents.

3.3.1.4 Metal Salts

Another effective and low-cost pretreatment found to be the use of metal salts such as $MgCl_2$, NaCl, and $CaCl_2$. The pretreatment with these salts has as a main target to exchange the H^+ ions of the active binding sites with Na^+, Mg^{2+}, or Ca^{2+} ions. This substitution can favor the biosorption of heavy metals, since the exchange of above-mentioned cations by the heavy metals ions can be easier and faster compared to the exchange of H^+.

The pretreatment of *Ficus carica* leaves (FCLs) with 0.1 M $MgCl_2$ resulted in a 1.7 fold increase of experimental q_e for Co^{2+}, from 20.2 mg/g (at optimum pH 4) to 33.9 mg/g (pH 6) (Dabbagh et al. 2016). The q_{max} based on the Langmuir model for the $MgCl_2$-modified material estimated to be 82.64 mg/g. This value is the highest compared to the values obtained from various other materials that have been reported as biosorbents of Co^{2+}. Based on the FTIR and XRF analysis results of the initial and the spend samples, the authors concluded that the sulfonic acid groups and the incorporated Mg^{2+} ions played the key role for the binding and removal of the cobalt ion via ion-exchange phenomenon. Unfortunately, the authors did not provide a comparison of the raw biomass with the biomass after the treatment, in order to determine the changes that were occurred with the use of the salts.

In another study, the pretreatment of *Marrubium globosum subsp. globosum* leaves powder with solutions of NaCl or $CaCl_2$ (0.5 M) resulted in an increased biosorption capacity of Cu^{2+} in comparison with raw biomass by 31.38% and 26.69%, respectively (Yazıcı et al. 2008). The higher performance of the NaCl modified sample rather than the sample treated with $CaCl_2$ was due to the weaker interaction of the monovalent sodium cations with the active binding sites of the biomass compared to the divalent calcium ions. As a result, the ion exchange of Na^+ with the Cu^{2+} is faster and more favorable compared to the ion exchange of Ca^{2+}. The same conclusions were reported from Chubar et al. (2004) in the case of the cork biomass pretreatment with the same agents (Chubar et al. 2004). In the case of NaCl, the biosorption capacity against Cu^{2+} was improved by 30% compared to the raw biomass, while the use of $CaCl_2$ did not lead to an increment of the biosorption performance.

The presence of cations like Na^+, K^+, Mg^{2+} and Ca^{2+} can interfere with the biosorption of heavy metals. It is possible that these cations are present in the real wastewater or they can be released during the biosorption of the heavy metals by the pretreated biomass with NaCl, KCl, $MgCl_2$ and $CaCl_2$. The biosorption capability for Cd^{2+} by natural and modified non-living leaves of *Posidonia oceanica* was examined with the individual presence of Na^+, K^+, Mg^{2+} and Ca^{2+} ions (Meseguer et al. 2016). The cadmium adsorption was slightly affected by the presence of potassium or sodium ions. At the highest studied concentration (800 mg/L) of Na^+ or K^+, the biosorption decrement was less than 10% for both monovalent cations. On the contrary, the presence of the divalent cations had an intensely negative effect on the uptakes, even at low concentration (100 mg/L) of them. At the highest studied concentration (800 mg/L), the decrease of the removal percentage was reached 60% in the case of Ca^{2+}, while the negative effect was even more pronounced in the case of Mg^{2+} (78%).

3.3.1.5 Pretreatment with Detergents/Organic Agents

The usage of commercial laundry detergent as pretreatment agent found to be another efficient strategy in order to improve the biosorption capability. Oil palm leaf powder (*Elaeis guineensis*) was modified with 2% solution of the anionic surfactant sodium dodecyl benzene sulfonate (SDBS) (Rafatullah et al. 2011). Even though the study did not offer a comparison of the materials before and after the treatment with SDBS, it is worthy to point out that the maximum adsorption capacity of Cu^{2+} was found to be 75.98 mg/g, based on the Freundlich model. Biosorption of Cu^{2+} onto *Marrubium globosumsubsp. globosum* (MGSG) leaves was also notably increased by 11.8% compared to the capacity of the raw biomass (8.54 mg/g, experiment in batch reactor), after the pretreatment with commercial laundry detergent solution (Yazıcı et al. 2008). The pretreatment with the detergent led to the greatest improvement compared to various agents that were tried in this study for chemical modification of the raw biomass, such as HCl, HNO_3, CH_2O_2, NaOH, $NaHCO_3$, NaCl, or $CaCl_2$. The excessive weight loss after the treatment (50%) suggests that putrefaction of biomass was occurred. The possible removal of proteins, polysaccharides and lipids that mask the binding sites and the formation of new functional groups can be the reasons behind the improved biosorption performance after the pretreatment. The pretreatment of cork biomass with the commercial laundry detergent solution led also to an improved removal of Cu^{2+} and Ni^{2+} performance (Chubar et al. 2004).

Finally, the pretreated biomass with organic agents presented to have efficient biosorption capabilities. In the case of *P. oceanica* leaves, the maximum biosorption capacity for Cd^{2+} increased from 0.69 mmol/g for raw biomass to 0.82 mmol/g (92.17 mg/g) for formaldehyde-treated biomass (Meseguer et al. 2016). Moreover, the modification of rubber (*Hevea brasiliensis*) leaves with formaldehyde solution led to a satisfactory biosorption performance of copper ions from aqueous solutions (Ngah and Hanafiah 2009). Monosodium glutamate modified rubber leaf powder (MGRL) revealed an elevated biosorption capability of Pd^{2+} (125.82 mg/g based on Langmuir model, and 94.82 mg/g based on batch experiments), which was higher than that of the citric acid modified rubber leaf biomass (Fadzil et al. 2016).

3.3.1.6 Alternative Reported Pretreatments

The leaves derived biomass or its pretreated counterpart can be modified to activated carbons with high porosity. Some examples, in which the finally obtained carbonaceous samples found to possess enhanced biosorption performance against various metals, are amorphous carbon derived from polyethylenimine-functionalized oil palm leaves and H_2SO_4 activated carbon derived from palm tree leaves (El-Sayed and Nada 2017; Soliman et al. 2016). However, it is out of the scopes of this study to examine in details the biosorption on carbons. Another strategy that was barely examined is the incorporation of nanoparticles into the biomass. An interested example is the magnetically modified *Aloe vera* leaves derived after treatment with

Fe_3O_4 nanoparticles, which exhibited a higher capacity for Pb^{2+}, Cu^{2+}, Cr^{3+} and Zn^{2+} compared to the raw biomass (Abedi et al. 2016). The benefit of the addition of the magnetic iron based nanoparticles is that the separation of the exhausted biomass will be an economically feasible procedure in some real applications.

3.3.2 General Results/Findings for Modified Leaf Biosorbents

The potential use of modified leaf biosorbents for heavy metal removal was examined under various operational conditions, while various experimental parameters were examined (different pH, temperature, contact time, initial solute concentration, and biosorbent dose). Another important experimental parameter not examined or taken into consideration in the most of the studies, but it was found to play a crucial role on the adsorption performance in others (Li et al. 2013), is the particle size of the biomass powder. Two different strategies during the preparation of the raw biomass was followed. The first one was to control the particle size of the biomass in a specific range by sieving. The most commonly range was between 250 and 500 μm. The second one is to collect and use the powder of less than a specific maximum in size value. Different maximum particle sizes were reported, such as 500, 180, 100, or even 80 μm. Not controlling the minimum size of the particles hides some risks during the biosorption experiments, especially on the correct flow in the column tests.

The study of heavy metal biosorption kinetics is important in order to determine the required equilibrium time of the process and to obtain information about the adsorption mechanisms and rate determining steps. The determination of biosorption rate can contribute to prediction of residence time of adsorbate at the solid-solution interface helping to design the appropriate water or wastewater treatment process. It was observed that the equilibrium time of heavy metal adsorption by modified leaves ranged between 20 and 180 min. The fast biosorption in the initial period of the process was followed by a slower biosorption due to slower diffusion of metal ions into the biosorbent interior. A very rapid biosorption of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cr^{3+} from aqueous solutions was observed by magnetically modified *Aloe vera* leaves ash, reaching equilibrium in 10 min (Abedi et al. 2016). This fast rate was attributed to the biosorption on the external surface. On the other hand, different treatments of the same biomass did not show to affect the equilibrium time as observed in H_2SO_4 and H_3PO_4 treated *Imperata cylindrica* leaf powder (Li et al. 2013).

The kinetic data of biosorption studies were summarized in Table 3.3, and they were evaluated by kinetic adsorption models, which assume chemical reactions or diffusion mechanisms as rate limiting steps. Regarding the chemical reaction based models used (pseudo-first order, pseudo-second order, Elovich and first order reversible model), it was observed that in the majority of studies biosorption of heavy metal was described by the pseudo-second order model assuming chemisorption as rate limiting step (Abedi et al. 2016; Dabbagh et al. 2016; El-Sayed and Nada 2017; Reddy et al. 2012). However, the pseudo-first order model described

Table 3.3 Isotherm, pretreatment methods, characterization techniques and maximum adsorption of modified leaf biosorbents

Biosorbent	Metal ion	Pretreatment	q_e or q_{max} (mg/g)	Isotherm model	Characterization technique	Reference
Spent tea leaves (*Camellia sinensis*)	Cu^{2+}	0.05 M $Ca(OH)_2$	7.81^a	Langmuir	SEM, S_{BET}, FTIR	Ghosh et al. (2015)
Oil palm leaf powder (*Elaeis guineensis*)	Cu^{2+}	Anionic surfactant (2% SDBS)	86.95^a 75.98*	Freundlich	SEM	Rafatullah et al. (2011)
Rubber (*Hevea brasiliensis*)	Cu^{2+}	37% Formaldehyde (HCHO)	8.36^a	Langmuir	FTIR, SEM-EDX, S_{BET}, carbon, hydrogen and nitrogen analyzer	Ngah and Hanafiah (2009)
Marrubium globosum subsb. *globosum*	Cu^{2+}	0.5 M NaOH	12.45^b	n.g.	FTIR	Yazıcı et al. (2008)
		0.5 M $NaHCO_3$	12.29^b			
		0.5 M H_2SO_4	9.55^b			
		0.5 M HNO_3	9.41^b			
		0.5 M Formic acid (CH_2O_2)	8.57^b			
		0.5 M NaCl	11.22^b			
		0.5 M $CaCl_2$	10.82^b			
		Commercial laundry detergent	12.46^b			
Activated carbonfrom palm tree leaves (*Phoenix dactylifera*)	Pb^{2+}	25% (w/w) H_2SO_4	61.15^a	Langmuir	FTIR, S_{BET}, SEM	Soliman et al. (2016)
Tephrosia purpuria	Pb^{2+}	0.1 M HNO_3	76.9^a	Langmuir	FTIR, SEM-EDAX	Madala et al. (2015)
Rubber leaf powder (*Hevea brasiliensis*)	Pb^{2+}	0.2 M Citric acid (CARL)	97.19^a 87.62^b	Freundlich	FTIR, SEM-EDX, S_{BET}, Elemental analyzer	Fadzil et al. (2016)
Rubber leaf powder (*Hevea brasiliensis*)	Pb^{2+}	Monosodium glutamate (MGRL)	125.82^a 94.82^b	Langmuir	FTIR, SEM-EDX, S_{BET}, Elemental analyzer	Fadzil et al. (2016)

(continued)

Table 3.3 (continued)

Biosorbent	Metal ion	Pretreatment	q_e or q_{max} (mg/g)	Isotherm model	Characterization technique	Reference
Rubber leaf powder (*Hevea brasiliensis*)	Pb^{2+}	Xanthation process	81.06^b 35^c	n.g.	TGA	Khalir et al. (2012)
Rubber leaf powder (*Hevea brasiliensis*)	Pb^{2+}	0.1 M $KMnO_4$ followed by 0.1 M Na_2CO_3	95.3^a	Langmuir	FTIR, SEM-EDX	Kamal et al. (2010)
Moringa oleifera tree leaf powder	Pb^{2+}	0.1 N NaOH followed by citric acid (CA)	186.63^a	Langmuir	SEM, FTIR, Elemental analysis	Reddy et al. (2010)
Moringa oleifera leaf powder	Cd^{2+}, Cu^{2+}, Ni^2	0.1 N NaOH followed by citric acid (CA)	159.88^a 146.87^a 138.04^a	Langmuir	FTIR, SEM, XRD	Reddy et al. (2012)
Aloe vera	Pb^{2+}	1 M H_3PO_4	$96.2\%^d$	n.g.	FTIR, SEM	Malik et al. (2015)
Oil palm leaves amorphous carbon	Pb^{2+}, Cr^{6+}	Polyethylenimine	143^a 109.6^b 125^a 108.8^b	Langmuir	HR-TEM, Raman, FTIR, S_{BET}	El-Sayed and Nada (2017)
Desmostachya bipinnata (kush grass)	Cd^{2+}	0.5 M NaOH	15.22^a	Langmuir	FTIR, SEM	Pandey et al. (2015)
Bambusa arundinacea (bamboo)	Cd^{2+}	0.5 M NaOH	19.70^a	Langmuir	FTIR, SEM	Pandey et al. (2015)
Posidonia oceanica	Cd^{2+}	0.1 N HCl	1.11^a 0.0823^b (mmol/g)	Sips, Redlich-Peterson, Toth	Elemental analysis, FTIR	Meseguer et al. (2016)
Posidonia oceanica	Cd^{2+}	Formaldehyde (HCHO)	0.82^a 0.0802^b (mmol/g)	Sips, Redlich-Peterso, Toth	Elemental analysis, FTIR	Meseguer et al. (2016)
Michelia champaca	Cr^{6+}	6 N HCl	$99.4\%^d$	n.g.	Field Emission SEM	Jayaraman (2015)
Michelia champaca	Cr^{6+}	1 N NaOH	$98.64\%^d$	n.g.	Field Emission SEM	Jayaraman (2015)
Imperata cylindrica	Ni^{2+}	Concentrated H_2SO_4	24.88^a 19.14^b	Freundlich, Langmuir	SEM, FTIR	Li et al. (2013)

Imperata cylindrica	Ni^{2+}	Concentrated H_3PO_4	24.69^a 19.28^b	Freundlich, Langmuir	SEM, FTIR	Li et al. (2013)
Ficus carica	Co^{2+}	0.1 M HCl, or 0.1 M $MgCl_2$	82.64^a 33.9^b	Dubinin-Radushkevich, Langmuir	FTIR, XRF	Dabbagh et al. (2016)
Aloe vera leaves ash (ALA)	Pb^{2+} Cu^{2+} Cr^{3+} Zn^{2+}	Fe_3O_4 nanoparticles	333.3^a 345.0^a 333.3^a 71.4^a	Langmuir	SEM, TEM	Abedi et al. (2016)
Banana leaves	Cu^{2+} Pb^{2+} Ni^{2+} Cd^{2+}	0.8 M $KMnO_4$	$Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$ [d]	n.g.	FTIR, TGA	El-Gendy et al. (2013)
Banana leaves	Cu^{2+} Pb^{2+} Ni^{2+} Cd^{2+}	0.8 M $KMnO_4$, $POCl_3$, pyridine	$Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$ [d]	n.g.	FTIR, TGA	El-Gendy et al. (2013)
Carbonized *Acacia nilotica*	Cu^{2+}	$ZnCl_2$	38.31^a	Freundlich, Frenkel-Halsey-Hill	SEM	Palanisamy and Santhi (2014)

In most cases the biosorption of the examined heavy metals onto leaf biosorbents at different experimental conditions obeyed the Langmuir isotherm. The maximum monolayer adsorption capacity obtained from the Langmuir isotherm for studied heavy metals ranged from 7.81 to 345 mg/g. FTIR, SEM and BET were widely used to characterize the leaf based biosorbents

Note: [a]q_{max} derived from Langmuir model; [b]experimental q_e; [c] breakthrough adsorption capacity (q_b) in fixed bed column experiment; [d] removal efficiency (%); * derived from Freundlich constant K_F; ** q_{max} derived from Sips model; *n.g.* not given in the study, *SEM/EDS* Scanning electron microscope/energy dispersive X-ray spectrometry, *FTIR* Fourier-transform infrared spectroscopy, *TGA* thermogravimetric analysis, *HRTEM* high-resolution transmission electron microscopy, *XRD* X-ray diffraction, *XRF* X-ray fluorescence, S_{BET} Brunauer-Emmett-Teller (BET) surface area) better the Cd^{2+} biosorption on HCl- and formaldehyde-treated leaves of *Posidonia oceanica* (Meseguer et al. 2016). The intraparticle diffusion models of Weber-Morris, Boyd and Bangham were applied in some studies to elucidate between film and diffusion mechanism (Kamal et al. 2010; Meseguer et al. 2016; Ngah and Hanafiah 2009). In some studies, the plots of Weber-Morris model showed a multi-linearity consisting of two or three steps. Based on Boyd model, intraparticle effective diffusion coefficients (D_{eff}) ranged from 2.7×10^{-6} to 3.0×10^{-6} cm^2/s and from 2.02×10^{-6} to 7.33×10^{-6} cm^2/s for Pb^{2+} and Cu^{2+} biosorption onto $KMnO_4$ and formaldehyde treated rubber leaf powder (*Hevea brasiliensis*), respectively. These D_{eff} values were much higher than the intraparticle diffusion range, suggesting that film diffusion also affected the heavy metal adsorption process (Kamal et al. 2010; Ngah and Hanafiah 2009).

The isotherm data at equilibrium were usually analyzed based on the two-parameter isotherm models of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (Table 3.3). In another study, the Harkin-Jura and Frenkel-Halsey-Hill two-parameter models were used to describe the Cu^{2+} adsorption by $ZnCl_2$ modified *Acacia nilotica* leaves (Palanisamy and Santhi 2014). The three parameter models of Sips, Redlich-Peterson and Toth were applied only in the case of Cd^{2+} biosorption onto modified leaves of marine phanerogam *Posidonia oceanica* and exhibited a better fit than the two-parameter ones (Meseguer et al. 2016).

As was observed for raw leaf biosorbents, the biosorption of heavy metals by the modified ones was dependent on solution pH. Maximum biosorption capacity for various metals was mostly observed in the pH range 5–6. However, the optimum adsorption of cobalt ions, Co^{2+}, onto $MgCl_2$ treated *Ficus carica* leaves was found to be at pH 6 whereas for raw leaves at pH 4 (Dabbagh et al. 2016).

Most studies using treated leaf biosorbents investigated the biosorption of one heavy metal. The affinity of metal ions by a biosorbent depend on the charge, ionic size, softness and hardness of each ion (El-Gendy et al. 2013). In a research work, The comparison of heavy metal biosorption in single and multi-metal systems (binary, ternary) was investigated (Abedi et al. 2016). Both raw and magnetically modified *Aloe vera* leaves presented a decrease of biosorption capacity in mixed metal cations systems in the order of $Cu^{2+} > Pb^{2+} > Cr^{3+} > Zn^{2+}$ for modified leaves and for $Pb^{2+} > Zn^{2+} > Cr^{3+} > Cu^{2+}$ for raw biomass. This was due to antagonistic effects (competitive adsorption) between the ions in the solution related to the hydrated ionic radius of each metal.

Furthermore, very limited studies have investigated modified leaf biosorbents in real industrial wastewater treatment. Industrial wastewaters contain various cations, anions or organic compounds which affect the selectivity and affinity of the biosorbent for the interested metal cations. The investigation of metal removal efficiency by a biosorbent in real wastewater is important for its full-scale application in wastewater treatment processes. Polyethylenimine-functionalized amorphous carbon derived from oil palm leaves has been tested in the treatment of real galvanization workshop and electroplating wastewater (El-Sayed and Nada 2017).

Among the studies presented in Table 3.3, very limited studies have studied the performance of leaf biosorbents in fixed bed columns. Continuous column processes are more practical for heavy metal ions removal from large quantities of industrial wastewater. The experiments were conducted by varying the initial metal concentrations at constant volumetric flow rate (Q: mL/min) or varying the flow rate at constant initial metal concentrations. Useful parameters can be obtained by column experiments such as breakthrough capacity, volume and time (Khalir et al. 2012). A breakthrough curve of "S" shape indicates a favorable adsorption process. Column studies showed that the breakthrough time decreased with increasing metal concentration and the lower is the flow rate the higher is the metal removal efficiency. In case of rubber leaf powder modified by citric acid, monosodium glutamate and xanthation process, the Thomas and Yoon-Nelson models fitted well the column data (Fadzil et al. 2016). It was found that Pb^{2+} adsorption capacity and removal performance of monosodium glutamate (MGRL) modified rubber leaf powder was superior to citric acid modified one (CARL). Thomas model is used to determine the maximum adsorption capacity q_0 (mg/g) and the adsorption rate constant k_{th} (mL/(min g)) assuming no axial dispersion, second order adsorption kinetics and Langmuir isotherm (Fadzil et al. 2016; Khalir et al. 2012). Yoon-Nelson model is used to determine a rate constant (k_{YN}: L/min), and the time (τ) required for the column to reach 50% adsorbate breakthrough (Fadzil et al. 2016). Column tests were performed for Cu^{2+} biosorption onto $ZnCl_2$ treated carbonized *Acacia nilotica* leaves varying the flow rate from 1 to 5 mL/min and the fixed bed layer thickness from 0.5 to 3 mm (Palanisamy and Santhi 2014). The modified biosorbent showed increasing percentage removal for Cu^{2+} when the bed layer thickness increased due to higher available adsorption sites allowing more time for the adsorbate to diffuse into the biosorbent. Compared to batch mode, the Cu^{2+} removal efficiency in the column studies was lower but a less adsorption time was observed.

3.3.3 Reusability/Regeneration

The reusability of biosorbents provide an economic advantage and is desired for the practical and commercial utility in wastewater treatment processes. Various studies have been performed regeneration and reuse of pretreated leaf biomass after metal loading. Desorption studies also help to determine the biosorption mechanisms such as ion exchange, complexation and physisorption. The most common eluents used are diluted HCl, NaOH, HNO_3, and EDTA solutions, usually in concentration up to 0.1 mol/L. Through desorption and recovery of adsorbed metals by using eluents the stability of the biosorbent is tested. Repeated exposure of biosorbents in acidic conditions due to strong desorption agents such as HCl, can affect the biomass rigidity due to biomass degradation and decrease of binding sites number (Ngah and Hanafiah 2009). Maximum desorption efficiency for Cu^{2+} ions (>90%) from loaded modified *Hevea brasiliensis* leaves was achieved by 0.1 M HCl, HNO_3 and EDTA solutions (Ngah and Hanafiah 2009). After three adsorption-desorption cycles, biosorption capacity slightly decreased from 1.93 to 1.81 mg/g. The desorption of Pb^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} from *Moringa oleifera* leaves was achieved by using 0.4 M HCl without significant reduction of biosorption capacity at four cycles (Reddy et al. 2010; Reddy et al. 2012). The desorption of Pb^{2+} and Cr^{6+} from loaded polyethylenimine-functionalized amorphous carbon derived from oil palm leaves were evaluated with 0.5 M HCl and 0.5 M NaOH (El-Sayed and Nada 2017). After the fifth cycle, a decrease of removal efficiency to 88% and 90% for Pb^{2+} and Cr^{6+}, respectively, was observed. Desorption of Cd^{2+} from the loaded modified *Desmostachya bipinnata* (kush grass) and *Bambusa arundinacea* (bamboo) leaves was 94% and 92% (Pandey et al. 2015).

3.3.4 Characterization of Modified Leaf Biosorbents

The characterization of leaf biosorbents aimed to understand their physicochemical properties, structural and morphological features, as well as the chemical composition, and was performed by using various techniques such Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy coupled with X-ray energy dispersive spectrometer (SEM-EDX), X-ray Diffraction (XRD), X-ray fluorescence (XRF), Raman spectroscopy and high resolution transmission electron microscopy (HR-TEM) (Table 3.3). Among them, SEM and FTIR analyses were used in most studies. Furthermore, the Brunauer-Emmet-Teller (BET) method for the estimation of specific surface area based on the N_2 gas adsorption isotherm data, the thermogravimetric analysis (TGA) and the elemental analysis (C, N, O, S) have been applied. These methods were used to compare either the biosorbent before and after pretreatment or to detect alterations on the biomass after the uptake of metals in order to determine the adsorption mechanisms. Based on these techniques, biosorption of heavy metals were found to be attributed to various metal-binding mechanisms such as ion exchange, surface adsorption and chemisorption (complexation). Another method to characterize the modified leaf biosorbents is by determining the pH of the point of zero charge (pH_{pzc}) which means the pH at which the biosorbent surface has a neutral electrical charge (Reddy et al. 2010). At this pH value, the acidic or basic functional groups of the biosorbent do not affect the solution pH (Rafatullah et al. 2011). At pH values higher than the pH_{pzc}, the biosorbent surface is negatively charged favoring the attraction of cations in solution.

In this paragraph, some results obtained via the less applied methods of XRD, XRF, TGA and elemental analysis are presented. Elemental analysis was performed to determine the percentage (%) composition of citric acid treated *Moringa oleifera* leaves for C, H, N, S and O (Reddy et al. 2012). The XRD patterns of *Moringa oleifera* leaf powder showed the absence of crystallinity indicating amorphous phases of the biomaterial (Reddy et al. 2012). The X-ray fluorescence technique was used to prove the cobalt (Co^{2+}) biosorption by raw and $MgCl_2$ treated *Ficus carica* leaves (Dabbagh et al. 2016). This analysis determined the biomass composition before and after sorption, and proved the ion-exchange of Co^{2+} with Mg^{2+} and Ca^{2+}. Thermogravimetric analysis (TGA) can be used to determine the thermal degradation of a biomaterial (Khalir et al. 2012). Hemicellulose starts to decompose at lower temperatures (220–315 °C) than cellulose (315–400 °C). Lignin decomposition takes place in a wide temperature range (200–720 °C). The mass loss at 50–180 °C is attributed to the loss of moisture and adsorbed water. The TGA analysis of xanthated rubber leaf powder (XRL) indicated a good chemical stability of XRL due to the adsorbent decomposition at a higher temperature (Khalir et al. 2012). Based on TGA, thermal stability of the carboxylated and phosphorylated banana leaves at high temperature was found to be higher than that for untreated banana leaves (El-Gendy et al. 2013).

Morphological changes on the surface of modified leaf biosorbents were determined by SEM images observing biomass structural alternations or degradation, color change, changes in the porosity and voids size, presence of fine particles assemblages, smoother or rougher surface etc. However, without the qualitative elemental analysis of the loaded biosorbent surface by EDX or XPS analysis, these observations remain subjective regarding the detection and location of heavy metals on the surface after biosorption. According to Reddy et al. (2012), a darker surface color after treatment of *Moringa oleifera* leaves with NaOH and citric acid was indicative of degradation of cellulose, hemicellulose and lignin (Reddy et al. 2012). According to SEM micrographs, the surface structure of raw *Imperata cylindrica* leaf powder was observed to be changed from rough to porous after sulfuric acid modification and to smooth with small porous after phosphoric acid treatment (Li et al. 2013). Both surfaces became smooth after Ni^{2+} biosorption. Surface morphology of SDBS-modified oil palm leaf powder (OPLP) was studied with SEM before and after Cu^{2+} adsorption (Rafatullah et al. 2011). SEM micrographs before adsorption showed a rough surface consisting of pores/cages of different sizes. After adsorption, the surface was observed to be covered with copper ions, however, without to confirm their presence via EDS analysis. Moreover, the authors conducted no FTIR study which could give a much clearer view about the changes of surface functional groups involved in copper adsorption.

Spherical magnetite nanonoparticles with smooth surface and slight aggregation were shown in the TEM images of magnetically modified *Aloe vera* leaves ash obtained after treatment of the raw ash with Fe_3O_4 nanoparticles (Abedi et al. 2016). The adsorption of Pb^{2+} and Cr^{6+} on the loaded polyethylenimine-functionalized amorphous carbon derived from oil palm leaves was confirmed by the EDX analysis of HR-TEM (El-Sayed and Nada 2017).

The major components of plant leaf biomass are cellulose, hemicellulose and lignin. Various functional groups such as hydroxyl, carboxylic, carbonyl, sulfate, phosphate, amides and amines, detected by FTIR, were responsible for ion exchange and complexation reactions with metals (El-Sayed and Nada 2017; Yazıcı et al. 2008). Carboxylic groups are contained in pectin hemicelluloses and lignin; phenolic groups in lignin and extractives; hydroxyl ones in cellulose, lignin, extractives and pectin; and carbonyl groups in lignin (Pandey et al. 2015). These active groups donate an electron pair in order to form surface complexes or exchange hydrogen ions for metal cations in the liquid phase (Reddy et al. 2012). Besides cations, amine group can adsorb anionic metal species through electrostatic interactions or hydrogen bonding (El-Sayed and Nada 2017).

Most studies have used the FTIR technique in order to compare the IR spectra of the pretreated biomass with the metal loaded one. Changes occurred in functional groups due to metal binding, which were indicated by the shift or disappearance of peaks in FTIR spectrum (Yazıcı et al. 2008). The biosorption of Cd^{2+}, Cu^{2+} and Ni^{2+} on citric acid treated *Moringa oleifera* leaves powder was confirmed by the changes (shift) in the peaks at 1732 and 3422 cm^{-1} indicating the binding of metal ions to carboxylic ($-COO^-$) and hydroxyl (-OH) groups, respectively (Reddy et al. 2012). According to FTIR results, hydroxyl and carboxylic groups were mainly responsible for Cu^{2+} biosorption onto modified *Marrubium globosum* leaves (Yazıcı et al. 2008). FTIR spectra showed that several functional groups such as carboxylic, amine, amide, phenol and sulphonyl contributed to Cd^{2+} biosorption onto *Posidonia oceanica* leaves (Meseguer et al. 2016). Phosphate (at 1200 cm^{-1}) and carboxyl (C=O of COOH at 1720 cm^{-1}) groups increased the heavy metal biosorption by $KMnO_4$ treated and phosphorylated banana leaves (El-Gendy et al. 2013).

3.4 Adsorption Thermodynamics

Thermodynamic studies are an indispensable component of predicting adsorption mechanism (i.e., physical or chemical). Physical adsorption arises from relatively weak interactions (i.e., van der Waals force), while chemical adsorption involves stronger chemical interactions (i.e., coordination) with attendant transfer of electrons between the adsorbent and adsorbate. A new classification system for biosorption mechanisms of heavy metal ions has been reported by Robalds et al. (2016). The thermodynamic parameters can be calculated according to the laws of thermodynamics through the following equations:

$$\Delta G^o = -RT \ln K_C \tag{3.1}$$

The relationship between ΔG°, ΔH° and ΔS° is described as follows:

$$\Delta G^o = \Delta H^0 - T\Delta S^0 \tag{3.2}$$

The well-known van't Hoff equation is obtained by substituting Eq. 3.1 into Eq. 3.2.

$$\ln K_C = \frac{-\Delta H^o}{R} x \frac{1}{T} + \frac{\Delta S^o}{R} \tag{3.3}$$

where R is the universal gas constant, and T is the absolute temperature in Kelvin.

The Gibbs energy change ($\Delta G°$) is directly calculated from Eq. 3.1, while the change in enthalpy ($\Delta H°$) and the change in entropy ($\Delta S°$) are determined from the slope and intercept, respectively, of a plot of ln K_C against $1/T$ (Eq. 3.3). It is well-known that the equilibrium constant (K_C) must be dimensionless. In the literature, the thermodynamic parameters can be calculated from K_C values derived from the adsorption-isotherm constants (i.e., Langmuir, Freundlich, Frumkin, Flory–Huggins, Redlich–Peterson, and Henry) or the partition coefficient (Tran et al. 2017).

Changes in the thermodynamic partition coefficient with changes in temperature were first reported by Biggar and Cheung (1973). The partition coefficient (K_p) is defined as follows:

$$K_p = \frac{a_s}{a_e} = \frac{\gamma_s C_s}{\gamma_e C_e} \tag{3.4}$$

where a_s is the activity of the adsorbate adsorbed onto the adsorbent; a_e is the activity of the adsorbate in solution at equilibrium; γ_s is the activity coefficient of the adsorbate adsorbed onto the adsorbent; γ_e is the activity coefficient of the adsorbate in solution at equilibrium; C_s is the concentration of adsorbate adsorbed onto the adsorbent at equilibrium (mg/L); and C_e is the concentration of adsorbate in solution at equilibrium (mg/L). C_s is defined by the mass balance of adsorbate that disappears from the solution, which should appear on the adsorbent.

When the concentration of adsorbate in the solution approaches zero, which results in $C_s \rightarrow 0$ and $C_e \rightarrow 0$, the activity of coefficient γ approaches unity, Eq. 3.4 can be written into:

$$\underset{Cs\rightarrow 0}{Lim} \frac{C_s}{C_e} = \frac{a_s}{a_e} = K_p \tag{3.5}$$

In this method, K_p values can be obtained plotting $\ln(C_s/C_e)$ versus C_s and extrapolating C_s to zero. If a straight line fits the data with a high coefficient of determination (R^2) and its intersection with the vertical axis provides the value of $\underline{K\mathrm{p}}$, the partition coefficient will be in unison with the equilibrium constant K_C.

On the basis of the method proposed by Biggar and Cheung (1973), Khan and Singh (1987) developed the other method for calculating the thermodynamic parameters (Eq. 3.6). The distribution coefficient (also known as the Henry constant) is defined as the following equation:

$$K_d = \frac{q_e}{C_e} \tag{3.6}$$

In this method, K_d values are obtained by plotting $\ln(q_e/C_e)$ against C_e and extrapolating to zero C_e. If a straight line fits the experimental data with a high regression coefficient (R^2), then its intersection with the vertical axis provides the value of K_d. However, the distribution coefficient K_d is a dimensional; therefore, it is necessary to convert K_d (dimensional) into K_C (dimensionless) by several appropriate methods (Tran et al. 2017). Notably, the distribution and partition coefficients are only appropriate to determine the thermodynamic parameters if the initial used adsorbate concentration is low (infinite dilution). In this situation, the distribution coefficient K_d and partition coefficient K_p will be in unison with the equilibrium constant K_C.

The thermodynamic parameters of biosorption process of heavy metals (i.e., Cd^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) onto the raw and modified biosorbents derived from leaves are summarized in Tables 3.4 and 3.5. Clearly, the sign and magnitude of thermodynamic parameters are strongly dependent on the properties of both biosorbent and adsorbate. For example, the enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) of Pb^{2+} biosorption onto *Azadirachta indica* leaves were 10.9 kJ/mol and −0.029 kJ/mol × T (Bhattacharyya and Sharma 2004), while the corresponding values of Ni^{2+} biosorption were −58.2 kJ/mol and −0.183 kJ/mol × T (Bhattacharyya et al. 2009), respectively. In contrast, Reddy et al. (2010) investigated the adsorption behaviors of various divalent toxic metal ions onto chemically modified *Moringa oleifera* leaves, concluding that the biosorption process exhibited the same sign of thermodynamic parameters. The $\Delta H°$ (kJ/mol) and $\Delta S°$ (kJ/mol × T) were obtained as follows: 17.5 and 0.074 for Pb^{2+} adsorption, 15.3 and 0.063 for Cd^{2+} adsorption, 12.8 and 0.053 for Cu^{2+} adsorption, and 10.3 and 0.043 for Ni^{2+} adsorption, respectively (Table 3.5). The results demonstrated that the modified *Moringa oleifera* possessed the similar adsorbing sites on its surfaces toward the heavy metal ions.

Generally, the removal process of heavy metals from aqueous solutions (adsorption onto biosorbent) is spontaneous in nature, which is supported by the negative $\Delta G°$ values (Tables 3.4 and 3.5). Additionally, the effects of operation temperatures on the amount of metal ions adsorbed onto biosorbent are reflected through the sign of enthalpy change. The adsorption capacity of biosorbent increased when the temperature increased, suggesting that the biosorption process is endothermic ($\Delta H° > 0$). In contrast, the negative $\Delta H°$ reflects the exothermic nature of the biosorption process, which is demonstrated by a decrease in adsorption capacity at higher temperatures. For example, Chen et al. (2010) investigated the adsorption characteristics of Pb^{2+} ions using natural fallen *Cinnamomum camphora* (NCM) leaves at different temperatures. Their results demonstrated that the maximum adsorption capacity ($Q°_{max}$; calculated from the Langmuir isotherm model) of NCM leaves increased with the increase in temperature, suggesting that the Pb^{2+} biosorption process was endothermic ($\Delta H° = 15.02$ kJ/mol). The $Q°_{max}$ (mg/g) of NCM leaves exhibited the following other: 75.82 mg/g at 333 K > 74.13 mg/g at 323 K > 73.58 mg/g at 313 K > 73.15 mg/g at 303 K, which is consistent with a decrease in (1) the equilibrium constant K_C (dimensionless): 109,000 > 98,480 > 79,600 > 64,590, and (2) the adsorption energy E (calculated from the Dubinin–Radushkevich isotherm model): 15.89 kJ/mol > 15.58 kJ/mol > 14.68 kJ/mol > 14.06 kJ/mol.

Furthermore, the sign of entropy change plays a contributing role in reflecting whether the organization of the adsorbate at the solid/solution interface during the biosorption process becomes less random ($\Delta S° < 0$) or more random ($\Delta S° > 0$). As showed in Tables 3.4 and 3.5, the raw and modified biosorbents exhibited a positive $\Delta S°$ value in most observed cases, suggesting the organization of the metal ions at the solid/solution interface becomes more random during the biosorption process.

Table 3.4 Thermodynamic parameters for the adsorption process of heavy metals onto the raw leaf biosorbents

	T (K)	Derivation of K_C (unit)	Thermodynamic parameters			Reference
			ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol × K)	
1. Lead (Pb^{2+})						
Cinnamomum camphora	303	K_L (L/mol)	−23.9	15.1	0.129	Chen et al. (2010)
	313		−25.3			
	323		−26.7			
	333		−27.8			
Solanum melongena	303	K_L (L/mg)	−8.75	3.69	0.039	Yuvaraja et al. (2014)
	313		−8.51			
	323		−7.98			
Ficus religiosa	303	K_d (L/g)	−2.95	−105	−0.350	Qaiser et al. (2009)
	313		−0.12			
	323		4.94			
Tea waste	288	K_d (mL/g)	−14.8	25.1	0.138	Wan et al. (2014)
	298		−14.6			
	308		−12.8			
	318		−12.6			
	328		−11.3			
Azadirachta indica	308	K_d (mL/g)	−4.69	10.9	−0.029	Bhattacharyya and Sharma (2004)
	313		−4.26			
	318		−3.96			
2. Cadmium (Cd^{2+})						
Syzygium cumini	303	K_p (No)	−1.40	3.70	0.017	Rao et al. (2010)
	313		−1.58			
	323		−1.74			
Eriobotrya japonica	293	K_p (No)	−7.02	29.7	0.125	Awwad and Salem (2014)
	303		−8.21			
	313		−9.55			
Carpinus betulus	298	K_p (No)	−4.29	−13.06	−0.029	Zolgharnein et al. (2013)
	308		−4.04			
	318		−3.65			
	328		−3.44			
Date tree	298	K_p (No)	−7.37	21.59	0.095	Boudrahem et al. (2011)
	308		−7.52			
	313		−7.92			
	333		−10.8			
Tea waste	288	K_d (mL/g)	−12.5	10.5	0.079	Wan et al. (2014)
	298		−12.4			
	308		−12.2			
	318		−12.1			
	328		−11.8			

(continued)

Table 3.4 (continued)

	T (K)	Derivation of K_C (unit)	Thermodynamic parameters			Reference
			ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol × K)	
Eriobotrya japonica powder	293	K_p (No)	−6.33	12.3	0.064	Al-Dujaili et al. (2012)
	303		−6.98			
	313		−7.60			
Eriobotrya japonica ash	293	K_p (No)	−5.87	10.0	0.054	Al-Dujaili et al. (2012)
	303		−6.43			
	313		−6.96			
3. Copper (Cu^{2+})						
Boston fern	303	K_p (No)	−10.4	−28.4	−0.061	Rao and Khan (2017)
	313		−8.35			
	323		−8.37			
Tea waste	288	K_d (mL/g)	−8.50	11.4	0.064	Wan et al. (2014)
	298		−7.78			
	308		−7.51			
	318		−7.59			
	328		−7.56			
Azadirachta indica	303	(K_L) L/mol	−19.8	15.4	0.116	Febriana et al. (2010)
	323		−22.0			
	343		−24.4			
4. Zinc (Zn^{2+})						
Tectona grandis L.f.	303	K_L (L/mg)	−11.9	−4.45	0.054	Kumar et al. (2006a)
	313		−12.5			
	323		−13.0			
	333		−13.6			
5. Nickel (Ni^{2+})						
Azadirachta indica	303	K_d (L/g)	−2.61	−58.2	−0.183	Bhattacharyya et al. (2009)
	308		−1.69			
	313		−3.88			
	323		1.06			
	328		1.41			
	333		2.69			
Tea factory waste	298	K_p (No)	−3.82	17.07	0.022	Malkoc and Nuhoglu (2005)
	318		−5.34			
	333		−6.27			
6. Cr(VI)						
Colocasia esculenta	303	K_d (L/g)	−8.32	0.75	0.025	Nakkeeran et al. (2016)
	313		−4.41			
	323		−1.43			
	333		−0.79			

(continued)

Table 3.4 (continued)

	T (K)	Derivation of K_C (unit)	Thermodynamic parameters			Reference
			ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol × K)	
Mango	303	K_p (No)	−7.15	97.1	0.344	Saha and Saha (2014)
	308		−9.27			
	313		−10.7			
7. Mercury (II)						
Bamboo	293	K_d (L/g)	−0.87	10.3	0.023	Mondal et al. (2013)
	300		−1.25			
	307		−2.03			

Thermodynamic parameters estimated for the biosorption of heavy metals onto the herein reported raw materials in a temperature range from 288 to 343; the results revealed that in most cases biosorption was spontaneous, endothermic with increased randomness at the solid/solution interface during the biosorption

Table 3.5 Thermodynamic parameters for the adsorption process of heavy metals onto the modified leaf biosorbents

	Chemical	T (K)	Derivation of K_C (unit)	Thermodynamic parameters			Reference
				ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol × K)	
1. Lead (Pb^{2+})							
Moringa oleifera	HNO_3	293	K_L (L/g)	−3.94	17.5	0.074	Reddy et al. (2010)
	NaOH	303		−4.92			
		313		−5.39			
Hevea brasiliensis	NaOH	303	K_d (mL/g)	−5.48	21.4	0.052	Khalir et al. (2012)
	CD	313		−4.95			
2. Cadmium (Cd^{2+})							
Desmostachya bipinnata	NaOH	298	K_L (L/g)	−0.39	5.50	0.002	Pandey et al. (2015)
		308		−1.51			
		318		−1.11			
Bambusa arundinacea	NaOH	298	K_L (L/g)	−0.66	9.28	0.003	Pandey et al. (2015)
		308		−1.73			
		318		−2.05			
Moringa oleifera	HNO_3	293	K_L (L/g)	−3.68	15.3	0.063	Reddy et al. (2012)
	NaOH	303		−4.50			
		313		−4.95			
		323		−5.42			

(continued)

Table 3.5 (continued)

				Thermodynamic parameters			
	Chemical	T (K)	Derivation of K_C (unit)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol × K)	Reference
3. Copper (Cu^{2+})							
Hevea brasiliensis	H_2SO_4,	300	K_L (L/mol)	−23.5	3.20	0.089	Ngah and Hanafiah (2009)
	HCHO	310		−24.4			
		320		−25.3			
Moringa oleifera	HNO_3	293	K_L (L/g)	−3.17	12.8	0.053	Reddy et al. (2012)
	NaOH	303		−3.75			
		313		−4.25			
4. Mercury (Hg^{2+})							
Bamboo	TX-100	293	K_d (L/g)	−1.07	15.9	0.098	Mondal et al. (2013)
		300		−2.76			
		307		−3.96			
Bamboo	SDS	293	K_d (L/g)	−1.15	32.9	0.106	Mondal et al. (2013)
		300		−3.00			
		307		−4.19			
5. Nickel (Ni^{2+})							
Moringa oleifera	HNO_3	293	K_L (L/g)	−2.68	10.3	0.043	Reddy et al. (2012)
	NaOH	303		−3.08			
		313		−3.56			
Waste tea	Formaldehyde	313	K_d (L/g)	−30.4	−23.7	0.022	Shah et al. (2015)
		323		−31.1			
		333		−31.8			
		343		−31.5			
		353		−31.9			
		363		−31.6			
Nymphaea alba	$MgCl_2$	303	K_d (L/g)	−1.73	0.21	0.002	Zahedi et al. (2015)
		308		−1.59			
		323		−1.68			

Thermodynamic parameters estimated for the biosorption of heavy metals onto the herein reported modified materials in a temperature range from 293 to 363; the results revealed that in all cases (except one) biosorption was spontaneous, endothermic with increased randomness at the solid/solution interface during the biosorption

Note: *SDS* Sodium dodecyl sulphate, *TX-100* Triton X-100, *CD* carbon disulfide

A plot of ΔH° versus ΔS° shows a strong linear relationship ($R^2 > 0.911$) (Fig. 3.3) which is known as enthalpy-entropy compensation (Anastopoulos and Kyzas 2014, 2015, 2016; Anastopoulos et al. 2015, 2017; Bhatnagar and Anastopoulos 2016; Chang et al. 2016). This phenomenon sounds strange and it is difficult to explain since the results came from different studies with various experimental conditions. One possible explanation is that both ΔH° and ΔS° calculated from the same equation.

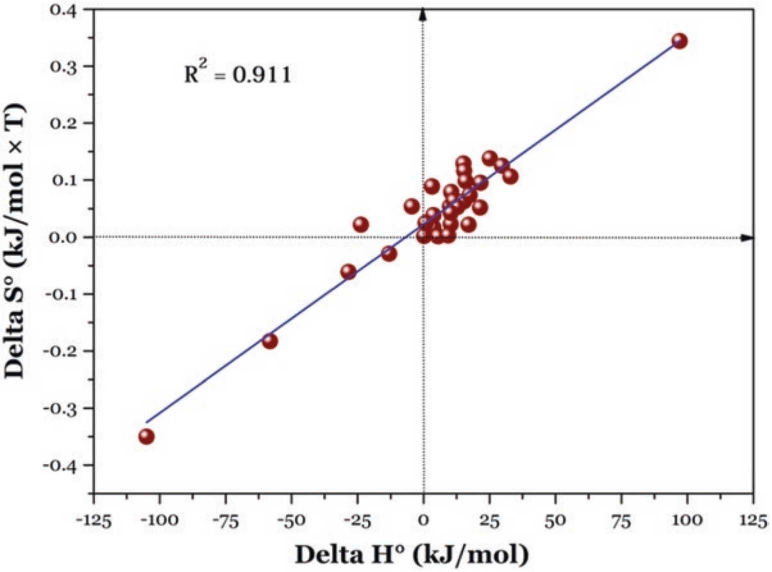


Fig. 3.3 The enthalpy–entropy compensation plot for the biosorption of heavy metals onto raw and modified leaf biosorbents (n = 33) in a temperature range between 288 and 363 K. The results showed that there is a strong linear correlation (y = 0.00331x + 0.02266, $R^2 = 0.911$), suggesting that thermodynamic studies must be taken into consideration with caution

Other significant points are that the sign and magnitude of $\Delta S°$ and $\Delta H°$ demonstrated a confused representation. This is because the thermodynamic parameters (Tables 3.4 and 3.5) were calculated from the equilibrium constant K_C derived from different methods (K_L, K_p, and K_d) and units (L/mol, L/mg, and L/g). Furthermore, the operation condition of thermodynamic adsorption experiments is dissimilar. For example, Rao et al. (2010) applied the distribution coefficient ($K_d = q_e/C_e$) at an initial cadmium concentration of 100 mg/L to calculate the thermodynamic parameters. Contrastingly, Pandey et al. (2015) applied the Langmuir constant at different initial cadmium concentrations (from 10 to 100 mg/L) to calculate the thermodynamic parameters.

Therefore, to obtain an appropriate calculation method, previous studies suggested several factors need to be considered thoroughly. First, the equilibrium constant (K_C) must be dimensionless. Second, the linear regression coefficient (R^2) of the van't Hoff equation must be high. Third, the concentration of adsorbate used in the biosorption equilibrium study (adsorption isotherm) is low or high. If the initial concentrations of adsorbate are very high, the distribution and partition coefficients might not be appropriate for calculating the thermodynamic parameters (Tran et al. 2016, 2017).

3.5 Conclusions

This chapter focused on the use of leaf biosorbents in the removal of heavy metal contaminants from aqueous solutions. Biosorption properties of leaf biosorbents have been evaluated mostly by laboratory scale batch sorption experiments. Different parameters such as initial metal concentration, contact time, solution pH, adsorbent dosage, temperature, etc. were found to affect significantly the biosorption process. Surface modification was found to enhance the biosorption capability of raw leaves. Batch equilibrium approach is fast and simple, but it gives only a rough idea of whether the studied adsorbent could be used in real wastewater treatment systems. Therefore, it is necessary to carry out studies which give more detailed information about the suitability of the particular biosorbent to be used in these systems. These studies, besides pilot scale and full-scale system studies may include the use of real wastewater; column studies and optimization of the mechanical and biosorption properties of the biosorbent. Langmuir isotherm and pseudo-second kinetic model were found to give the best fit to the experimental data. In addition to two-parameter isotherm models (Langmuir, Freundlich, Temkin) and pseudo-kinetic models, three-parameter- isotherm models and diffusion kinetic models are highly suggested for better understanding of the adsorption mechanism. The thermodynamic parameters can be calculated from the K_C equilibrium constants derived from the Langmuir constant, distribution coefficient, and partition coefficient. The biosorption process of heavy metals onto raw and modified leaf biosorbents is generally spontaneous in nature ($-\Delta G°$). The magnitude of $\Delta H°$ is less than 40 kJ/mol, suggesting that the biosorption mechanism mainly involves physical adsorption. The organization of the heavy metal ions at the solid/solution interface generally becomes more random during the biosorption process ($+\Delta S°$). However, most the biosorption enthalpy was calculated based on the van’t Hoff approach. Further experiments should be continued to determine adsorption enthalpy by other methods, such as calorimetric measurements, for comparison or propose a standard protocol for determining the thermodynamic parameters. The regeneration capability of the materials targeted to be used for adsorption application is an essential aspect with an effect on the economic feasibility. For that reason, the determination of the reusability/regeneration should be also examined in detail. The final disposal of the exhausted adsorbents is also a vital environmental concern that should be also taken into consideration. Future work will also focus on the examination of the fate of the heavy metals after the application of leaves in soil environment.

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Chapter 4
Cellulose Based Green Adsorbents for Pollutant Removal from Wastewater

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Contents

Abstract Water pollution is a major problem affecting people across the world. Heavy metals and dyes are major pollutants that pose potential threat to the health of humans and ecosystems. Several treatment technologies are available to reduce the pollutant concentration in water and wastewater. However, many of these processes are costly, have high energy requirements and generate toxic sludge and wastes that need to be carefully disposed. Addressing these problems invoked the need for green methods that are more efficient, cost effective and environment friendly for water purification. Adsorption is regarded as a green, clean and versatile method for wastewater treatment. Cellulose based materials attained considerable

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attention for water purification because of its abundant availability, biodegradability and non-toxic nature. This chapter reviews the application of cellulose based materials and their modified forms as adsorbents for the removal of dyes and toxic heavy metals from wastewater. The adsorption efficiency of green adsorbents, cellulose based green adsorbents and their modified forms are compared. The adsorption capacity of the adsorbent is enhanced by reducing the cellulosic dimension to the nanolevel. Moreover, further chemical modification of nanocellulose adsorbents result in maximum adsorption.

4.1 Introduction

Issues related to the quality of water are one of the major problems faced by humanity in the twenty-first century. The quality of our water resources are deteriorating day by day due to various anthropogenic activities, increasing industrialization and unplanned urbanization. Dyes are complex organic compounds which are purged from various industrial sources such as textile, cosmetic, paper, leather, rubber and printing industries to color their products. Dye bearing effluent is a significant source of water pollution. Human activities have also resulted in substantial amounts of heavy metals being released into the hydrosphere causing ecotoxicological hazards due to their tendency to accumulate in vital organs and high toxicity (Abdel-Raouf and Abdul-Raheim 2017). Wastewater effluents containing dyes and heavy metals cause potential hazard to the environment and human health. Recently, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. These include chemical precipitation, ion exchange, coagulation flocculation, membrane separation, electrochemical treatment and adsorption (Barakat 2011). However, most of them require substantial financial input and their use is restricted because of cost factors overriding the importance of pollution control. Amongst all the treatment processes mentioned, adsorption is found to be effective, cheap, simple, and relatively lower operation cost of dye removal (Meshko et al. 2001). Different types of materials have been developed as adsorbents for effective adsorption of pollutants. In recent years, development of green adsorbents received widespread attention as they are valued for their renewability, low cost and non-toxicity (Chang and Juang 2004). Green adsorbents produced from sustainable raw materials are manufactured in a more energy conservative way, pose few health problems, is recyclable and is compostable to be supplied to the market using less materials. Cellulosic adsorbents have the proficiency to meet almost all the requirement for being green. Cellulose is the most abundant, natural biopolymer which is renewable, biodegradable and non-toxic. The primary occurrence of cellulose is the existing lignocellulosic material, with wood as the most important source. One of the promising applications of lignocellulosic material is as an adsorbent for water purification or wastewater treatment due to its wide availability, renewability, sustainability and the possibility of surface modification. Several researches have been devoted to review the removal of organic and inorganic pollutants using lignocellulosic adsorbents (Abdolali et al. 2014). However, untreated lignocellulosic biomass is generally not functional and the adsorption capacity varies depending on the biomass source. When the size is minimized to the nanoscale, the high specific surface area of the polysaccharide adsorbents contribute to enhancing the adsorption capacity. This led to the emergence of nanocellulose as a new generation of bio based adsorbents with potential applications in wastewater treatment. Within the past decade, cellulose in the form of cellulose nanocrystals and cellulose microfibrils has been extensively studied due to its wide industrial application such as enzyme immobilization, adsorption, catalysis, drug delivery, biosensors and bio-imaging (Lam et al. 2012). These nanomaterials have been extensively explored by researchers as an adsorbent for removal of various kinds of hazardous pollutants and the studies indicate that these materials possess high adsorption capacity, are environmental friendly and inexpensive (Lam et al. 2012). Cellulose based materials are more attractive for water purification when it makes modifications in its structure in order to improve their existing properties or adding new potentialities to this material (Silva et al. 2013). The presence of abundant hydroxyl groups on the surface of micro or nanoscale of cellulose provides a unique platform for significant surface modification to graft a myriad of functional groups or molecules onto the cellulosic structure thereby immobilizing pollutants.

This chapter provides an overview of the recent progresses related to the application of cellulose based materials and their modified forms as an adsorbent for the removal of toxic heavy metals and dyes from wastewater. It contains a general introduction to the pollutants, heavy metals and dyes and the various techniques for pollutant removal from wastewater with special reference to adsorption. Herein the adsorption efficacies of various green adsorbents, cellulose based green adsorbents, modified cellulose based adsorbents and modified nano/microbased adsorbents have been discussed.

4.2 Major Water Pollutants

In recent years, growth in industrial activity, intensification of agriculture and growing volumes of sewage from rapidly urbanizing areas has led to the release of various pollutants into aquatic environment, such as toxic heavy metals, dyes, organic compounds like phenols, pesticides, humic substances, detergents etc. These pollutants are characterized not only by their persistence against chemical or biological degradation, but also high environmental mobility and strong tendency for bioaccumulation in the food chain. Among these various pollutants, heavy metals and dyes are the important members of pollutants which will be discussed.

Table 4.1 The source, route of entry and toxicity effect of some heavy metals

Heavy metal	Source	Route of entry	Toxicity effect
Arsenic	Pesticides, fungicides, metal smelters	Inhalation and ingestion	Irritation of respiratory system, liver and kidney damage, loss of appetite, nausea and vomiting
Cadmium	Welding, electroplating, pesticide fertilizer, Cd-Ni batteries	Inhalation and ingestion	Lung, liver and kidney damage; irritation of respiratory system
Chromium	Paints, electroplating and metallurgy	Inhalation, ingestion, and absorption through skin	Lung damage and irritation of respiratory system
Mercury	Pesticides, batteries, paper industry	Inhalation, ingestion and absorption through skin	Irritation of respiratory system; lung, liver and kidney damage, and loss of hearing and muscle coordination
Lead	Paint, pesticide, smoking, automobile emission, mining	Inhalation and ingestion	Lung and liver damage; loss of appetite, nausea
Nickel	Electrochemical industries	Inhalation	Lung, liver and kidney damage

4.2.1 Heavy Metals

The term “heavy metals” refer to any metallic element that has a density more than 5 g per cubic centimeter and is toxic or poisonous even at low concentration. These include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe), and the platinum group elements. Most of the metals are non-biodegradable, highly toxic and carcinogenic in nature. Toxic heavy metals reach through various food chains and cause toxic effects on the ecosystem as well as humans and animals (Barakat 2011). Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. At higher doses, heavy metals can cause irreversible brain damage. Therefore, it is necessary to treat metal-contaminated wastewater before its discharge into the environment. Table 4.1 (Abdel-Raouf and Abdul-Raheim 2017) lists those heavy metals that are relevant in the environmental context, their source and toxicity effects.

4.2.2 Dyes

Dyes have been extensively used for thousands of years for textile, paint, pigment and many other applications (Liu et al. 2011). To meet industrial demand, it is estimated that 1.6 million tons of dyes are produced annually and 10–15% of this volume is discarded as wastewater (Hunger 2003). As a result, dyes are major water

Table 4.2 The specific properties, applications and toxicities of various types of dyes

Dye	Examples	Properties	Application	Toxicity
Acidic	Acid red 183, acid orange 10, acid orange 12, acid orange 8, acid red 73, acid red 18, sunset yellow, acid green 27, methyl orange	Water soluble, anionic	Nylon, wool, silk, paper, leather, ink-jet printing	Carcinogenic (benign and malignant tumors)
Cationic	Methylene blue, janus green, basic green 5, basic violet 10, Rhodamine 6G	Water soluble, releasing colored cations in solution. Some dyes show biological activity	Paper, polyacrylonitrile, modified nylons, modified polyesters, as antiseptics	Carcinogenic (benign and malignant tumors)
Disperse	Disperse orange 3, disperse red, disperse red 1, disperse yellow 1	Water insoluble, non-ionic; for hydrophobic aqueous dispersion	Polyester, nylon, cellulose, cellulose acetate, acrylic fibers	Allergenic (skin), carcinogenic
Direct	Congo red, direct red 23, direct orange 39, direct blue 86	Water soluble, anionic, improves wash fastness by chelating with metal salts	Cotton, regenerated cellulose, paper, leather	Bladder cancer
Reactive	Reactive black 5, reactive green 19, reactive blue 4, reactive red 195, reactive red 198, reactive blue 19, reactive red 120	Extremely high wash fastness due to covalent bond formation with fiber, brighter dyeing than direct dyes	Cotton, wool, nylon, ink-jet printing of textiles	Dermatitis, allergic conjunctivitis, rhinitis, occupational asthma

pollutants. Excessive exposure to dye causes skin irritation, respiratory problems, and some dyes even increase the risk of cancer in humans (Rai et al. 2005). In addition, the presence of dyes in wastewater also contributes to high chemical oxidation demand and causes foul odor (Midha and Dey 2008). Thus, it is of utmost importance to remove dyes from wastewater effectively to ensure safe discharge of treated liquid effluent into watercourses. Dyes are mainly classified into (a) anionic (direct, acidic, and reactive dyes) (b) Cationic (all basic dyes) and (c) Non-ionic (disperse dyes). Table 4.2 lists the various types of dyes, their applications and toxicities (Tan et al. 2015).

4.3 Methods for Pollutant Removal

In response to the rising demands of clean and safe water, improving wastewater treatment is a key intervention strategy to control and eliminate diseases. Many different technologies are available for treating the pollutant-laden wastewater. Some

Table 4.3 Treatment technologies for the removal of pollutants from wastewater and associated advantages and disadvantages

Technology	Advantages	Disadvantages	Reference
Chemical precipitation	Simple operation	Sludge generation	Aderhold et al. (1996)
	Not pollutant selective, low capital cost	Sludge disposal cost	
		High maintenance costs	
Coagulation–flocculation	Bacterial inactivation capability	Chemical consumption	Aderhold et al. (1996),
	Good sludge settling and dewatering characteristics	Increased sludge	
	Simple, economically feasible	High cost, sludge disposal problem	Wang et al. (2005)
Adsorption	Broad spectrum of pollutants, High capacity, Fast kinetics	Performance depends on type of adsorbent	Crini (2006)
	Low cost, easy operating conditions	Chemical derivatisation to improve its sorption capacity	Ali and Gupta (2006)
Membrane filtration	Small space requirement	High initial cost	
	Low waste	High maintenance & operation cost, Membrane fouling	
	Low chemical consumption	Limited membrane life-time	

of the widely used treatment technologies are biological treatments (McMullan et al. 2001), membrane process (Dialynas and Diamadopoulos 2009; Barakat 2011), chemical and electrochemical technology (Ku and Jung 2001), reverse osmosis (Sonune and Ghate 2004), ion exchange (Maranon et al. 1999), electro dialysis, electrolysis and adsorption procedures (Barakat 2011). Of these, reverse osmosis, electrodialysis, electrolysis and ion exchange are costly involving complicated procedures for treatment. Major limitations of many of these processes include high cost, high energy requirement and generation of toxic sludge and wastes that demand careful disposal. Table 4.3 collects some of the common technologies that have been adopted by researchers for the removal of heavy metals and dyes from wastewater along with their advantages and disadvantages.

4.3.1 Conventional Methods

The conventional processes for removing pollutants from wastewater include many processes such as chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition. Chemical precipitation is most widely used for pollutant removal from inorganic effluent. Adjustment of pH to the basic conditions is the major parameter that significantly improves pollutant removal by chemical precipitation. Figure 4.1 shows the various processes involved in the chemical precipitation process (Wang et al. 2005). However, this method requires a large amount of

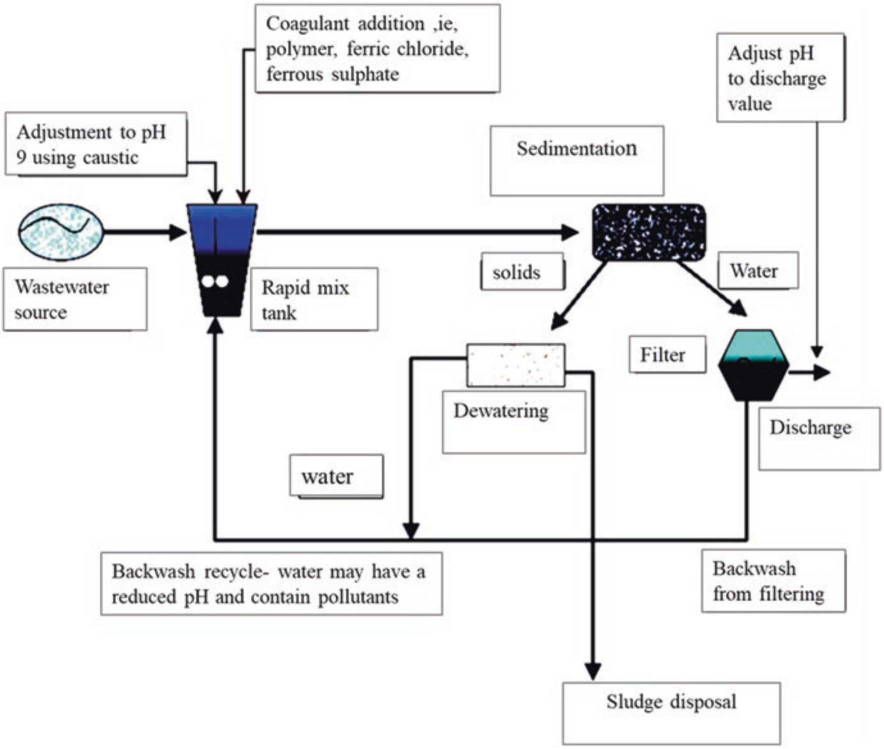

Fig. 4.1 Processes of a conventional precipitation treatment plant

chemicals to reduce the pollutant to an acceptable level for discharge. Other drawbacks include excessive sludge production that requires further treatment, slow precipitation, poor settling and the long-term environmental impacts of sludge disposal (Aziz et al. 2008).

Ion exchange is another alternative for the removal of pollutants from effluent. An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated pollutant solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is non selective and is highly sensitive to the pH of the solution. Electrolytic recovery or electro-winning is one of the many technologies used to remove pollutants from process water streams. This process uses electricity to pass a current through an aqueous pollutant bearing solution containing a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit that is strippable and recoverable. A noticeable disadvantage was that corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced (Babel and Kurniawan 2003).

Among the various decontamination techniques, adsorption process is regarded more prospective for water treatment due to its ease of operation, convenience and simplicity of design (Faust and Aly 1981).

4.3.2 Adsorption

Adsorption is a fast, inexpensive and widely used method as it can be applied for the removal of a wide spectrum of soluble and insoluble contaminants and biological pollutants with high removal efficiency (Ali and Gupta 2006). Moreover, its high efficiency in pollutant removal without the production of toxic by-products makes adsorption one of the most popular methods for water decontamination. The process of adsorption is a mass transfer process involving the transfer of a substance from solution phase and resulting in the deposition at the surface of the other phase. The substance being adsorbed is termed the adsorbate and the adsorbing surface is called adsorbent. If the interaction between the adsorbate and the adsorbent are due to the weak van der Waal's forces, then the process is physisorption or physical adsorption. Contrarily, if the attraction forces between the adsorbate and adsorbent are due to chemical bonding, then chemisorption. The general mechanism of adsorption involves the transfer of the pollutant from bulk solution to the outer surface of the adsorbent, internal mass transfer from the outer surface to its inner pores of the adsorbent and the adsorption of adsorbate particles onto the active pores of the adsorbent. The overall rate of the reaction is determined by either film formation or intraparticle diffusion or both.

The ideal materials for the adsorption of pollutants should meet several requirements such as inexpensiveness, good mechanical and structural integrity to overcome water flow for a long time, high adsorption capacities with high rates, have a large surface area and possess a regeneration aptitude using cost-effective approaches. Different materials tested as possible wastewater adsorbents are depicted in Fig. 4.2 (Mahfoudhi and Boufi 2017).

The main advantage of adsorption recently became the use of low-cost materials with satisfactory adsorption properties and environmentally-friendly nature. As per these requirements, nowadays researchers are switching onto green adsorbents due to their abundance, biodegradability and non-toxic nature. Under this term, green adsorbents include low-cost materials originated from: (i) natural sources (Sharma et al. 2011) (ii) agricultural residues and wastes in particularly lignocellulosic biomass (Sud et al. 2008; Abdolali et al. 2014) and (iii) low-cost sources (Bhatnagar and Sillanpää 2010) from which activated carbon adsorbents will be produced. These green adsorbents were found to be inferior in terms of their adsorption capacity than the commercial adsorbents such as modified chitosans, activated carbons, structurally-complex inorganic composite materials etc., but their cost-potential makes them competitive. Cellulosic adsorbents have the proficiency to meet almost all the requirement for being green. With responsible and thoughtful research, development and deployment, cellulosic materials have the potential to become sustainable, green materials of choice for high end applications such as water purification.

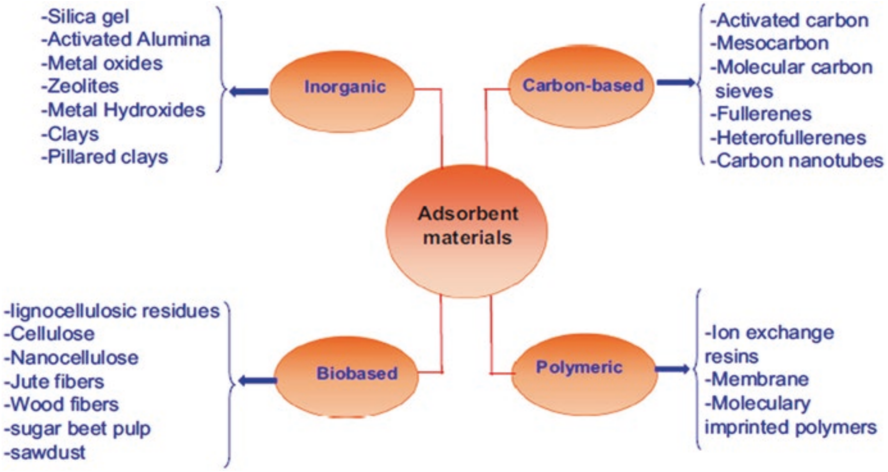

Fig. 4.2 The most commonly used adsorbents

4.3.2.1 Adsorption by Green Adsorbents

Recently, a great deal of interest in the research for the removal of heavy metals and dyes from industrial effluent has been focused on the use of green adsorbents in particular from natural sources, agricultural residues and wastes particularly lignocellulosic biomass and low-cost sources from which activated carbon adsorbents will be produced. Figure 4.3 compiles the various green adsorbents that have been used for wastewater treatment.

Barka et al. investigated the biosorption of methylene blue, eriochrome black T and alizarin S dyes from aqueous solutions using dried prickly pear cactus cladodes as a low-cost, natural and eco-friendly biosorbent (Barka et al. 2013). The maximum adsorption capacities were reported to be 189.83 mg/g for methylene blue, 200.22 mg/g for eriochrome black T and 118.35 mg/g for alizarin S. In another study, Ferrero explored the adsorption of methylene blue onto ground hazelnut shells Ferrero (2007). It was observed that adsorption capacities of methylene blue for hazelnut shells was 41.3 mg/g, which was five times higher than the respective amount reported for activated carbon obtained from the same material. Hameed investigated the feasibility of using papaya seeds for methylene blue adsorption and observed a high adsorption capacity of 556 mg/g (Hameed 2009a). McKay and co-workers reported high adsorption capacities for methylene blue and Safrarine dye using some green adsorbents such as tea wood bark, rice husk, cotton waste, hair and bituminous coal (McKay et al. 1999). The adsorption capacities for Safranine dye were found to be 1119, 838, 875, 190 and 120 mg/g and for methylene blue were 914, 312, 277, 158 and 250 mg/g for tea wood bark, rice husk, cotton waste, hair and bituminous coal, respectively. El Haddad and co-workers explored animal bone meal as a novel green adsorbent for the removal of Rhodamine B from wastewaters (El Haddad et al. 2016). The adsorption capacities obtained at different temperatures were close to 65 mg/g. Vijaya Kumar studied the adsorption of Violet 54

Fig. 4.3 Various green adsorbents

using a musa spp. waste adsorbent but the adsorption capacity was found to be 36.49 mg/g which was quite low (Kumar et al. 2010). Some disperse dyes namely Begacron Blue BBLS 200% and Miketon Polyester Scarlet RCS were removed with palm ash by Hasnain Isa and co-workers with adsorption capacities of 49.5 and 61 mg/g respectively (Isa et al. 2007). El-Mekkawi and Galal investigated that the adsorption capacity of rutile TiO_2 and Degussa P25 TiO_2 for the removal of Direct Fast Blue B2RL and an adsorption capacity of 56 and 144 mg/g respectively (El-Mekkawi and Galal 2013). Table 4.4 depicts the adsorption capacities of various green adsorbents for the removal of dyes and heavy metals. Comparatively, the green adsorbents show higher adsorption ability for dyes than the metal ions after modification as in the case of azolla, the adsorption capacity further enhances.

Interesting works have been reported regarding the adsorption of various heavy metals onto green adsorbents. In a study by Salam and co-workers showed the adsorption behavior of some adsorbents such as peanut husk charcoal, fly ash, and natural zeolite, with respect to copper and zinc ions, in order to consider their application to the purification of metal finishing wastewater (Salam et al. 2011). The results showed that peanut husk charcoal, fly ash and natural zeolite all hold potential to remove cationic heavy metal species from industrial wastewater in the following order: fly ash (0.18 mg/g) < peanut husk charcoal (0.36 mg/g) < natural zeolite

Table 4.4 Adsorption capacities of various green adsorbents for the removal of dyes and heavy metals

Green adsorbent	Dye/ heavy metal	Adsorption capacity (mg/g)	Reference
Cactus cladodes	Methylene blue	189.83	Barka et al. (2013)
	Eriochrome black T	200.22	
	Alizarin S	118.35	
Hazelnut shells	Methylene blue	41.3	Ferrero (2007)
Papaya seeds	Methylene blue	556	Hameed (2009a)
Tea wood bark	Methylene blue	914	McKay et al. (1999)
Rice husk		312	
Cotton waste		277	
Hair		158	
Bituminous coal		250	
Tea wood bark	Safrarine	1119	McKay et al. (1999)
Rice husk		838	
Cotton waste		875	
Hair		190	
Bituminous coal		120	
Animal bone meal	Rhodamine B	65	El Haddad et al. (2016)
Musa spp	Violet 54	36.49	Kumar et al. (2010)
Palm ash	Begacron Blue BBLS 200%	49.5	Isa et al. (2007)
	Miketon Polyester Scarlet RCS	61	
Rutile TiO_2	Direct Fast Blue B2RL	56	El-Mekkawi and Galal (2013)
Degussa P25 TiO_2	Direct Fast Blue B2RL	144	
Sludge	Cr(VI)	26.31	Bhattacharya et al. (2008)
Rice husk ash		25.64	
Activated alumina		25.57	
Fuller's earth		23.58	
Fly ash		23.86	
Saw dust		20.70	
Neem bark		19.60	
Treated olive stones	Cd(II)	49.3	Aziz et al. (2009)
Orange waste	Cd(II)	48.33	Pérez-Marín et al. (2007)
Azolla + $MgCl_2$	Pb	33	Khosravi and Rakhshaee (2005)
	Cd	29	
	Cu	40	
	Zn	24	
Azolla + $MgCl_2$ in the presence of H_2O_2	Pb(II)	228	Khosravi and Rakhshaee (2005)
	Cd(II)	86	
	Cu(II)	62	
	Zn(II)	48	

(1.18 mg/g). However, the adsorption capacities were extremely low and could not be attractive, not only for batch experiments but also for industrial use.

Bhattacharya et al. (2008) investigated the removal of Cr (VI) from aqueous solution with batch adsorption techniques using different low-cost adsorbents. He used some low-cost adsorbents such as clarified sludge, rice husk ash, activated alumina, fuller's earth, fly ash, saw dust and neem bark to determine the adsorption efficiency for Cr (VI). These adsorbents demonstrated low adsorption capacities of 26.31, 25.64, 25.57, 23.58, 23.86, 20.70 and 19.60 mg/g for clarified sludge, rice husk ash, activated alumina, fuller's earth, fly ash, saw dust, and neem bark. Aziz and co-workers investigated the adsorption of cadmium from treated olive stones and the adsorption capacity was 49.3 mg/g (Aziz et al. 2009). Heavy metals such as Cr(III), Cu(II) and Zn(II) were able to be removed from wastewater using hydrochloric acid treated carrot residues (Nasernejad et al. 2005). Acid treatment was performed in order to remove tannins, resins, reducing sugars and coloured materials. The adsorption of metal ions onto carrot residues was possible due to the presence of carboxylic and phenolic groups which have cation exchange properties. It was observed that adsorption of the metals increased at higher pH values of the solutions. Maximum adsorption capacities were 45.09, 32.74 and 29.61 mg/g for Cr (III), Cu (II) and Zn (II) respectively. Perez-Marin et al. showed that the untreated orange waste could only adsorb 48.33 mg/g Cd (II) (Pérez-Marín et al. 2007). Another interesting green adsorbent is azolla, a small aquatic fern which is commonly used as a fertilizer in botanical gardens and as green manure in rice fields. Azolla treated with $MgCl_2$ was used to remove Pb, Cd, Cu and Zn (Khosravi and Rakhshaee 2005). The adsorption values of Pb, Cd, Cu and Zn by azolla treated with $MgCl_2$ were approximately 33, 29, 40 and 24 mg/g respectively. These values increased with increasing concentration of $MgCl_2$ due to better ion exchange behavior between heavy metals and Mg^{2+} ions on the cell walls of azolla. No remarkable effect on the heavy metal removal was observed when azolla was treated with H_2O_2. However, the highest metal removal was reported on treating azolla with 2 M $MgCl_2$ in the presence of 8 mM H_2O_2. The maximum adsorption capacities for Pb (II), Cd (II), Cu (II) and Zn (II) were 228, 86, 62 and 48 mg/g respectively. In another study, adsorption of divalent heavy metal ions particularly Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} onto acid and alkali treated banana and orange peels was performed by Annadurai and co-workers (Annadurai et al. 2003). The adsorbents were modified with nitric acid and sodium hydroxide. In general, the adsorption capacity decreases in the order of $Pb^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+}$ for both adsorbents. Banana peel exhibited higher maximum adsorption capacity for heavy metals compared to orange peel. The reported maximum adsorption capacities were 7.97, 6.88, 5.80, 4.75 and 2.55 mg/g for Ni, Zn, Cu and Pb respectively using banana peel as adsorbent and 7.75, 6.01, 5.25, 3.65 and 1.82 mg/g for Ni, Zn, Cu and Pb respectively using orange peel as adsorbent. Nitric acid treated peels showed better adsorption capacities followed by sodium hydroxide treated peels and water treated peels. Based on regeneration studies, it was reported that the peels could be used for two regenerations for removal and recovery of heavy metal ions. Among the naturally occurring adsorbents, peat is a partially fossilized plant matter. It is formed in poorly oxygenated wetlands, where the rate of accumulation of plant matter is greater than that of decomposition. Allen et al. reported the sorption of three basic dyes, namely basic blue 3, basic yellow 21 and basic red 22 onto peat (Allen et al. 2004). Chitin is a natural polysaccharide found particularly in the shells of crustaceans such as crab and shrimp, the cuticles of insects, and the cell walls of fungi. It is the second most abundant polysaccharide after cellulose. It has gained importance in environmental biotechnology due to its very good adsorption capacity towards dyes (Annadurai et al. 1999) and metal ions. Akkaya et al. investigated the adsorption of reactive yellow 2 and reactive black 5 by chitin (Akkaya et al. 2007). Clay minerals and zeolites were reported to be unconventional adsorbents for the removal of dyes from aqueous solutions due to their cheap and abundant resources along with higher surface areas (Liu and Zhang 2007). Clay materials with sheet-like structures (Tahir and Rauf 2006) and needle like structure (Huang et al. 2007) have been increasingly explored by researchers because they are cheaper than activated carbons and possess high specific surface area (Zhao and Liu 2008). On the other hand, zeolites are three dimensional, microporous, crystalline solids with well-defined structures that can absorb dyes with a capacity of up to more than 25% of their weight in water.

4.3.2.2 Adsorption on Cellulose-Based Green Adsorbents

Cellulose based materials are available in abundant quantity, cheap and have low or little economic value. Different forms of cellulosic materials are used as adsorbents such as fibers, leaves, roots, shells, barks, husks, stems and seed as well as other parts also. Natural and modified types of cellulosic materials are used in different pollutant detoxifications in water and wastewater.

Plant stalks are cellulosic materials consisting of cellulose, hemicelluloses and lignin. Jalali and Aboulghazi (2013) investigated the feasibility of sunflower stalks for lead (Pb) and cadmium (Cd) metal ion adsorption. Batch adsorption studies were conducted to study the effect of contact time, initial concentration, pH and adsorbent doses on the removal of Cd (II) and Pb (II) metal ions at room temperature. The maximum sorption capacities for Pb (II) and Cd (II) were reported to be 182 and 70 mg/g respectively. In another study, oil palm shell was evaluated as an adsorbent for the removal of Cu (II) from synthetic waste water (Chong et al. 2013). An adsorption capacity of 1.756 mg/g was reported for Cu (II). They also used the same adsorbent for Pb (II) removal and reported an adsorption capacity of 3.309 mg/g for Pb (II) metal ion. Rice husk is another cellulosic material consisting of 32.24% cellulose, 21.34% hemicelluloses, 21.44% lignin, 15.05% mineral ash and a high percentage of silica in its mineral ash. Pretreatment of rice husk can remove lignin and hemicelluloses, decrease cellulose crystallinity, and increase the porosity and surface area. Rice husk can easily be converted into rice husk ash at 300 °C which contains 92–95% silica. Untreated rice husk was used for the removal of Cr (III) and Cu (II) from synthetic wastewater (Sobhanardakani et al. 2013). The maximum sorption capacity of 22.5 and 30 mg/g were obtained for Cr (III) and Cu (II) respectively. In another study, tartaric acid-modified rice husk was used for the removal of Cu (II) and Pb (II) ions from aqueous solutions (Malik et al. 2016). He reported that the maximum metal uptake was found to be 29 and 108 mg/g at 27 °C for Cu (II) and Pb (II) metal ions respectively. Sugarcane bagasse, an agro waste from sugar industries has been extensively studied because of its low price and high availability all over the world. It was used by Alomá et al. (2012) in the removal of Ni (II) ions from the aqueous solution. The adsorption capacity for Ni (II) ion removal at pH 5 at 25 °C was approximately 2 mg/g. The process was observed to be exothermic and spontaneous. Yu et al. (2015) used sugarcane bagasse modified with pyromellitic dianhydride modified sugarcane bagasse and unmodified form for the removal of heavy metals such as Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2}. It was found that adsorption of these four metal ions increased with an increasing solution pH and dosages. The adsorption capacities of modified bagasse were 1.06, 0.93, 1.21 and 1.0 mmol/g and for unmodified bagasse 0.04, 0.13, 0.10,and 0.07 mmol/g for Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} respectively. Orange peel suggests high metal adsorption potential due to its high content of cellulose, pectin, hemicelluloses and lignin. Sivaraj et al. (2001) studied the effectiveness of orange peel in adsorbing acid violet 17 dyes from aqueous solutions. The adsorption capacity was 19.88 mg/g at pH 6.3. Adsorption was found to increase with increasing pH. Furthermore, maximum desorption of dye was achieved in water medium at pH 10.0. Orange peel waste was also examined for the removal of congo red, procion orange and rhodamineB dyes (Namasivayam et al. 1996). Acidic pH was found to be favorable for the adsorption of three dyes. Arami et al. (2005) also studied the use of orange peel as low-cost adsorbent for the removal of direct red 23 and direct red 80 from aqueous solutions. The adsorption capacity was found to be 10.72 and 21.05 mg/g respectively for the two studied dyes at initial pH 2. Banana peel, a commonly produced fruit waste, was examined as an adsorbent for the removal of Cd(II) from environmental and industrial wastewater (Memon et al. 2008). An adsorption capacity of 35.52 mg/g was reported for Cd (II). They used the same adsorbent for Cr (VI) removal and reported an adsorption capacity of 131.56 mg/g in case of Cr (VI) (Memon et al. 2009). Table 4.5 shows the adsorption capacity of various lignocellulosic adsorbents, the major source of cellulose, for the removal of dyes and heavy metals.

Most of the adsorption studies have been focused on untreated plant wastes because of low cost, easy availability and easy to handle. But only a few untreated adsorbents show good adsorption potential and performance of these adsorbents has been remarkably affected upon physical and chemical treatment. Pretreatment of cellulose based adsorbents can also remove lignin, hemicelluloses thereby decreasing cellulose crystallinity and increasing the porosity or surface area.

Table 4.5 Compilation results on the removal of various dyes and heavy metals by different cellulose-based adsorbent

Cellulose-based adsorbent	Dyes/heavy metals	Adsorption capacity (mg/g)	References
Jute fiber	Congo red	8.116	Roy et al. (2013)
Rice husk	Direct red 31	74.07	Safa et al. (2011)
Citrus waste	Reactive blue 19	37.45	Asgher and Bhatti (2012)
Sunflower seed hull	Methylene violet	92.59	Hameed (2008)
Grass waste	Methylene blue	457.64	Hameed (2009b)
Spent tea leaves	Methylene blue	300.05	Hameed (2009c)
Mango seed	Victazol orange	44.8	Alencar et al. (2012)
Wheat straw	Cr(VI)	47.16	Dhir and Kumar (2010)
	Ni(II)	41.84	Dhir and Kumar (2010)
Rice husk	Cr(III)	22.5	Sobhanardakani et al. (2013)
	Cu(II)	30.0	
Mango peel	Pb(II)	99.02	Iqbal et al. (2009)
Mosambi (sweet lime) peel	Cr(VI)	250	Saha et al. (2013)
Sugarcane bagasse	Ni(II)	2.0	Alomá et al. (2012)
Sunflower stalk	Cd(II)	69.80	Jalali and Aboulghazi (2013)
Oil palm shell	Cu(II)	1.75	Chong et al. (2013)
	Pb(II)	3.39	
Bamboo leaf powder	Hg(II)	27.11	Mondal et al. (2013)
Cauliflower waste	Pb(II)	47.63	Hossain et al. (2014)
Coir fibers	Ni(II)	2.51	Shukla and Pai (2005)
	Zn(II)	1.53	

4.3.2.3 Adsorption by Modified Cellulose

Cellulose by itself cannot be satisfactorily applied for adsorbing pollutants and thus many attempts have been made to utilize cellulose as a pollutant adsorbent through chemical and physical modification. Cellulose is abundant in hydroxyl groups which can anchor other functionalities through a variety of chemical modifications. Modification of cellulose involves the direct modification and monomer grafting. Direct cellulose modification in the preparation of adsorbent materials are esterification, etherification, halogenation, oxidation, alkaline treatment, and silynation (O’Connell et al. 2008; Hokkanen et al. 2016).

Zhang et al. (2014a) produced a novel adsorbent using acrylic acid and carboxymethyl cellulose for the removal of methyl orange, disperse blue 2BLN and malachite green chloride. The removal ratio of adsorbent to methyl orange, disperse blue 2BLN and malachite green chloride reached to 84.2%, 79.6% and 99.9% respectively. In another study, acrylonitrile was grafted to the cellulose surface using the photografting technique wherein the cyano groups were amidoximated with hydroxylamine (Kubota and Shigehisa 1995). The ability of these cellulose amidoximated adsorbents to adsorb Cu (II) was investigated and the maximum adsorption capacity was found to be 51 mg/g. Later, the resultant acrylonitrile -grafted celluloses were treated with triethylene tetraamine. The sample containing triethylene tetraamine groups exhibited an adsorption capacity of 30 mg/g for Cu(II) (Kubota and Suzuki 1995). Goel et al. (2015) converted cotton textile waste to a cationized adsorbent, poly [2 (Methacryloxy) ethyl] trimethylammonium chloride for treatment of dye waste water. It was then investigated for the removal of acid blue 25 and acid blue 74 from aqueous solutions. The cellulosic adsorbent with 25% grafting yield exhibited equilibrium adsorption capacities of ~540.0 mg/g and ~340.0 mg/g for acid blue 25 and acid blue 74, respectively. The desorption percentage for the dyes was found to be more than ~95% and ~50% for acid blue 25 and acid blue 74, respectively. In another study, a reactive cloth filter was fabricated by grafting acrylonitrile/methacrylic acid onto cotton cloth. The irradiation technique was used for grafting. After subsequent amidoximation, the material was used for the recovery of uranium from radioactive waste obtained from nuclear fuel fabrication laboratories. Musyoka et al. (2014) functionalized cellulose through esterification with furan-2, 5-dione for the removal of methyl violet dye. This functionalized cellulose adsorbent showed higher dye removal capability of 106.38 mg g^{-1} than the non-functionalized cellulose of 43.668 mg g^{-1}. Chemically modified cellulose bearing Schiff's base and carboxylic acid groups was synthesized for the removal of Cu(II) and Pb (II) from aqueous solutions (Saravanan and Ravikumar 2016). This novel green adsorbent was synthesized by periodate oxidation of cellulose followed by condensation reaction with p-aminobenzoic acid for the Schiff's base forming reaction. Bediako et al. developed an adsorbent via carbomethylation and cross linking reactions from waste lyocell fabric to produce carbomethyl cellulose adsorbent. Adsorption studies were conducted for the removal of Cd (II). Moreover this adsorbent displayed approximately 17 times greater metal uptake than the original material and at neutral and alkaline pH, maximum Cd (II) uptake was displayed. Hokkanen et al. used aminopropyltriethoxysilane modified microcrystalline cellulose for the removal of Ni(II), Cu(II) and Cd(II) ions from aqueous solutions (Hokkanen et al. 2014). Aminopropyltriethoxysilane is a silane coupling agent bearing one amino group in one molecule. Silane is easily hydrolyzed to the silanol group and can be further dehydrated with surface hydroxyl groups of cellulose. Also the amino groups could bind the metal ions, improving the adsorption capacity. The maximum removal capacities of this adsorbent for Ni (II), Cu (II) and Cd (II) ions were 2.734, 3.150 and 4.195 mmol/g respectively (Table 4.6).

4.3.2.4 Adsorption by Modified Nano/Microcellulose

Cellulose based adsorbents in the form of porous macro-sized particles were found to increase the surface area and enhance the adsorption capacity. However, diffusion within the particles has limitations and can lead to a decrease in the adsorption

Table 4.6 Adsorption capacities (in mg/g) of various modified cellulose adsorbents for the removal of heavy metals and dyes

Cellulose adsorbent	Modifying agents	Heavy metal/dye	Maximum adsorption capacity (mg/g)	Reference
Cellulose	1. Acrylonitrile 2. Hydroxylamine (amidoxime)	Cu(II)	0.47	Kubota and Shigehisa (1995)
Cellulose	Glycidylmethacrylate	Cr(VI)	2.38	Anirudhan et al. (2013)
Cellulose	Acrylonitrile N,N-methylenebisacrylamide (amino)	Cd(II)	0.19	Zheng et al. (2010)
Cellulose bead	1. Acrylonitrile	Cr(III)	73.5	Liu et al. (2001)
	2. Sodium hydroxide (carboxyl)	Cu(II)	70.5	
Cellulose pulp	1. Acrylic acid 2. Acrylamide carboxyl (amino)	Cu(II)	0.74	Bao-Xiu et al. (2006)
Cellulose	1. Glycidyl methacrylate (imidazole)	Cu(II)	60	Navarro et al. (1999)
		Co(II)	20	
	2. Polyethylene imine (amine)	Zn(II)	27	
Cellulose	Acrylic acid (carboxyl)	Cu(II)	5.17	Hajeeth et al. (2013)
		Ni(II)	4.71	
Cellulose	Methyl benzalaniline	Cu(II)	157.3	Saravanan and Ravikumar (2015)
		Pb(II)	153.5	
Cellulose powder	Acrylic acid (carboxyl)	Pb(II)	55.9	Güçlü et al. (2003)
		Cu(II)	17.2	
		Cd(II)	30.3	
Cotton cellulose	Acrylamide (amino)	Hg(II)	712	Biçak et al. (1999)
Cellulose	Succinic anhydride (carboxyl)	Cu(II)	0.47	Gurgel et al. (2009)
		Cd(II)	0.76	
		Pb(II)	0.99	
Cellulose	Succinic anhydride + triethylenetetramine (carboxyl, amine)	Cr(VI)	0.82	Gurgel et al. (2009)
Cellulose	Triethylenetetramine (amine)	Cu(II)	0.89 & 1.09	Gurgel et al. (2009)
		Cd(II)	0.60 & 0.77	
		Pb(II)	0.71 & 0.93	
Cellulose bagasse	HCl, HNO_3, NaOH tartaric, citric and oxalic acids (carboxyl)	Zn(II)	0.12	Velazquez-Jimenez et al. (2013)
		Cd(II)	0.13	
		Pb(II)	0.17	
Cellulose	Glycidyl methacrylate diethylenetriamine acetic acid (carboxyl)	Malachite green basic fuchsine	3.16 1.36	Zhou et al. (2013)

(continued)

Table 4.6 (continued)

Cellulose adsorbent	Modifying agents	Heavy metal/dye	Maximum adsorption capacity (mg/g)	Reference
Cellulose	Succinic anhydride + sodium bicarbonate (Carboxylate)	Co(II)	2.46	Melo et al. (2011)
		Ni(II)	2.46	
Wood pulp	Succinic anhydride (carboxyl)	Cd(II)	169	Geay et al. (2000)
Wood pulp	Citric acid (carboxyl)	Cu(II)	24	Low et al. (2004)
		Pb(II)	83	
Cellulose	1. Sodium methylate	Hg(II)	1.44	(Navarro et al. 1999)
	2. Epichlorohydrin			
	3. Polyethyleneimine			
Cellulose powder	Acrylonitrile hydroxylamine (amidoxime)	Cu(II)	3.76	Saliba et al. (2005)
		Cr(III)	3.90	
Cellulose (Juniper fiber)	Sodium hydroxide (hydroxyl)	Cd(II)	0.26	Min et al. (2004)
Wood sawdust cellulose	Sodium hydroxide (hydroxyl)	Cd(II)	0.65	Šćiban et al. (2006)
Sawdust cellulose	Sodium hydroxide (hydroxyl) untreated	Cd(II)	0.65	Memon et al. (2007)

capacity and rate. Moreover, adsorbents have to be easily separated from the effluent and be easily regenerated with a minimum loss in the adsorption capacity. For this reason, many studies involving the application of nanosized adsorbents, in particular for the wastewater treatment, has gained much attention. At the nanoscale level, materials are characterized by different physical, chemical, and biological properties compared to their larger size counterparts. These adsorbents offer high specific surface area associated with sorption sites and short intraparticle diffusion distance which may lead to a fast kinetics compared to the conventional adsorbents (Tashiro and Kobayashi 1991; Pan et al. 2003; Mohmood et al. 2013; Qu et al. 2013). Such unique properties of this nano/microcellulose enhance their potential to solve the current pollution problems. The presence of abundant hydroxyl groups on the surface of nanocellulose function as metal-binding sites on the biomass and provides a unique platform for significant surface modification to graft a myriad of functional groups onto the cellulosic structure. The surface modifications of nano/microcellulose include sulfonation, TEMPO-mediated oxidation, phosphorylation, esterification, etherification, silyation, amidation, etc.

Sun et al. prepared a cellulosic adsorbent by halogenation of microcrystalline cellulose followed by the functionalization with pyridone diacid for the removal of Pb (II) and Co (II) from aqueous solutions (Sun et al. 2017). The maximum adsorption capacities of this adsorbent towards Pb (II) and Co (II) ions were determined to be 177.75 and 122.70 mg/g, respectively, which are greater than most of the reported cellulosic adsorbents. The content of carboxyl groups in this cellulosic adsorbent was determined to be 1.32 mmol/g, which was responsible for the high adsorption towards metal ions. The adsorption equilibriums for both Pb (II) and Co (II) were reached within 10 min. The adsorbent could be regenerated in 0.1 mol/L hydrochloric acid solution. Isogai et al. (2011) categorized 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidized cellulose nanofibrils as novel bio based nanomaterials prepared by the position selective catalytic oxidation of C6 primary hydroxyls on the cellulose microfibril surface using TEMPO-mediated oxidation. These fibers were then used to remove Pb (II), Ca (II) and Ag (I) from aqueous solutions (Saito and Isogai 2005). The ion exchange behavior of carboxylate groups in the TEMPO-oxidized fibrous cellulose was compared with that of the fibrous carboxyl methyl cellulose with almost the same carboxylate content as that the former. The studies revealed that TEMPO oxidized cellulose had higher metal ion contents than the fibrous carboxyl methyl cellulose. Sehaqui et al. conducted a study on the adsorption of Cu(II) on TEMPO-oxidized fibrous cellulose and observed that the Cu(II) adsorption onto the nanofibers increased nearly with the carboxylate content for pH values between 3 and 7 (Sehaqui et al. 2014). Carboxylate groups on the surface of TEMPO oxidized nanofibers effectively adsorbed radioactive UO_2^{2+} which was about 167 mg/g at pH 6.5. The high adsorption capability for $UO_2^{2+}$was attributed to the very high surface to volume ratio, the high surface charge density and hydrophilicity of cellulose nanofibers (Ma et al. 2011). In another study, TEMPO-oxidized fibrous cellulose modified with polyethyleneimine via crosslinking with glutaraldehyde also exhibited a higher adsorption of Cu(II) at pH 5 than the polyethyleneimine grafted cellulose (Zhang et al. 2016). Liu et al. (2014) reported that cellulose nanocrystals obtained by sulphuric acid hydrolysis displayed a higher uptake capacity for adsorption of silver ions of 34.35 mg/g at pH 6.5. However for cellulose nanofibrils obtained through mechanical grinding, the adsorption capacity for Ag (I) was only 15.45 mg/g at pH 5.45. For both the above bio nanomaterials, the best adsorption performance was observed near neutral pH. The adsorption capacities decreased significantly under acidic pH as the H^+ ions competes with Ag^+ ions on being adsorbed onto the negatively charged $–SO_3$ functional groups on the cellulose nanocrystal surface. The negative surface charge density was higher for cellulose nanocrystal than for cellulose nanofibrils. The positive-negative interactions were the predominant mechanism of silver adsorption onto the nanocellulose. Yu et al. (2013) reported that cellulose nanocrystals were chemically modified with succinic anhydride, which upon further treatment with sodium bicarbonate resulted in the sodic nanoadsorbent. Batch experiments were conducted with succinic anhydride treated nanocrystals and the resultant sodic nanoadsorbent for the removal of Pb^{2+} and Cd^{2+}. The maximum adsorption capacities of the former for Pb^{2+} and Cd^{2+} was 367.6 mg/g and 259.7 mg/g respectively and that for the sodic nanoadsorbent for Pb^{2+} and Cd^{2+} was 465.1 mg/g and 344.8 mg/g respectively. Hokkanen et al. investigated the removal of Zn (II), Ni (II), Cu (II), Co (II) and Cd (II) from aqueous solutions using succinic anhydride modified mercerized nanocellulose. Mercerization increases the specific surface area thereby making the hydroxyl groups of cellulose more accessible for succinylation. The maximum metal ion adsorption ranged from 0.72 to 1.95 mmol/g in the order of Cd > Cu > Zn > Co > Ni. The modified adsorbent could be regenerated after ultrasonic treatment with regeneration efficiencies ranging from 96% to 100% (Hokkanen et al. 2013). Sheikhi et al. (2015) showed that the functionalization of crystalline nanocellulose can be done by selectively oxidizing the C_2 and C_3 hydroxyl groups followed by oxidizing the aldehyde groups to form 2, 3-dicarboxyl groups in aqueous acid medium. This functionalized nanocellulose demonstrated a maximum adsorption capacity for Cu^{2+} of 185 mg/g at pH 4. In another study, the amino – functionalized bacterial cellulose, upon reaction with epichlorohydrin and diethylenetramine exhibited a maximum adsorption capacity for Cu^{2+} of 63 mg/g at pH 4.5 and 87 mg/g for Pb^{2+} (Shen et al. 2009). Liu et al. (2015) investigated the potential of nanocellulose and enzymatically phosphorylated nanocellulose for the removal of Ag^+, Cu^{2+} and Fe^{3+} from industrial effluents. Phosphorylated nanocellulose efficiently scavenged multiple metal ions with the metal ion selectivity in the order $Ag^+ > Fe^{3+} > Cu^{2+}$. Enzymatically phosphorylated nanocellulose displayed a higher adsorption capacity for Ag^+, Cu^{2+} and Fe^{3+} at pH = 4 of 136 mg/g, 117 mg/g and 115 mg/g respectively whereas nanocellulose exhibited 120 mg/g, 114 mg/g and 73 mg/g for Ag(l), Cu(ll) and Fe(lll) respectively. Xanthated nanobananacellulose displayed the maximum adsorption capacity for Cd (ll) to be 154.26 mg/g at pH 6.0 from aqueous solutions. The high adsorption capacity of this biosorbent resulted from the sulphur groups which had strong affinity for Cd(ll) (Pillai et al. 2013). Bisphosphonate nanocellulose obtained from periodate oxidized and sodium alendronate aminated cellulose fibers by mechanical disintegration method efficiently removed vanadium with a maximum adsorption capacity of 194 mg/g at pH 2. The maximum removal of vanadium occurred at low pH which is due to the complexation of vanadium with bisphosphonate groups and the electrostatic interaction between cationic vanadium and anionic acid groups (Sirviö et al. 2016). Zhang et al. (2014b) grafted (poly) acrylic acid onto the surface of cellulose nanofibril from bamboo to remove Cu (II) from aqueous solutions. This functionalized nanocellulose exhibited adsorption capacity about 3 times higher that of pristine bamboo cellulose nanofibrils. Hokkanan et al. investigated the adsorption properties of aminopropyltriethoxysilane modified microfibrillated cellulose (APS/MFC) in aqueous solution containing Ni (ll), Cu (II) and Cd(II) ions. The adsorption of metals onto this adsorbent was due to the presence of amino groups on aminosilane and/or hydroxyl groups on cellulose fiber. The selectivity sequence of the metal ions was in the order Ni (II) > Cu (II) > Cd (II) for the adsorbent. The maximum removal capacities of the APS/MFC adsorbent was 2.734, 3.150 and 4.195 mmol/g for Ni(II),Cu(II) and Cd(II) respectively (Hokkanen et al. 2014). Magnetic iron nanoparticle modified microfibrillated cellulose was adopted for the removal of arsenic (V) from aqueous solutions (Hokkanen et al. 2016). Mautner et al. (2016) synthesized phosphorylated nanocellulose papers for copper adsorption from aqueous solutions for copper removal from contaminated water via electrostatic interactions. Cellulose nanofibrils were modified with phosphate groups by reacting cellulose nanofibril derived from cellulose sludge, with phosphoric acid. Phosphorylated cellulose nanofibril nanopapers, manufactured via a papermaking process exhibited lower permeance as compared to unmodified cellulose nanofibril nanopapers. The nanopaper ion-exchangers were demonstrated to be able to adsorb copper ions in dynamic filtration experiments on passing water containing copper ions through the nanopapers. It was found that nanopapers were able to adsorb copper from aqueous solutions up to 200 mg per one m^2 filtration area equivalent to almost 20 mg copper per one g phosphorylated cellulose nanofibril. Also it was observed that phosphate groups on the surface of the nanopaper contributed to a greater extent to the overall copper adsorption than functional groups within the bulk of the nanopapers. Furthermore, the nanopapers could be regenerated by washing with phosphoric acid and reused without significant loss in adsorption capacity. Moreover, the adsorption capacity for copper was reduced by only 10% when calcium ions were present in the same concentration.

The above studies suggest that nanocellulose have the potential to adsorb a wide range of heavy metal ions, including Ag(I), Cu(II), Fe(III), Ni(II), Cd(II),Cr(III) and Zn(II), but have varying adsorption capacity. Generally, cellulose nanocrystals have better adsorption behavior than native cellulose nanofibers, which is attributed to the surface functionalities and specific surface area. The metal adsorption behavior of nanocellulose was found to be pH dependent and the best adsorption performance was observed near neutral pH.

Organic dye pollutants display cationic, anionic, or non-ionic properties and pose a significant environmental problem in many parts of the world. Cationic dyes are removed using nanocellulose functionalized with anionic moieties. Carboxylated nanocellulose has been extensively studied for the sorption of cationic dyes. Carboxylated nanocellulose synthesized via TEMPO-mediated oxidation, resulted in a significantly higher uptake of 769 mg/g at pH 9 of the cationic dye methylene blue, compared to nanocellulose with sulfate groups on their surfaces with an adsorption capacity of 118 mg/g at pH = 9 (Batmaz et al. 2014). Cellulose nanocrystals prepared by esterification with maleic anhydride, displayed a high uptake capacity for several cationic dyes (Qiao et al. 2015). Carboxylated cellulose nanocrystals prepared using ammonium persulfate by the one-step oxidation showed an adsorption capacity of 101 mg/g for methylene blue at a neutral pH (Leung et al. 2011; He et al. 2013). He et al. prepared carboxylated nanocellulose from microcrystalline cellulose using ammonium persulfate and the negatively charged carboxyl groups on the surface of nanocellulose binded to positively charged methylene blue molecules. The maximum adsorption capacity was reported to be 101.2 mg/g (He et al. 2013). Batmaz et al. used pristine nanocellulose derived from sulfuric acid hydrolysis of pulp fiber for the adsorption of methylene blue. The nanocellulose was decorated with negative sulfate ester groups that served as the binding sites for the methylene blue molecules. The adsorption capacity could be enhanced by introducing more negative carboxyl groups via TEMPO oxidation of pristine cellulose nanocrystals. The adsorption capacity for pristine nanocellulose and carboxylated nanocellulose were found to be 118 and 769 mg/g respectively (Batmaz et al. 2014). Carboxylated nanocellulose produced by citric acid/hydrochloric hydrolysis of microcrystalline cellulose was used for the adsorption of methylene blue (Yu et al. 2016). Novel carboxylate functionalized nanocellulose produced via grafting maleic anhydride was used for the adsorption of multiple cationic dyes, such as methylene blue, crystal violet, malachite green and basic fuchsin (Qiao et al. 2015). Anionic dyes are usually removed using nanocellulose functionalized with cationic moieties. Cationic nanocellulose prepared via successive sodium periodate oxidation, followed by reaction with ethylenediamine, displayed a maximum uptake of 556 mg/g of acid red GR (Jin et al. 2015a). Amine functional groups usually display maximum adsorption at lower pH and a significant decrease in the uptake capacity is observed at higher pH values. Cationic nanofibers obtained through quaternization with glycidyltrimethylammonium chloride exhibited an uptake of 664 mg/g and 683 mg/g of Congo red and acid green 25, respectively, in less than a minute (Pei et al. 2013). Nanocrystalline cellulose forming cross linked microgels with polyvinylamine exhibited a high affinity for both cationic and anionic dyes, with maximum adsorption uptakes for acid red GR, Congo red 4BS, and reactive light yellow K-4G, of 896 mg/g, 1469 mg/g, and 1250 mg/g, respectively (Jin et al. 2015b). The same functionalization method was explored by Zhu et al. (2016) on dialdehyde functionalized cellulose powder, but using hyper-branched polyethyleneimine. The adsorbent displayed a high Congo red adsorption of 2100 mg/g and a high cationic basic yellow adsorption of 1860 mg/g. Eyley et al. used imidazolium grafted nanocellulose for the adsorption of anionic dye, Orange II. Here the imidazolium groups were introduced by a heterogeneous Cu(I) catalyzed azide-alkyne cycloaddition reaction on nanocellulose (Eyley and Thielemans 2011). Jin et al. (2015a) synthesized amino functionalized nanocellulose by grafting ethylenediamine on sodium periodate oxidized pristine nanocellulose and the adsorption of anionic dyes such as Congo red 4BS, acid red GR and reactive yellow K-4G was studied. Hashim and El-Shishtawy prepared cationized cellulose via the reaction of microcrystalline cellulose with 3-chloro-2-hydroxypropyl triethylammonium chloride.

In another study by Hu et al. (2014) microcrystalline cellulose was functionalized with quaternary amine groups and used as an adsorbent to remove congo red dye from aqueous solution. The ultrasonic pretreatment of microcrystalline cellulose was investigated during its functionalization and an adsorption capacity of 304 mg/g at initial pH under a dose of 0.1 g/L and initial concentration of 80 mg/L was exhibited. After functionalization, the spectroscopic results indicated that the quaternary amine group was successfully grafted onto the cellulose, the surface was transformed to be coarse and porous, and the crystalline structure of the original cellulose was disrupted.

Table 4.7 shows the adsorption capacities of nano/microcellulose and their modified counterparts. Nanocellulose, particularly, cellulose nanocrystals when chemically modified with succinic anhydride and then with sodium bicarbonate resulted in the modified nanoadsorbent which displayed the maximum adsorption capacity for metal ions. That is 465.1 mg/g and 344.8 mg/g for Pb^{2+} and Cd^{2+} respectively. Among the dyes, carboxylated nanocellulose synthesized via TEMPO-mediated oxidation, resulted in the maximum adsorption capacity of 769 mg/g for the cationic dye methylene blue.

Table 4.7 Modified and unmodified nanocellulose adsorbents for the removal of heavy metals and dyes

Nano/ microcellulose adsorbent	Modification	Heavy metal/dye	Maximum adsorption (mg/g)	Reference
TEMPO-oxidised nanocellulose	_	UO_2^{2+}	167	Ma et al. (2011)
Nanocellulose	Succinic anhydride	Pb(II)	367.6	Yu et al. (2013)
		Cd(II)	259.7	
	Succinic anhydride + sodium bicarbonate	Pb(II)	465.1	
		Cd(II	344.8	
Bacterial cellulose	Epichlorohydrin + diethylenetramine	Cu(II)	63	Shen et al. (2009)
		Pb(II)	87	
Nanocellulose	–	Ag(I)	120	Liu et al. (2015)
		Cu(II)	114	
		Fe(III)	73	
Nanofiber	Enzymatic phosphorylation	Ag(I)	136	
		Cu(II)	117	
		Fe(III)	115	
Nanocellulose	Xanthation	Cd(II)	154.26	Pillai et al. (2013)
Aminated nanocellulose	Sodium periodate + sodium alendronate	Vanadium	194	Sirviö et al. (2016)
Microfibrillated cellulose	Aminopropyltriethoxysilane	Ni(II)	2.734	Hokkanen et al. (2014)
		Cu(II)	3.150	
		Cd(II)	4.195	
Nanocellulose	–	Ag(I)	34.4	Liu et al. (2014)
Nanocellulose	Phosphorylation	Ag(I)	136	Liu et al. (2015)
		Cu(II)	117	
		Fe(III)	115	
Pristine nanocellulose	_	Ag(I)	56	
		Cu(II)	20	
		Fe(III)	6.3	
Microcrystalline cellulose	Halogenation + pyridine diacid	Pb(II)	177.75	Sun et al. (2017)
		Co (II)	122.70	
Nanocellulose	TEMPO oxidation	Methylene blue	769	Batmaz et al. (2014)
Nanocellulose	–	Methylene blue	118	
Nanocellulose	Maleic anhydride	Crystal violet	244	Qiao et al. (2015)
Nanocellulose	Ammonium persulphate oxidation	Methylene blue	101	He et al. (2013)

(continued)

Table 4.7 (continued)

Nano/ microcellulose adsorbent	Modification	Heavy metal/dye	Maximum adsorption (mg/g)	Reference
Crystalline nanocellulose	Sodium periodate oxidation + ethylene diammine	Acid red GR	556	Jin et al. (2015a)
Crystalline nanofiber	Glycidyl trimethyl ammonium chloride	Congo red	664	Pei et al. (2013)
		Acid green25	683	
Crystalline nanocellulose microgels	Polyvinyl amine	Acid red GR	896	Jin et al. (2015b)
		Congo red 4BS	1469	
Dialdehyde functionalized cellulose powder	Hyperbranched polyethyleneimine	Congo red	2100	Zhu et al. (2016)
		Basic yellow	1860	
Microcrystalline cellulose	Ammonium persulphate	Methylene blue	101.2	He et al. (2013)
Pristine crystalline nanocellulose	Sulphuric acid hydrolysis	Methylene blue	118	Batmaz et al. (2014)
Pristine crystalline nanocellulose	TEMPO oxidation	Methylene blue	769	Batmaz et al. (2014)
Microcrystalline cellulose	–	Methylene blue	4.95	Tan et al. (2016)
Microcrystalline cellulose	Quaternary amine groups + ultrasonication	Congo red	304	Hu et al. (2014)

4.4 Conclusion

Among the various available methodologies for pollutant removal from wastewater, adsorption is regarded better to the conventional methods because of the effective, economical and eco-friendly nature of the technique. Green adsorbents have garnered attention due to its low cost and environmentally friendly features. Cellulose-based adsorbents obtained from lignocellulosic materials contain a variety of functional groups which could be modified. Upon chemical modification, the adsorption capacity of these adsorbents have enhanced as a result of the increase in active binding sites on modification and addition of new functional groups that favor the higher uptake of pollutants. Currently, research is focused to synthesize modified cellulose and nanocellulose based adsorbents for wastewater treatment. Among the various cellulose adsorbents reviewed, modified cellulose nanocrystals offered greater adsorption capacities for pollutant removal from wastewaters.

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Chapter 5
Activated Carbon from Food Waste

Ramonna Kosheleva, Athanasios C. Mitropoulos, and George Z. Kyzas

Contents

Abstract Activated carbons are considered to be the most successful adsorbent materials due to their high adsorption capacity for the majority of pollutants, e.g. dyes, heavy metals, pharmaceuticals, phenols. They possess large surface area, and different surface functional groups, which include carboxyl, carbonyl, phenol, quinone, lactone and other groups bound to the edges of the graphite-like layers. Therefore, they are regarded as good adsorbents both in liquid and gas phases. The most widely used carbonaceous materials for the industrial production of activated carbons are coal, wood and coconut shell. These types of precursors are quite expensive and often imported, in many places; hence making it necessary, particularly for developing countries, to find a cheap and available feedstock for the preparation of activated carbon for use in industry, drinking water purification and wastewater treatment. In order to reduce the synthesis cost of activated carbons, some green final products are recently proposed, using several suitable agricultural by-products (lignocellulosics) – i.e. including olive-waste cakes, cattle-manue compost, bamboo

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materials, apple pulp, potato peel – as activated carbon precursors. In this chapter, special attention is given to activated carbons based on some of agricultural wastes from the Mediterranean region, which can be characterized as green.

5.1 Introduction

With the growth of mankind, society, science, technology our world is reaching to new high horizons but the cost which we are paying or will pay in near future is surely going to be too high. Among the consequences of this rapid growth is environmental disorder with a big pollution problem. Environmental pollution is the contamination of the physical and biological components of the earth/atmosphere system to such an extent that normal environmental processes are adversely affected. The introduction of contaminants into the environment causes harm or discomfort to humans or other living organisms damaging the environment. Environmental pollution is categorised in three main groups; air, water and soil pollution. In general, any human activity releases pollutants, with the most severe being sulphur dioxide, nitrogen dioxide, carbon monoxide, ozone, volatile organic compounds, insecticides and herbicides, food processing waste, pollutants from livestock operations, heavy metals, chemical waste and others. With the rapid push of globalization, wide application of new technologies and the increasing pressure from resource and environment, it has been realized that the natural environment is irreversible and critically important for urban development, thus is the call for urban transition towards greening (McGranahan 2015). Green technology, also referred to as environmental technology or clean technology, is an encompassing term. It deals with using science and technology in order to protect the environment. A lot of techniques fall under this term such as the use of green chemistry, environmental monitoring, and more. Specifically, Green Chemistry is defined as the design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances (Sheldon 2008), governed by 12 principles. One of them is the usage of renewable feedstock for material synthesis (Anastas and Eghbali 2010). The major renewable feedstock on the planet both for material and energy is bio-mass, the material available from living organisms. This includes wood, crops, agricultural residues, food (Kamm et al. 2000; Fornasiero and Graziani 2011). Research of the past two decades have shown that bio-mass as feedstock has many applications including transport fuel production (McKendry 2002), chemicals (Tong et al. 2010), electricity generation (Chaudhuri and Lovley 2003) as well as materials production for usage in many industrial applications (Agbor et al. 2011).

According to Environmental and Energy Study Institute, a list of some of the most “common” bio-mass feedstocks is comprised of (i) grains and starch crops (sugar cane, corn, wheat, sugar beets, industrial sweet potatoes), (ii) agricultural residues (corn stover, wheat straw, rice straw, orchard pruning), (iii) food waste (waste produce, food processing waste), (iv) forestry materials (logging residues, forest thinning), (v) animal byproducts (tallow, fish oil, manure), (vi) energy crops (switchgrass, hybrid poplar, willow, algae) and (vii) urban and suburban wastes (municipal solid wastes, lawn wastes, wastewater treatment sludge, urban wood wastes, disaster debris, trap grease, yellow grease, waste cooking oil). Biomass derived from plants, the so-called lignocellulosic bio-mass, is the most abundant and bio-renewable bio-mass on earth (Isikgor and Becer 2015). The major components of woody plants, as well as grasses and agricultural residues are three structural polymers; lignin (10–25%), hemicellulose (20–30%) and cellulose (40–50%) (Pérez et al. 2002). Apart of these three components, which vary regarding the source, there are also some minor non-structural components such as proteins, chlorophylls, ash, waxes, tannins (in the case of wood) and pectin (in most of fibers). Among the three fractions of the lignocellulosic materials, lignin has been identified as the main component in lignocellulosic bio-mass responsible for the adsorption process (Mohamad Nor et al. 2013). Specifically, lignocellulosic wastes are a low cost natural carbon source for the production of various materials including activated carbon. In addition, lignocellulosic precursors and biomass sources have become important materials to produce activated carbon because their use creates many benefits, mainly environmental. Nowadays, it is possible to find numerous research papers devoted to the synthesis characterization and applications of novel precursors to produce activated carbon. Except from the treatment conditions, the biomass source determines many of the properties of the final material. In fact, although the lignin is considered to be the major contributor for activated carbons production, properties such as the mean pore size versus the specific porous volume are effected by all precursor's components whatever is its weight contribution (Cagnon et al. 2009).

Activated carbon is a well-known material used in an increasing number of environmental applications; namely water and waste water treatment, gas filters, green gases capturing. High surface area, a microporous structure, and a high degree of surface reactivity make activated carbons versatile adsorbents, particularly effective in the adsorption of organic and inorganic pollutants from aqueous solutions ref. In recent years, scientific interest on lignocellulosic precursors for activated carbon production used as storage material of several gases as well as catalytic reactor has been increased (Fiuza et al. 2015; Ruiz et al. 2017), leading to replacement of less cost effective materials such as metal organic frameworks (Llewellyn et al. 2008; Kuppler et al. 2009; Sumida et al. 2012) or less eco-friendly (in sense of production of raw material or activation treatment) such as fly ash (Lu and Do 1991).

Activated carbon is the generic term used to describe a family of amorphous carbonaceous adsorbents with a highly crystalline form and well developed internal pore structure. Any organic material can be the starter material (precursor) of activated carbon production after being subjected to carbonization and activation of its organic substances (Bansal and Goyal 2005). Traditionally, typical precursors for activated carbon production were coal (Teng et al. 1998), peat (Veksha et al. 2009), and lignite (Shrestha et al. 2013). Mainly due to economical as well as environmental issues, the replacement of those raw materials with low-cost and environmental friendly precursors is mandatory. To this end, in recent years there has been a growing interest in the production of activated carbons from agricultural and forestry wastes (Dias et al. 2007). In the context of the present chapter, as agricultural wastes are considered residues of agricultural by products (not for consumption) i.e. peels, stems and fruit core. The following sections describes the treatment and activation processes of carbonaceous materials of various precursors. Furthermore, comparison of final properties regarding treatment conditions as well as the source is provided too. Related industrial applications are discussed.

5.2 Activated Carbon from Lignocellulosic Biomass

The production of activated carbons from lignocellulosic materials is a two phase process; it involves carbonization at low temperatures (700–800 K), in the absence of oxygen, to eliminate volatile materials, and subsequent activation at higher temperatures (1100–1300 K) to increase the porosity and the surface area of the solid. The process of activation can be carried out through different ways: (i) with chemical agents (e.g. KOH, H_3PO_4, $ZnCl_2$), known as chemical activation; (ii) with CO_2, air or water vapor for physical or thermal activation or; (iii) these two methods combined (Marsh and Rodríguez-Reinoso 2006). Although physical activation is a low-cost process with a lower environmental impact, chemical activation of is preferred because of porosity improvement (adsorption capacity) of the final material (Rodríguez-Reinoso and Molina-Sabio 1992).

Recent studies have shown that extraction of valuable solutions from agricultural by product could also act as reagents of biochar activation, minimizing further the cost and the impact to the environment (Treviño-Cordero et al. 2013). To this end, the pre-treatment process of biomass should follow (among others) the following criteria: (i) affordable with low energy and resource consumption, (ii) low water and chemical consumption in order to minimize or even eliminate liquid waste stream, (iii) low operation risk and safe to operate as well as (iv) low cost of the construction materials in order to be considered cost effective and eco-friendly. It is worth to mention that the challenge is to develop adsorbents which are not only cost effective and environmentally friendly, but also possess high efficiency, selectivity and regeneration δrate and cycles (Ince 2014). There is numerous literature about the influence of preparation conditions of carbonaceous materials on the physicochemical properties of the produced material e.g. surface area, pore size distribution. Another critical factor is physicochemical properties of the precursors itself; depending on weather conditions, harvesting methods and even on the season that it is collected, agricultural precursors' properties such as initial moisture, oxygen content, and derived components fraction of cellulose, hemicellulose, lignin may vary (Huggins et al. 2011; Balan 2014).

5.3 Lignocellulosic Precursors for Activated Carbons Process

Activated carbons have a highly developed porosity and an extended interparticulate surface area. As it was already mentioned, preparation involves two main steps: the carbonization of the carbonaceous raw material at temperatures below 800 °C in an inert atmosphere and the activation of the carbonized product. Thus, all carbonaceous materials can be converted into activated carbon, although the properties of the final product will be different, depending on the nature of the raw material used, the nature of the activating agent, and the conditions of the carbonization and activation processes.

Carbonization of bio-mass has a number of advantages over common biological treatments regarding time and required equipment. Also, high process temperatures can destroy pathogens and such potential organic contaminants as pharmaceutically active compounds that could be present (Libra et al. 2011). On the other hand, the preparation of activated carbon is usually conducted at relatively high temperatures, consequently there is also a considerable risk of overheating, leading to complete combustion of the carbon (Foo and Hameed 2011). Besides of pyrolysis in furnaces, there have been developed other carbonization technologies; to name a few of the most promising technologies there is hydrothermal carbonization, microwave heating. When compared to fermentation and anaerobic digestion, hydrothermal carbonization is referred to as the most exothermic and efficient process for carbon fixation. In addition, some feed stocks are toxic and cannot be converted biochemically. Microwave technology is gaining importance as a promising technology for research and industrial applications. Microwave heating offers a potential means of cost reduction as it is capable of reducing the heating period, energy consumption, and gas consumption. Additionally, microwave irradiation may promote rapid and precise temperature control and compact equipment size. However, application of microwave technology for carbonization process has not been implemented until recently, hence there are very few studies that report its use for preparation of activated carbon (Foo and Hameed 2011; Thue et al. 2016).

Physical activation of carbonized material involves the implementation of hot gases or water vapor steams (Román et al. 2008; Zhang et al. 2014; Vivo-Vilches et al. 2015). This generally is carried out by using one or a combination of carbonization in the presence of an inert gas to convert this organic precursor to primary carbon, which is a mixture of ash, tars, amorphous carbon, and crystalline carbon, and activation/ oxidation where high temperature in the presence of carbon dioxide, steam is required. Undesirably, in the step of carbonization, some decomposition products or tars are deposited in the pores (Rodríguez-Reinoso and Molina-Sabio 1992; Maciá-Agulló et al. 2004).

Chemical activation on the other hand, prohibits the formation of tar; in this way a carbonized product with a well-developed porosity may be obtained in a single operation (Lozano-Castelló et al. 2001; Kalderis et al. 2008). Chemical activation takes place prior to carbonization wherein the agricultural waste is impregnated with certain chemicals, which is typically an acid such as H_3PO_4, a strong base such as KOH, and NaOH or a salt such as $ZnCl_2$. Then the agricultural precursor is carbonized at lower temperatures (450–900 °C). Number of studies conducted, indicate that the carbonization/activation step proceeds simultaneously with the chemical activation (Milenković et al. 2009; Ludwinowicz and Jaroniec 2015). It is also believed that the chemical incorporated to the interior of the precursor particles reacts with the products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinking of the particle; in this way the conversion of the precursor to carbon is high, and once the chemical is eliminated after heat treatment, a large amount of porosity is formed (Kumar and Jena 2016; Shamsuddin et al. 2016). Chemical activation is preferred over physical activation owing to the lower temperature and shorter time needed for activating the material. The chemical activation method presents many advantages over the physical activation method and therefore it has been employed enormously in many studies when the preparation of activated carbon from agricultural wastes is concerned. In addition, activated carbon obtained by chemical activation exhibits a larger surface area and better developed mesoporosity than physical activation (Aygün et al. 2003; Valix et al. 2004). On the other hand, from the economical point of view, chemical activation requires the use of agents that rise the total cost of the production process (Zhang et al. 2004; Dias et al. 2008).

As it was mentioned in previous section, the suitability of an activated carbon for different applications is matter of many parameters. Although carbonization/activation conditions play the most important role in adsorbent's efficiency, they are not the only major contribution towards porous structure of activated carbon; the original nature and structure of the precursor also is significant. The proximate analysis along with ultimate analysis of the precursor are common properties investigated in the related literature. Proximate analysis involves the determination of moisture content, volatile matter, fixed carbon and ash content of the raw material (Jin et al. 2012; Koay et al. 2013).

From the economical aspect, biomaterials are promising precursors for adsorbents because of their abundance. To preserve their cost effective treatment, especially regarding large scale applications, the source should be taken into account. For instance, although some agricultural wastes (i.e. coconut shells (Shrestha et al. 2013; Nandeshwar et al. 2016), hazelnut husk (Imamoglu and Tekir 2008; Milenković et al. 2009; Kwiatkowski and Broniek 2017), rice husk (Foo and Hameed 2011; Menya et al. 2018; Rwiza et al. 2018) and others) are acknowledged as highly efficient precursor, in many cases it has to be imported, resulting in an increase of cost. Therefore, agricultural/household residuals, including fruit and vegetable peels are considered as good alternatives. Moreover, regions such as Mediterranean, can take advantage of residuals produced from regional commodities like olive or peach stones. Properties of such agricultural wastes are collected

Table 5.1 Surface area of various agricultural wastes abundant in Mediterranean region

Precursor	Surface area (m^2/g)	Reference
Orange peels	1090	Fernandez et al. (2014)
Orange peels	1477	Xie et al. (2014)
Olive stones	1031.5	Román et al. (2008)
Olive stones	790.25	Kula et al. (2008)
Cherry stones	1200	Lussier et al. (1994)
Peach stones	608	Duranoğlu et al. (2010)
Potato peels	904–1041	Kyzas et al. (2016)

form recent studies. Table 5.1 summarizes some of the most investigated agricultural wastes as activated precursors; only obtained surface is presented because properties such as pore size, contaminant uptake and are omitted because such characteristics depend mainly on process conditions. Effect of process conditions will be discussed in a following section.

5.4 Characterization of Lignocellulosic Based Activated Carbons

As it was mentioned, characterization of adsorbents derived from lignocellulosic based materials should be comprised of both physicochemical analysis of precursors and textural analysis after processing. Analysis of raw material determining moisture, percentage of main polymeric structure as well as density and other compounds presence is required. Proximate analysis conducted prior to carbonization phase and ultimate analysis after that provide important information about the final product properties (Wilkins et al. 2001; Fu et al. 2013; González and Pliego-Cuervo 2013; Kumar and Jena 2016). The impact factor of those measurements on the understanding of effects that treatment processes have is discussed in depth through literature.

Given an example is the work by Sentorun and his associates (2006), where it was found that the initial sulfur content influenced the obtained porosity properties and surface area of the final material. One interesting outcome of the specific study is the effect of raw material treatment on the final properties (after activation). Here, the apricot stones were dried under two different environments prior activation process; sun-dried and SO_2-dried apricot stones. As it is illustrated in Figs. 5.1 and 5.2, the two pre-treatment methods resulted with very different materials regarding porosities and internal microstructure. Investigation of the effect of process variables such as activation temperature, soak time, and particle size range on microstructural characteristics of the adsorbent was studied as well. The highest BET surface area carbon (1092 m^2/g) was obtained from the low sulfur content (0.04%) apricot stone with a particle size range of 1–3.35 mm at the activation conditions of 800 °C for 4 h.

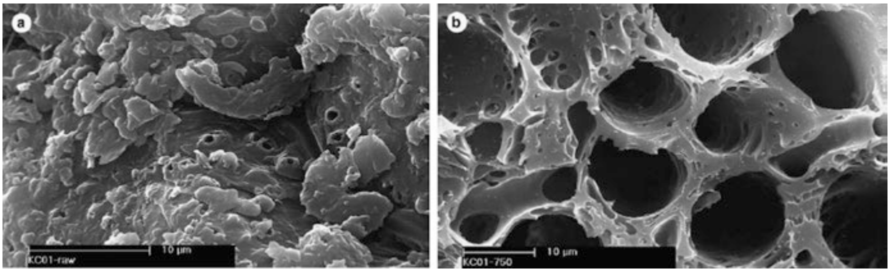

Fig. 5.1 Scanning Electron Microscopy (SEM) micrograph of sun-dried apricot stone (**a**) prior activation, (**b**) after activation; prior activation the sun-dried raw material presents almost no porosity and a thick wall structure while after activation a wide porosity is observed. (Reprinted with permission by Elsevier (Şentorun-Shalaby et al. 2006))

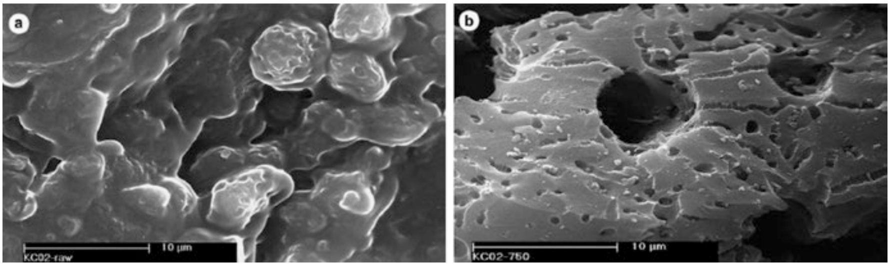

Fig. 5.2 Scanning Electron Microscopy (SEM) micrographs of SO_2-dried apricot stone (**a**) prior activation, (**b**) after activation; high ash and Sulphur content of the precursor leads to the appearance of anon-porous cloudy surface (**a**) while activated material does not present a well-developed porous network compared to sun-dried material (Fig. 5.1). (Reprinted with permission by Elsevier (Şentorun-Shalaby et al. 2006))

Temperature during carbonization phase plays significant role in the final material's properties. Biochar yield increases with a decrease in pyrolysis temperature, an increase in the residence time, and a preferable low heating rate (Tripathi et al. 2016). The highest treatment temperature is regarded to have the greatest effect on the physical properties of biochar produced (Mukome et al. 2013). In a recent study, Palanisamy et al. reported that biochar of *C. vulgaris* prepared at higher temperatures (450–600 °C) contained a higher proportion of organic matter (C, H and N) than those produced at lower temperatures.

Kyzas et al. (2016) conducted experiments involving potato peels for metal ion removal. In this work, potato peels were cleaned and dried for 24 h for moisture reduction. The activation agent used was H_3PO_4. All conditions kept same (amount of dried material, activation agent) and three samples were produced at different heating temperature (400, 600, 800 °C). Comparison of the samples regarding, among others, the surface area of the material, revealed that the higher surface area resulted for the sample treated at 600 °C, while at higher temperature the surface area of the sample was less than 1 m^2/g. Size distribution analysis confirms the

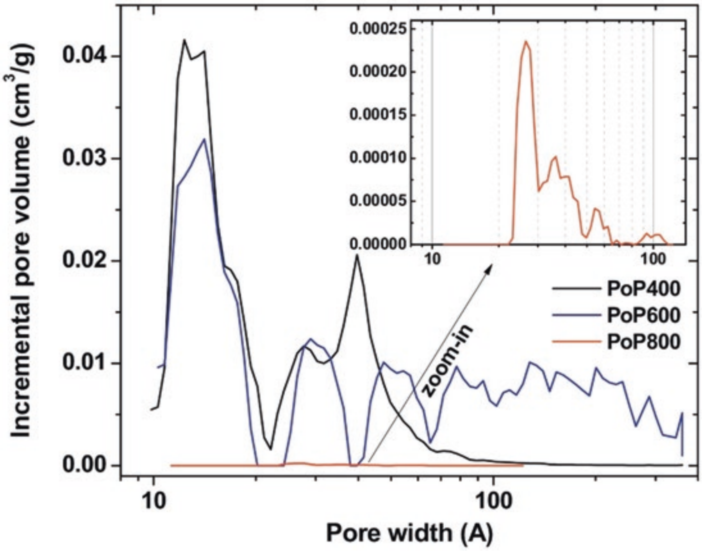

Fig. 5.3 Pore size distribution curves of potato peels (denoted as PoP in the graph) carbons activated at 400 °C, 600 °C and 800 °C. PoP400 is defined by micro-meso porosity while PoP600 curve shows a structure combined of all three groups of pores. (Reprinted with permission by Elsevier (Kyzas et al. 2016))

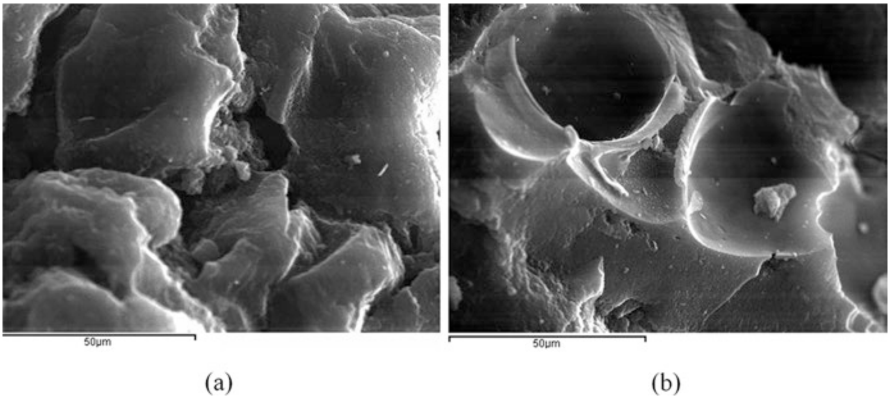

Fig. 5.4 Scanning Electron Microscopy (SEM) micrographs of surface morphology of potato peels samples; (**a**) potato peels treated at 400 °C, (**b**) potato peels treated at 600 °C. (Reprinted with permission taken by Elsevier (Kyzas et al. 2016))

aforementioned results as it is shown in Fig. 5.3. This last observation may be attributed to overheating of the sample leading to precursor's combustion.

The two samples were further examined by means of SEM (Fig. 5.4). As it is obvious from Fig. 5.4 (taken by Kyzas et al. 2016), potato peels treated at 600 °C perform larger porous. Relevant studies have been conducted including many different lignocellulosic materials and the influence of treatment conditions on the produced activated carbons.

Köseoğlu and Akmil-Başar (2015) reported the effect of treatment temperature on orange peel activation. Chemical activation using zinc chloride ($ZnCl_2$) and potassium carbonate (K_2CO_3) was performed. The activation temperatures and impregnation ratios were selected at the range of 500–1000 °C and 1:1, respectively. The carbon content of activated carbons resulted 70% while BET surface area of activated carbons prepared with K_2CO_3 and $ZnCl_2$ activation is 1352 and 1215 m^2/g, respectively. An increase in the temperature for both K_2CO_3 and $ZnCl_2$ led to a decrease in the yields of the activated carbons. The overall yield of material, estimated to be greater for activated carbons by $ZnCl_2$ than those activated by K_2CO_3, although it does not play any role in performance.

Besides, the activation temperature, the time and heating rate are important preparation variables for obtaining activated carbon with specific characteristics (Yorgun and Yıldız 2015). According to the literature review, chemically activated carbons have developed surface areas ranging from very poor surface area to as high as 3000 m^2/g, a broad range of pore size distribution from a few nm to a few micrometers and pore volume from 0.1 to 2.5 cm^3/g. From released scientific reviews, it is possible to note that activation with alkaline agents produces the highest surface area values. Secondly, treatment with acids and acid salts supplies also high surface areas; for instance, impregnation of Chinese fir using H_3PO_4 yields to 2518 m^2/g, impregnation of lignin with H_2SO_4 produces 1946 m^2/g, the use of $FePO_4$ on peach stone provides 2160 m^2/g, use of $CaHPO_4$ on pistachio shell supplies 1919 m^2/g, and the use of K_2CO_3 on wasted tea yields 1722 m^2/g. Finally, activation of coconut shells with $ZnCl_2$ and with a mixture $ZnCl_2/H_2O_2$ yields to 2450 and 2050 m^2/g, respectively. Additionally, depending on the activation agent, the carbon surface exhibits numerous functional groups, mainly acidic, which favor specific interactions allowing it to act as an ionic interchanger (Toles et al. 2000; Bharathi and Ramesh 2013). Physical activation of lignocellulosic chars with steam or CO_2 causes different effects on the development of microporosity. In early stages of activation process, CO_2 develops narrow micropores, while steam widens the initial micropores of the char. At high degrees of burn-off, steam generates activated chars which exhibit larger meso- and macropore volume than those prepared by CO_2 (Liou 2010). As a result, CO_2 creates activated chars with larger micropore volume and narrower micropore size than those activated by steam. At this point is possible to note that physically activated carbons have smaller surface area values than those obtained from chemical (i.e H_3PO_4, KOH, NaOH and $ZnCl_2$) activation. However, there have been reported high surface area adsorbents from lignocellulosic precursors activated physically (Maciá-Agulló et al. 2004). On the other hand, oxidizing treatments using water steam and CO_2 atmospheres, yield average surface area values, comparable with those obtained from the activation using acid salts; such as K_2CO_3 or $CaHPO_4$. In this sense, water steam of date pits yields surface area of 1467 m^2/g and CO_2 activation of olive stones yields 1355 m^2/g (Román et al. 2008). Other option to design activated carbons with controlled porosity and larger surface areas is the combination of both, chemical and physical activations, simultaneously or by step (Şentorun-Shalaby et al. 2006). For instance, simultaneous physical and chemical activation process have been described a few years ago to improve the mesoporosity in activated carbons from lignocellulosic materials, such as coconut shells and palm stones. According to the authors, $ZnCl_2$ and KOH can be used as chemical activating agent coupled with CO_2. However, the use of $ZnCl_2$ has two advantages of higher mesoporosity and much higher yield of activated carbon. But, the emission of heavy metallic zinc may cause serious environmental problem. KOH/CO_2 activation has a significant contribution to the development of microporosity as well as mesoporosity. In their work, $ZnCl_2/CO_2$ activation of coconut shells yields surface area of 2191 m^2/g whereas the KOH/CO_2 activation of palm stones yields 2390 m^2/g.

5.5 Activated Carbon for Water Purification and Wastewater Treatment

Various industrial processes such as mineral processing, metal mining, tanning in the leather industry, dyeing in textile industry and pigment manufacture, contribute in the discharge of pollutants which can be classified as inorganic (heavy metals, sulphates, nitrates), organic (dyes, phenols, pesticides) and biological (viruses, bacteria).

There have been developed many processes that have been utilized to remove chemical pollutants from different aqueous matrices include, but not limited to, membrane filtration, precipitation, ion exchange, solvent extraction and adsorption (Fu and Wang 2011). Some of the drawbacks associated with these processes include: low removal efficiencies, high cost of regeneration, deposition of sludge, high energy demand, and high reagent requirements, amongst others. Multiple researches lend credence to the postulation that adsorption still remains one of the preferred techniques for pollutant removal from aqueous media since it is safer and easier to use (Cooney 1998).

Over the years, the literature has been enriched with various applications which are based on the adsorption techniques for the removal of pollutants from aqueous waste streams. This amount of knowledge has shown that agricultural-based adsorbents are promising alternatives to the conventional treatment techniques because of their inherent advantages such as minimization of chemical or biological sludge, high efficiency for dilute solutions, no additional nutrients requirements, ease of operation, possibility of adsorbent regeneration,and ultimately, the fact that these materials are non-hazardous to the environment contributes to their growing popularity (Yu et al. 2000; Celik and Demirbaş 2005; Demirbas 2008). This insistence for the use of adsorption as a technique for decontamination of aqueous environments is mainly due to the availability of biomaterials/biomass used as adsorbents, high adsorption capacities and the almost zero cost.

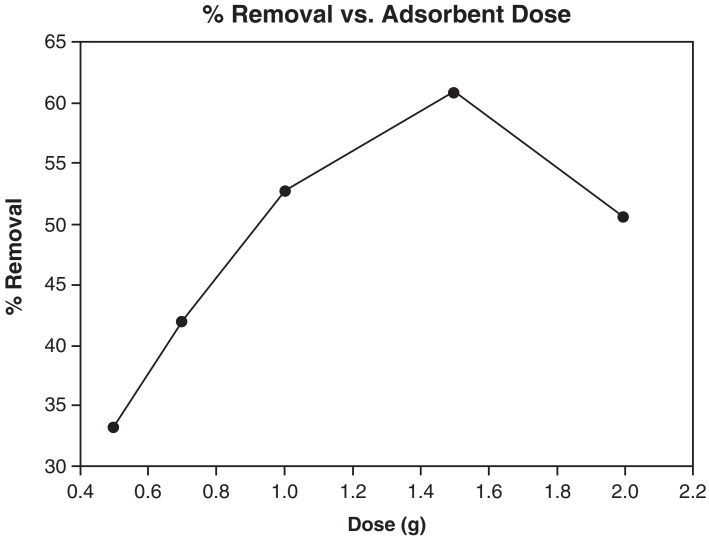

Fig. 5.5 Effect of adsorbent dose on dye removal efficiency. (Reprinted with permission by Springer (AbdurRahman et al. 2013))

5.5.1 Dyes Removal

Dyes are widely used in industries such as textiles, rubber, plastics, printing, leather, cosmetics, to color their products. As a result, they generate a considerable amount of colored wastewater. Besides aesthetic issues, dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration. Among side-effects, there are allergic dermatitis, skin irritation, cancer, mutation.

AbdurRahman et al. (2013), studied the removal of various dyes from textile wastewater by adsorption on orange peels. Obtained results indicate that the adsorption of dyes onto orange peels is influenced by pH values, amount of adsorbents and contact time. Also, the adsorption of dyes onto orange peels follows the Langmuir isotherm model. Additionally, it is reported that for higher removal of dyes from textile effluents adsorbent dose of 1.5 g was favorable (Fig. 5.5). The uptake of the dye increased with increasing contact time and the optimum contact time was obtained at 2 h. Also, the adsorption was found to be higher for pH 7 (Fig. 5.6). Authors concluded that even though the removal efficiency of orange peels is not much higher than other bio-adsorbents, it is preferred for its available.

Another work has been conducted for removal of methylene blue from an aqueous solution (Amela et al. 2012) by biosorption on banana and orange peels waste. Kinetic study is also carried out to observe the effects of various process parameters. The maximum values of adsorption capacities for activated banana peel was 19.671 and 18.647 mg/g for natural banana peel at pH 4–8, 20 °C. The results follow kinetic of pseudo second-order rate equation (Fig. 5.7). The suitability of the

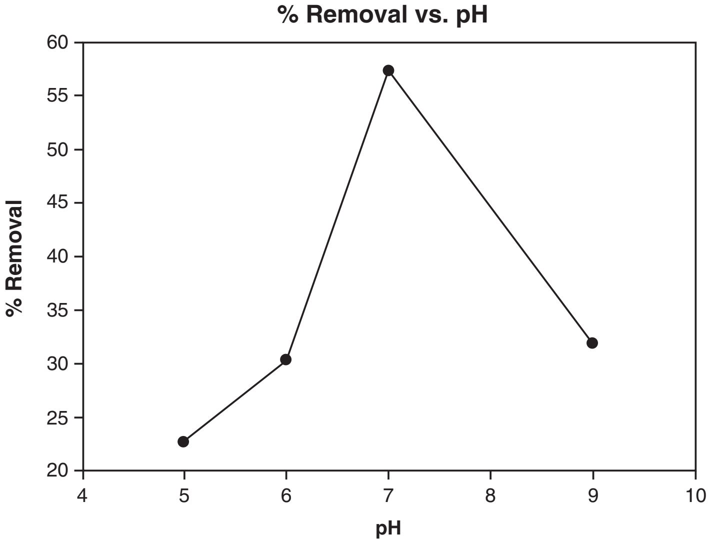

Fig. 5.6 Effect of pH on dye removal; the adsorbent dosage was 1.5 g (previously found) for 90 min of contact time. (Reprinted with permission by Springer (AbdurRahman et al. 2013))

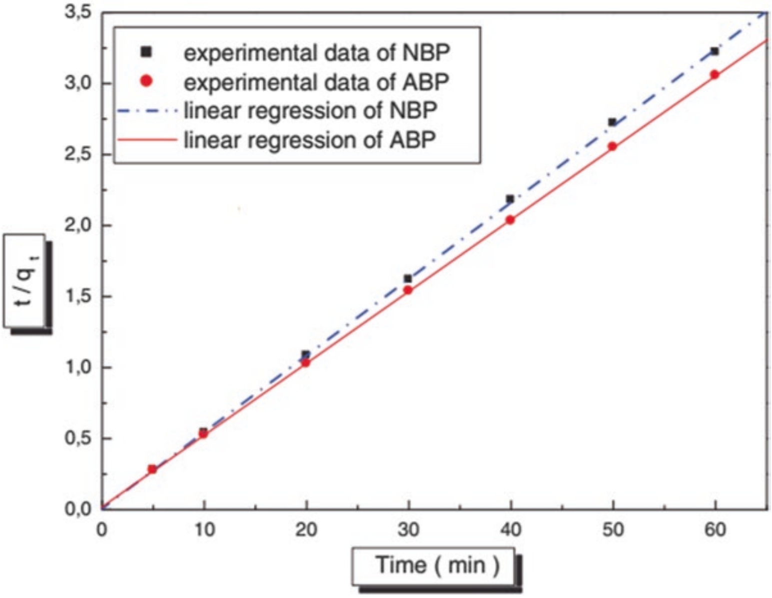

Fig. 5.7 Kinetics of Methylene blue ions onto banana peels (activated and natural –ABP, NBP respectively) test for pseudo second order equation. (Reprinted with permission by Elsevier (Amela et al. 2012))

adsorbent was tested by fitting the adsorption data with four isotherms, namely Freundlich, Langmuir and Temkin. The characteristic parameters for each isotherm have been determined. The Freundlich equation represented the best fit of experimental data for activated banana peel than the other isotherm equations, and Langmuir equation described the adsorption of natural biosorbent.

Namasivayam et al. (1998), examined the adsorption of direct red and acid brilliant blue by waste banana pith. Varying the agitation time, dye concentration, adsorbent dose and pH results were obtained; adsorption capacity was 5·92 and 4·42 mg dye per gram of the adsorbent for direct red and acid brilliant blue, respectively. Adsorption of dye followed first-order kinetics. An acidic pH was favorable for the adsorption of both dyes. An alkaline pH was favorable for desorption of the dyes.

Removal of ultramarine blue dye from aqueous solution using yam peels waste was investigated in the study conducted by Owamah et al. (2013). The effect of adsorbent concentration, dye concentration, time and pH were evaluated. Maximum adsorption occurred at pH of 10. A general increase in adsorption with increase in adsorbent concentration, dye concentration, time and temperature, respectively was also reported. The pseudo second order model with R^2 of 0.98 indicates that adsorption occurred mainly by intra-particle diffusion. The Freundlich and Langmuir isotherms were found suitable for describing the adsorption.

Valorization of olive stones as an agricultural waste into an efficient granular activated carbon for the removal of Methylene blue in batch and fixed bed modes from aqueous solutions was proposed by Benallou Benzekri et al. (2018) The activated carbon preparation was carried out in two steps: an impregnation with 50% phosphoric acid at 170 °C for 2.5 h followed by physical activation using steam at 750 °C. Activated carbons resulted in specific surface areas of 1031.5 and 1029.2 m^2/g, respectively. The Langmuir model was found to describe correctly the isothermal adsorption of Methylene blue for both adsorbents and resulted in adsorption capacities of 107 and 121 mg/g for the commercial one.

Chemically modified olive stones investigated regarding the sorption efficiency towards cadmium and safranine removal from their respective aqueous solutions. Treated Olive stones material was prepared by treatment of olive stones with concentrated sulfuric acid at room temperature followed up by a subsequent neutralization with 0.1 M NaOH aqueous solution. Results indicated that treated olive stones exhibited efficiency in terms of sorption capacities toward the two pollutants (128.2 and 526.3 mg/g for cadmium and safranine, respectively).

In order to valorize olive stones and to show its potential use in the sorption of two dispersed dyes, it was transformed in activate carbon and characterized by Hemsas et al. (2014). The adsorption capacity of activated carbon for the dyes removal was found to be affected by the solution's pH. Acidic pH was found the favour disperse dyes removal. Over 95% removal was achieved for both the dyes at pH 3. The equilibrium time for both dyes was 30 min. Both Langmuir and Freundlich isotherms could be used to describe the adsorption of the dyes. Freundlich adsorption model succeeded in fitting the adsorption isotherms of dyes on olive stones activated carbon in single-solute systems, and prediction of the competitive adsorption behavior of dyes with the Freundlich-based Sheindorf-Rebuhn-Sheintuch model gave acceptable results.

Uğurlu et al. (2007) studied the removal of a reactive dye from aqueous solution by adsorption onto activated carbon from olive stone. Different amounts of activating agent ($ZnCl_2$) and adsorbent particle size were studied to optimize adsorbent surface area. The adsorption experiments were conducted at different process parameters such as adsorbent dose, temperature, equilibrium time and pH. The experimental results showed that at equilibrium time 120 min, optimum pH ranged between 3 and 4, and adsorbent dosage was 2.0 g per 200 mL. While the kinetic data support pseudo-second order, a pseudo-first order model shows very poor fit. In addition, the thermodynamic parameters such as isosteric enthalpy of adsorption $(\Delta H_{ads})_y$, isosteric entropy of adsorption $(\Delta S_{ads})_y$ and free energy of adsorption ΔG0ads were calculated. BET surface area measurements were made to reveal the adsorptive characteristics of the produced active carbon. The surface area of the activated carbon produced with 20% w/w $ZnCl_2$ solution was 790.25 m^2/g.

Survey on the feasibility of the biosorption of two acid dyes (Acid blue 113 and Acid black 1) from aqueous solution using biomass prepared from potato peel waste was attempted by (Hoseinzadeh et al. 2014). Adsorption isotherms were constructed and the kinetics of dye adsorption were studied. Langmuir and Freundlich isotherms, pseudo-first-order, and pseudo-second-order kinetic models were studied. The maximum biosorption was observed at a pH of 2 and 3 for Acid blue 113 and Acid black 1, respectively. The biosorption of two dyes increased with increasing contact time and reached equilibrium after two hours, approximately. Pseudo-second-order kinetic and the Langmuir isotherm model was shown to have better fit for the adsorption of Acid blue 113 and Acid black 1 on used potato peel waste.

Interesting findings are also provided by Atttia et al. (2008), in their work of activated carbon production from peach stones. The acid used for activation was H_3PO_4 at constant temperature but at different concentrations. The obtained results of the materials characteristics such as porosity, surface area reveal that impregnation ratio effects positively the process. On the other hand, increase of temperature conditions and post heat treatment effect negatively the same properties. Equilibrium adsorption of methylene blue proved good uptake of the bulky dye, which improved considerably with impregnation concentration that was related to enhanced porosity. Increased impregnation ratio improved column performance, as well as forcing N_2 pyrolysis or extra heat-treatment. Activated carbon impregnated with 70% H_3PO_4 and carbonized at 500 °C exhibited the best properties which prevailed upon raising treated dye concentration to 150 and 200 mg/L, although degraded its capacity due to the limited mass of adsorbent and to the short contact time.

5.5.2 Heavy Metals Removal

The release of heavy metals into our environment is still large. In certain areas of the world it is even increasing. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. It is well known that some metals can have poisonous or otherwise toxic to human beings and ecological environments, include chromium, antimony, copper, lead, mercury, cadmium, manganese. Studies on heavy metal adsorption by activated carbon from agricultural wastes have shown remarkable removal efficiency even compered to commercial ones (Babel and Kurniawan 2004; Kołodyńska et al. 2017). Among others, most common metals constituting in water pollution are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), mercury (Hg) and their ions. Related studies are presented for heavy metals adsorption by activated carbons from various fruit and vegetable peels as well as stones that can be found abundant in Mediterranean region.

According to Khalfaoui and Meniai (2012), orange peels can efficiently remove copper ions from aqueous solutions. In fact the use of orange peels without any pretreatment leads at the most a copper retention percentage of the order of 75%, whereas percentages over 99% could be achieved by means of chemical activations with sulfuric acid, caustic soda, methanol and acetic anhydride. Remarkably, results showed that saturation was reached after 10 and 5 min, for the cases of no pretreatment and the chemical activation of the orange peels, respectively. The pH study indicated that a value between 4 and 6 seemed to be the most adequate. The results did also show that the copper initial concentration value did have an influence on the retention capacity for the natural solid support. The sorption kinetic study showed that the process could be considered of a pseudo-second order, whereas the obtained equilibrium data were best fitted to the Freundlich model.

Liu et al. (2013) have conducted experiments of cysteine-modified orange peel for the removal of Cu(II) from aqueous solutions compared to diethylenetriamine-modified orange peel. Both materials were systematically evaluated via their capabilities for adsorbing Cu(II), including the key influential parameters such as initial pH, contact time and initial Cu(II) concentration. This work suggests that the sorption of Cu(II) onto both materials fits well with the pseudo-second-order equation, and the corresponding sorption isotherm can be classified to a Langmuir. The maximum capacities of both materaials for adsorbing Cu(II) were found to be 95.23 and 83.68 mg/g, respectively, about three times higher than that of unmodified orange peels. The sorption efficiency of cysteine-modified orange peel drops by merely about 3% after five cycles, implying a promising usage in the removal of Cu(II) from wastewater in practice.

The performance of a microporous activated carbon prepared chemically from olive stones for removing Cu(II), Cd(II) and Pb(II) from single and binary aqueous solutions was investigated by Bohli et al. (2015). Adsorption kinetic rates were found to be fast and kinetic experimental data fitted very well the pseudo-second-order equation. The adsorption isotherms fit the Redlich–Peterson model very well and maximum adsorption amounts of single metal ions solutions follow the trend

Pb(II) > Cd(II) > Cu(II). In another work, Bohli et al. (Bohli and Ouederni 2016) modified surface structure of activated carbon from olive stones using ozone (O_3) in the gaseous phase and in liquid phase using nitric acid (HNO_3) were examined. The activated carbon parent exhibits a high surface area of 1194 m^2/g and shows a predominantly microporous structure. They also revealed that acidic treatment lead to fixation of high amount of surface oxygen functional groups, thus making the carbon surface more hydrophilic. The obtained data from Co(II), Ni(II), and Cu(II) heavy metal ions removal were well fitted to the Redlich-Peterson and Langmuir equation. Further investigation on ability to remove metal ions from binary systems presented an important maximum adsorbed amount as compared to single systems.

Potato peels charcoal (PPC) was investigated as an adsorbent of Cu(II) from aqueous solutions by Aman et al. (2008). Study of the effects of various parameters such as temperature, pH and solid liquid ratios concluded to an optimum pH value found to be 6.0. The thermodynamic parameters such as standard Gibb's free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were evaluated by applying the van't Hoff equation. The equilibrium data at different temperatures were analyzed by Langmuir and Freundlich isotherms.

Although there is a great amount of literature for lignocellulosic activated carbons used efficiently in aqueous solution, development of such adsorbents for gas phase applications is in immature level. The main drawback for gas phase applications of lignocellulosic based activated carbon was considered the low surface area of produced material. Nowadays, research on surface modification of activated carbon from agricultural precursors has open the way for efficient application in air pollution control (Mohamad Nor et al. 2013). The potential use of those adsorbents as catalysts for flue gas, gas storage material of CH_4, CO_2 and other has attract scientists' interest for further study. Reports for efficient CO adsorption (Grigor'ev et al. 2003), CO_2 capture (Fiuza et al. 2015) and other flue gas compounds (H_2S, NO_x) (Ghouma et al. 2017).

Among the various harmful gases, nitrogen oxides (NO_x) have a negative impact through the smog and acid rain formations as well as the decrease of the superior ozone layer (Wilkins et al. 2001; Blondeau et al. 2005). The most recent work for NO_x adsorption from automotive gas exhaust was conducted by Ghouma et al. (2017). In this study, adsorption of NO_2 at room temperature and very low concentration was performed onto three different activated carbons. The importance of textural and surface properties was realized. The results obtained during the different experiments indicate that both of these properties are responsible of NO_2 uptake and reduction to NO. The reduction rate of NO_2 is found to be very high when the activated carbon is prepared by H_3PO_4 activation. Adsorption capacity was found to be higher for one of the subjected activated carbons, attributing this fact to the presence of high amount of basic groups. The difference observed for the breakthrough curve of NO_2 for AC-CO_2 and AC-H_2O is explained by the mesoporous structure of the AC-H_2O sample, which enables a better diffusion of NO_2 inside the activated carbon particles. The particular study is considered to be the only that examines NOx adsorption onto lignocellulosic based activated carbon.

Ahmed et al. (2015) tested nanofibers for lead removal from wastewaters. Here, activated carbon was used as substrate for nanofibers growth. Pb^{2+} was the target pollutant of the study. After experiments of pH, contact time, adsorbent dosage and agitation speed, optimal conditions for sorption were determined. Specifically, the best performance was obtained when the dosage of adsorbent was 0.25 g/L at solution pH 5.5 and 200 rpm for 60 min of contact.

At this point, it will be good to just report some cases of organic components removal. Organic compounds are another severe source of water pollution. Polycyclic aromatic hydrocarbons (PAH) were efficiently removed from water samples by solid phase extraction. Razmi et al. (2016) proposed a new nanocomposite of graphene quantum dots and eggshells for extract PAH. Effect of initial pH of the solution, adsorbent amount within the column as well as the flow rate of the sample on the total extraction efficiency was investigated. Characterization by SEM revealed that although eggshells examined separately presented an irregular crystal structure when mixed with graphene quantum dots a uniform distribution was achieved resulting in an effective contact of the effluent. This study concluded that taking into consideration both the ease of preparation and well adsorption desorption performance, graphene quantum dots-eggshell nanocomposite can be considered suitable for extraction of various aromatic hydrocarbons from water.

Also, in a review article for nitrogen and phosphorous containing pollutants removal, several adsorbents are presented by Prashantha Kumar et al. (2017). Among adsorbents such as zero-valent metal, metal oxides/metal hydroxides, there is a reference to carbon based materials too. Specifically, carbon nanotubes and chitosan based nanocomposite present high uptake values compared to other carbon based materials including graphene (Prashantha Kumar et al. 2017). From all carbon based materials, carbon nanotubes have gained a great attention the past decade. Due to their versatility, carbon nanotubes find many applications including water desalination (Hebbar et al. 2017).

5.6 Conclusions

Activated carbons are considered to be the most successful adsorbent materials due to their high adsorption capacity for the majority of pollutants (dyes, heavy metals, pharmaceuticals, phenols). Their large surface area, and different surface functional groups, which include carboxyl, carbonyl, phenol, quinone, lactone and other groups bound to the edges of the graphite-like layers. Numerous agro-food wastes as summarized in this Chapter regarding their adsorption potential to many pollutants. The most important conclusion is that some basic characteristic of adsorption as capacity and kinetics are directly influenced by the structural characteristics of the prepared materials. It is mandatory to note that the system of adsorbent-adsorbate is unique and therefore to make a safe comparison, the adsorption conditions must be exactly the same. Otherwise, the comparison is faulty.

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Chapter 6
Water Depollution Using Activated Carbons from Aerogels and Bones

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Abstract The presence and removal of different inorganic and organic contaminants in water bodies has been a problem studied in recent years. Different techniques have been developed to eliminate these contaminants, and adsorption is one of the most projected techniques. The removal of heavy metals and phenolic compounds has had good results using activated carbons of different precursors. Activated carbons obtained from different precursors, both natural products and synthetic products is a subject in constant development today.

Here we presented materials that was obtained from animal bones with yields around 50%; with different chemical and textural properties. The samples have a volume of micropores between 0.228 and 1.417 $cm^3.g^{-1}$ and values of 99–180 $m^2.g^{-1}$ area, depending on the precursor and the carbonization atmosphere, the materials obtained are basically mesoporous. The advances we have obtained in the adsorption of phenolic compounds with activated carbon from bone char are shown. The maximum adsorption capacities of 2,4-dinitrofenol correspond to chicken bones CO_2 17.90 $mg.g^{-1}$ and the minimum for bones of Bovine N_2 8.08 $mg.g^{-1}$. For chicken phenol CO_2 10.52 $mg.g^{-1}$ maximum and minimum for bovine N_2 5.92 $mg.g^{-1}$.

For carbon aerogels, with the increase of the resorcinol/catalyst ratio, two series of aerogels are generated: one in which microporous materials are obtained and a second series where they are characterized by the development of mesoporosity. Thus, in the series II of aerogels, as the resorcinol/catalyst ratio increases, the adsorption capacity of the Ni^{2+} ions of the aqueous solution increases, obtaining the greater adsorption capacity of 14.51 mg g^{-1} of Ni^{2+} for the sample AeW600, which is the one with the highest mesoporosity. A detailed study is made of the characterization of the materials obtained using different conventional and non-conventional techniques, as well as the analysis of the adsorption capacities of the contaminants of interest on the porous materials.

In the end, an exploration is presented with the use of molecular dynamics simulation with mathematical models to propose a mechanism of how adsorption occurs on the surface of solids.

6.1 Introduction

The industrial development that was generated indulge the nineteenth century, caused not only the man had a “lifestyle” more comfortable, but that unfortunately we broke the balance of living systems, altering in a very worrying way the life on the planet. There are many examples of this phenomenon, within which we can mention the alteration of the temperature, which have caused the stations in certain countries are today extreme, taking temperatures in winter very low and summers with high temperatures. In tropical countries nor have dealt with this type of alteration of the climate where floods and droughts are very common, generating diseases and ruin. Additionally, in the countries called "industrialized" as a product of their development, e.g. with control elements as, pesticides, fungicides, nuclear tests, etc., have degraded the ozone layer and have contaminated the ground. Many are the industries of these countries that generated and continue to generate a large amount of pollution affecting the life on our planet. To contaminate the immediate nature of this has an impact on human life because we nourish ourselves of crops and animals, thus moving this pollution to human beings. It is for this reason that today humanity has had to face many new diseases due to this misunderstood "industrial development", which has been unreasonable.

There are various contaminants found in the bodies of water, due to the lack of compliance with the rules governing certain countries particularly those who are on the road to development especially metal ions, volatile organic compounds VOC's, dyes and a high content of surfactants molecules, among others. These contaminants are present along all the rivers and alter the balance in ecosystems dramatically to such an extent that life in some of them disappears.

It is necessary to think about this type of development and generate solutions to achieve a sustainable system. Find solutions that do not adversely affect the environment. That allow to create economically viable systems.

Various proposals have been designed with the aim of controlling, reducing and in some cases, eliminate pollutants, so check these environmental problems, which have caused this part of chemistry. It is organized in several sub-areas within which it is worth mentioning green chemistry, area that aims to synthesize and prepare chemical type substances not only to achieve a healthy environment by removing pollutants with direct or indirect deleterious effects on humanity or at least minimize them, but that will decrease the existing pollution. For the control of pollutants, a broad type of materials has been synthesized and prepared. Materials such as catalysts, (Rodriguez-Reinoso 1998), carbon foams, activated carbon cloth (Rodriguez-Reinoso 2005, 2007), clays pillared clays, foams ceramics, zeolites (Gaulke et al. 2016), aerogels, xerogels (Maldonado-Hódar et al. 2013), among other special materials, have been used to reduce and control the environmental pollution generated by the chemical industry (Maya et al. 2015). Within these solids, which have been the most used are the activated carbons due to their chemical and textural features, including: large surface area, volumes and diameters of pores controllable through the process of preparation, as well as its surface chemistry.

The adsorption of organic solutes and metal ions, the heavy metals in aqueous solutions, is a branch that has been of great research and follow up in the application of activated carbon, due to the high adsorption capacities of this material, its fast kinetics of adsorption and its ease of regeneration, related to its porous structure, its surface area and the chemical structure of its surface.

This branch of the adsorption, covers a variety of systems of great magnitude, as the treatment of polluted waters and water for the human consumption, besides its use in the industries of food and pharmaceutic chemistry (Min-Woo et al. 2001).

Phenolic derivatives and metal ions are compounds that belong to a group of contaminants of toxic character and in almost all cases carcinogenic. Due to their physicochemical properties are not easily biodegradable and can be stored in individual organisms, for that reason is necessary to remove them from the effluents; The industrial sources of this type of pollutants are oil refineries, coal gasification plants, petrochemical units, leather processing plants and electroplating industries which generate large quantities of phenols and heavy metals, as well as phenolic derivatives and salts of metal ions.

This type of compounds is used in the synthesis of plastics, dyes, pesticides, insecticides, papermaking and electrolytic coatings among others; Therefore, its appearance is indicative of the degradation capacity of phenols and metallic ions by the environment (Dabrowski et al. 2005). These adsorption processes with activated carbon have a great advantage over other conventional treatment systems such as phytoremediation, electrochemical treatment, microbial isolates, coagulation-flocculation, biosorption, among others and it is the regeneration of the material to be used again in the same system for several more cycles, minimizing in this way the environmental impact that the activated carbon can have once used and giving the possibility to recover also the retained pollutants and reintroduce them in the same productive processes (Sowjanya 2013; Fonseca et al. 2014).

The adsorption is one of the processes that is using to design experiments that subsequently, according to the results, can be scaling to an industrial level. Physical chemistry is a phenomenon that offers good results for the elimination of a wide variety of pollutants and offers significant advantages over other types of techniques used for the control of the environment such as high removal of the treated effluent, low cost of operation and low sensitivity to the toxic.

The porous solids as the carbonized, activated carbons or carbon aerogel, e.g., are very using for this type of removals due to its high adsorption capacity and control that can performed during the preparation process to give you some chemical and textural features and thus obtain a material with high specificity and adsorption capacity very specific. To obtain a good activated carbon is required from a source that has a high percentage in coal. In this chapter, we will introduce two types of porous solids: charred of bone and carbon aerogel that we used in our research group.

On the other hand, theoretical studies based on molecular modeling and simulation tools are useful to obtain data to correlate the structural characteristics of the solids that we want to get, the conditions of synthesis, the mechanisms involved and the applications in the adsorption of molecules of interest (Enfremenko and Sheintuch 2006). Currently, with the increase of the computing potential and the ability to operate more complex calculations, the use of molecular dynamics simulations, unlike those that use statistical data and probabilities as Monte Carlo, provides a representation to “real-time” of the physical process in study (Georgakis et al. 2014). In this chapter we will analyze the mechanisms that are put at stake, mostly, when one considers the adsorption of phenol in aqueous solution, considering the environment involved in such a process surface chemistry and solvent effect (Húmpola et al. 2013). For this, it is necessary to discuss the experimental results, compared to the numerical simulations and computations based on the theory of the

Density Functional (DFT) and molecular dynamics (Bertoncini et al. 2002). In this regard, different groups are compared and the acids oxygenated surface effect of each one of them in the adsorption, determining the presence or not of such groups by titration of selective Boehm, for the purposes of power have a realistic profile of surface chemistry of the solid (Boehm 2002).

It then submits fundamental concepts of adsorption, preparation of the same and some applications.

6.2 Definition: Activated Carbons and Aerogels

6.2.1 Activated Carbon and Aerogels

The activated carbon is defined as a porous material to be prepared by reaction of materials whose majority component the coal, from plant, animal or agricultural is using oxidizing gases or by the carbonization of lignocellulosic materials impregnated with chemical dehydrating agents. All these materials thus obtained are structurally sound very untidy constituted mainly by carbon, and because of the process pyrolytic, exhibit a high degree of porosity and a high internal surface area, that can be used in adsorption processes and catalysis. One of the applications to which more he had been employed is the elimination of impurities of gases and liquids through a process of adsorption. Are the van der Waals forces, which generate an attraction of molecules on the surface of solid and do you have on it a higher concentration of adsorbate on the adsorbent, that adsorbate molecules within the fluid. Given the nature inert the surface of the carbon, the affinity toward low molecular weight molecules such as nitrogen or oxygen at ambient temperature or polar molecules such as water is very low. However, the affinity toward non-polar molecules and of a certain volume and molar mass e.g. hydrocarbons will be high. This difference in affinity makes the activated carbon is the preferred adsorbent, whenever that need to perform a separation/purification in the presence of moisture or in aqueous solution.

Although the activated carbon is considered the adsorbent universal, for the variety of applications that can be used the number of applications has been growing steadily over the past years, as progress has been made in the control of their properties (Rouquerol 1999; Leyva-Ramos et al. 2008). Traditionally it has been considered that the porosity and surface area were the parameters that define the quality, but today it is known that the surface chemistry of the activated carbon plays a very important role in its adsorption capacity (Pelaez-Cid et al. 2016; El-Shafey et al. 2016). In fact, the porosity is the necessary precondition for an activated carbon can carry out its mission to adsorb, but this is not enough and in many cases, the adsorption is not possible if its surface is not modified properly in order to interact in a specific way with the compound to adsorb (Anutosh 2016). In addition, the implementation of the activated carbons to new technological processes requires materials more sophisticated than the classic granular or powder coals. This has led to the development of new physical forms such as fibers, cloths, felts, monoliths, etc. even more the need has emerged to prepare carbon that can separate molecules depending on the size or molecular form, the so-called molecular sieves of coal, which play an important role in the process of purification and catalysis.

Another type of porous solids that have been used as adsorbent are xerogeles and aerogel. While his synthesis of known since many decades ago by (Lu et al. 1995; Reynolds et al. 1995; Pekala et al. 1998), several authors have explored their applications in the environmental part. In terms of its chemical structure, can be classified as inorganic gels and the organic gels (Schaefer et al. 1995; Gross et al. 1997). The inorganic gels have been widely studied and there are reports from the fifties, while the organic gels represent an interesting and special family of materials within the scale of nanocomposites, which develop according to its method of synthesis, nanoporous. Carbon gels are studied since it is now more than two decades due to its potential, as there is a wide diversity of gels, depending of the precursors used and of the method of preparation, of carbon gels are obtained from the polycondensation of hydroxylated benzenes, such as phenol, catechol, resorcinol, hydroquinone etc., and aldehydes such as formaldehyde, furfural, etc. in a solvent, followed by a drying stage and later carbonization (Pekala et al. 1995). In 1989 (Pekala 1989) synthesized the first organic gel obtained from the polycondensation of resorcinol and formaldehyde. Since then this organic gel has been studied, and today it is still producing alternatives to preparation process, through which they can achieve carbon gels with specific properties.

6.2.2 Structure

Activated carbons possess carbon, normally with a relatively low number of heteroatoms mainly hydrogen and oxygen and inorganic components that constitute what is called ash which depend on the material precursor. However, the main feature of the activated carbon is the porous structure.

The structure of the activated carbon, which is based on layers of graphene totally disordered, corresponds to that of a material not graphitizable, i.e. a material that has not passed by a state fluid during the carbonization process. The macromolecular structure of the precursor polymer or remains during the heat treatment, because it produces an interbreeding that prevents the fusion, with only the loss of small molecules by the pyrolysis. This interbreeding is one that leads to a rigid structure, with very little mobility, which prevents the order which occurs during the process of heat treatment for example, graphitization, and giving rise to a porous structure (Anutosh 2016). A structure that can be used to represent the activated carbon is that presented several authors in the literature as shown in Fig. 6.1. (Stoeckli 1990; Rodríguez-Reinoso and Sepulveda-Escribano 2001).

The porous structure of activated carbon is a function of the precursor used in the preparation, the activation method, as well as the degree of activation reached. This

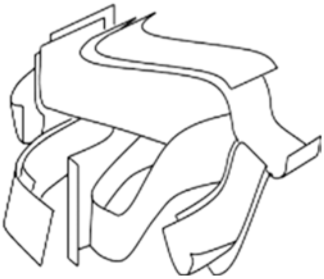

Fig. 6.1 Schematic model of the activated carbon structure, where the different layers are observed in a disorganized way. (Modify after Stoeckli 1990; Rodriguez-Reinoso and Sepulveda-Escribano 2001 without permission)

is the reason why the surface area and the porosity, volume of pores can vary so widely from one activated carbon to another and use in each application is determined by the size distribution of pores. Thus, while a microporous essentially carbon can be suitable for the adsorption of gases and vapors and, to some extent, for the separation of molecules of different dimensions, a carbon with a well-developed additional mesoporosity can be necessary to accelerate the adsorption kinetics of molecules of greater dimensions such as those that are usually found in aqueous solution (Bailey et al. 1999).

The presence of oxygen, hydrogen and nitrogen in the form of functional groups in the surface of the carbon has a great effect on the adsorbent properties, especially compared to polar molecules or polarizable (Wase and Forster 1997; Lopez and Echavarría 2003). The presence of these heteroatoms on the surface of the carbon can be caused by the precursor used in the production, the activation method, or the artificial introduction after the manufacturing process through the so-called post-treatments (Mwaniki 1992; Carballo 2002 Moreno-Castilla 2004).

The oxidation of the surface of the activated carbon, which is inherent to the production by physical activation controlled reaction of the charred with an oxidizing agent, involves the formation of different types of surface groups of oxygen (Figueiredo and Pereira 2010). On the other hand, these superficial groups are not formed exclusively by reaction with oxygen, but also by reaction with other oxidizing gases in the gas phase ozone, carbon dioxide, nitric oxide, etc. or in aqueous solution nitric acid, hydrogen peroxide, sodium hypochlorite, etc. The chemical nature and the amount of oxygen surface groups of as given carbon are a function of the surface area, particle size, ash content and the experimental conditions used in its manufacture. It is known that there is a variety of surface groups of oxygen, ranging from carboxyl groups to carbonyl, phenol, ether, chromene, etc. (see Fig. 6.2), which gives the carbon a character amphoteric, so that it can be acid or base in aqueous solution.

The carbon aerogels, as has been mentioned, are being investigating as possible materials for use in decontamination. The aerogels by its structure, materials are very light and with a potential for application in different areas of knowledge. This material by its properties is sometimes thought as a material “strange”. Its appearance varies according to the sources from which to split to perform their synthesis, e.g. can be used as an insulator from noise, thermal insulator, takes on different forms and for

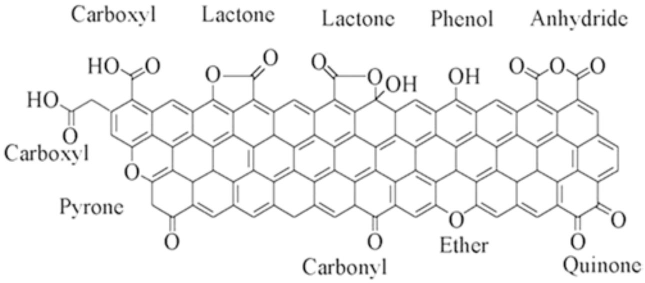

Fig. 6.2 Types of surface groups of oxygen in an activated carbon. (Modify after Figueiredo and Pereira 2010 without permission)

its porosity is a material that can adsorb and store different materials both from liquid or gaseous phase. Additionally, these have a low density and thermal conductivity.

Despite their names is a rigid material, solid and dry that has nothing to do with a gel in their physical properties.

6.2.3 Preparation and Synthesis

The activated carbons are prepared industrially from precursor's carbon-rich, mainly lignocellulosic materials such as wood, bone and fruit peel, sawdust, etc., peat, lignite, coals sub-bituminous, pitch of oil, coke, etc. The criteria that are often used to select the precursor are, among others, the following: low content in inorganic components, availability and low cost, not suffer degradation during storage, ease of activation the calcined coke is a material very difficult to activate, while timber is easily activated, and that will lead to good adsorbents. Lignocellulosic materials correspond to 47% of the total of precursors used in the worldwide manufacture of activated carbon and are followed by mineral coal, around 30% and peat. It should be noted that within a type of precursor, for example the lignocellulosic materials, there may be great differences between the different materials to be used. Thus, a high density is important because it contributes to the performance and final mechanical properties of carbon, while a high content of volatile matter is important because it can save energy in the manufacture and allows for better control of the activation process and the end performance. The materials with low density as the pine wood, which also contains a high percentage of volatile, lead to activated carbons with a high volume of pores and low density, but if the process is modified to reduce the loss of carbon during carbonization or if the carbon is densification, the quality of the active carbon can be considerably increased. On the other hand, the coconut husk and bones of fruits have a high density and quantity of volatile, adequate and therefore that produce granular activated carbons drives with high volume of pores, very suitable for many applications are two industrial methods of producing activated carbon, one called physical activation, also called thermal activation and another called chemical activation.

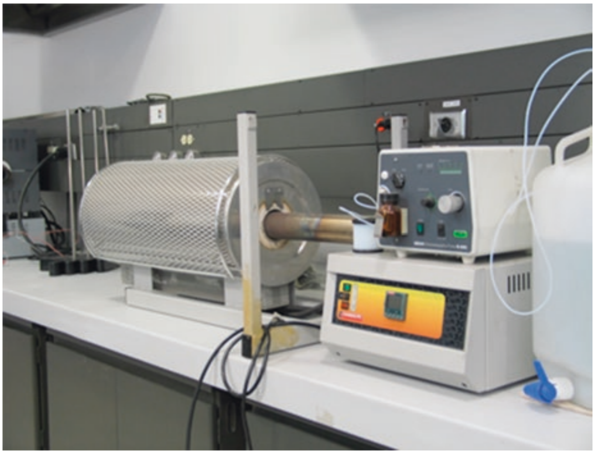

Fig. 6.3 Horizontal tubular reactor Carbolite used to obtain carbonaceous materials

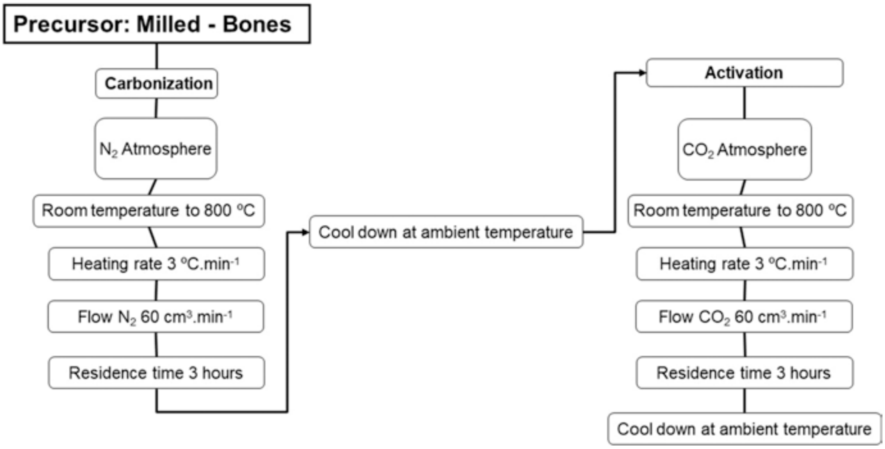

Fig. 6.4 Flow diagram for the carbonization process to obtain activated carbon

The granular bone carbonization used was prepared from bovine, porcine and chicken bones. These are manually cleaned to remove some of the fat and meat, cut into pieces of approximately 4–10 cm. Then are washed with boiling distilled water for 2 h several times to remove excess fat and transferred to a stove at a temperature of 80 °C for 48 h. The dried bones are split and ground to a particle size of 2 mm and are heat treated in an atmosphere of N_2 and CO_2, this process is carried out in a fixed bed horizontal tubular reactor shown in the Fig. 6.3 from room temperature to 800 °C, with a heating rate of 3 °C.min^{-1} and a flow of N_2 of 60 cm^3.min^{-1}, with a residence time of 3 h.

The samples obtained are characterized by the techniques described in this chapter. Figure 6.4 shows the flow diagram for the carbonization and activation process and Fig. 6.5 shows the precursor, granular material and activated carbon obtained.

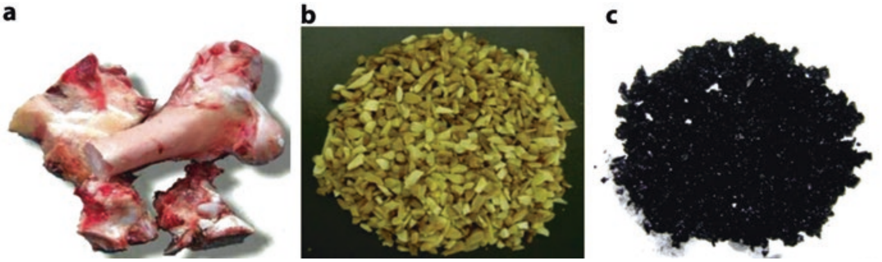

Fig. 6.5 (**a**) Precursor of bones, (**b**) granular material and (**c**) activated carbon obtained

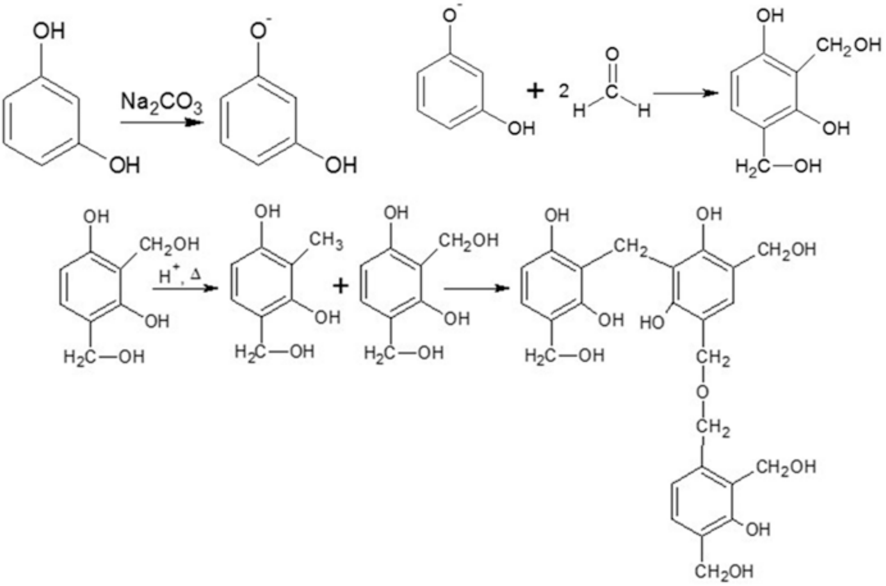

Fig. 6.6 Mechanism of reaction of polymerization gel resorcinol-formaldehyde. (Modify after Lin and Ritter 1997 without permission)

On the other hand, the usual procedure to synthesize carbon gels consists of mixing resorcinol and formaldehyde with a suitable molar relation in the presence of a catalyst, which in most cases is basic (see Fig. 6.6), though in occasions it can also use acid catalysts. The reaction between resorcinol and formaldehyde takes place in an aqueous medium, although organic solvents such as methanol, ethanol, acetone, ethanol can also be used (Al-Muhtaseb and Ritter 2003; Czakkel et al. 2005).

Once, the reagents are mixed, are introduce in a sealed container and are subjected to heating up to obtain a crosslinking and stable gel completely. At this stage have place the processes named gelation and cured. When the gel is way, the solution loses fluidity and the elapsed time is called the time of gelation. The curing of

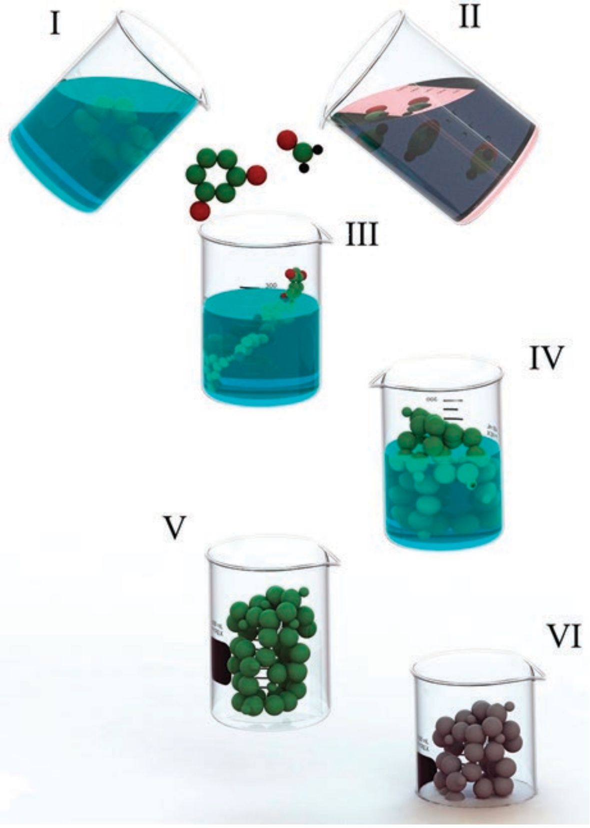

Fig. 6.7 Outline of the stages involved in obtaining carbon gels. *I–IV*, sol-gel reaction where the polymer intersects and form the gel resorcinol-formaldehyde. *V*, drying of the gel saturated with solvent. *VI*, carbonization of organic gel to obtain the gel of carbon. (Modify after Fonseca-Correa et al. 2016 without permission)

the gel is the process in which favored the crisscrossing in the structure of the organic gel and the formed polymer stabilizes (Kim et al. 2001).

As shown in the Fig. 6.7, in the process of obtaining organic gels from resorcinol and formaldehyde can differentiate the three main stages (Fonseca-Correa et al. 2016).

During the development of each one of these stages, it affects the final structure of the gel as also will be affected and the final properties chemicals. The object of the activation is the increase in the surface area obtained in the synthesis and increase the porosity that has been able to close during the drying processes and carbonization (Job et al. 2005). Within the activation methods that can be used for this type of materials is the physical activation. In the physical activation, the gases used are air, water vapor or CO_2. Chemical activation can also be used, as is done with lignocellulosic precursors, in the preparation of activated carbons (Navarrete et al. 2005; Vargas et al. 2011).

Resorcinol-formaldehyde gels are synthesized from resorcinol (R) at 98% purity, formaldehyde (F) solution at 37% purity and sodium carbonate at 99,9% purity, all reagents brand Aldrich™. 0,1120 mol of resorcinol and different quantity of sodium carbonate was dissolved in deionized water to obtain different ratios resorcinol/catalyst: 25, 50, 100, 200, 400, 600, 800 and 1500. Then, formaldehyde was added to obtain ratio R/F = 0,5 with vigorously stirrer. Solutions are placed in Pyrex glass and let it heal for 1 day at 25 °C, 2 days at 50 °C and 3 days at 70 °C. Gels were washed with ethanol and after with acetone.

Drying is done at supercritical conditions, 38–40 °C, 90–100 atm. Organic aerogel synthesized were then pyrolyzed in nitrogen atmosphere at 5 °C/min to during 3 h with flow 100 mL min^{-1} at 850 °C in oven Carbolite MFT type 12/38/400 to obtain carbon aerogel.

According resorcinol/catalyst ratio carbon aerogels are named: AeW25, AeW50, AeW100, AeW200, AeW400, AeW600, AeW800 and AeW1500.

6.3 Adsorption Phenomenon

The adsorption is a process of effective separation, for the treatment of industrial and domestic effluents. In the adsorption from aqueous phase, considers factors such as: the adsorbent characteristics and the adsorbate, the chemistry of the dissolution and the temperature. According to the foregoing, the characteristics that correspond to the adsorbent are: its porous texture and surface chemistry; adsorbate: its molecular size, solubility, polarity, hydrophobicity, pK$_a$ and nature of the substituents, if it is an aromatic molecule; pH of the dissolution and its ionic strength (Weber and Morris 1963; Moreno-Castilla 2004) (Fig. 6.8).

When preparing and/or synthesize porous solids is fundamental aim is to design them so that adsorb contaminants "objective", to adsorb phenols and Ni^{2+} on charred bones and carbon aerogel respectively.

Phenols, nitro phenols and Ni^{2+} are common pollutants in wastewater generated from oil, petroleum, coal, paper, textile, synthetic rubber, electroplating industries, industries of painting and pharmaceutical industries, among others. The wastewater

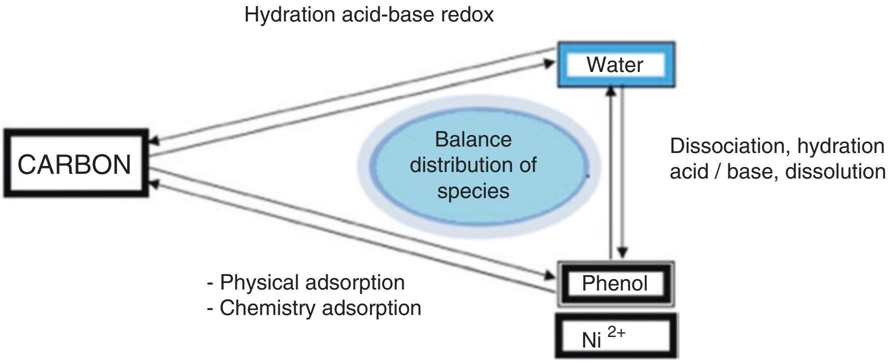

Fig. 6.8 Simultaneous processes that occur when the carbon has immersed in aqueous solution where is present the adsorbate

containing these compounds have a serious environmental problem due to its high toxicity and possible accumulation.

Several techniques of recovery, such as chemical precipitation, membrane filtration, adsorption, redox or ion exchange, nano filtration and reverse osmosis, among others has been proposed for this purpose. However, these techniques require a high investment and demand for technical resources and energy. For this reason, in the last decades, have developed new solid materials that have allowed the reduction of pollution in aqueous phase and gas. Within these new materials are the porous solids in all its forms, which have been widely studied and implemented due to its growing demand and its great versatility. These porous solid currently used in the operation of cleaning systems of air, as catalytic media and in the chemical industry for the removal of organic and inorganic compounds (Rodriguez-Reinoso 2007). Prepare solids with a suitable degree of porosity granular or powder usually very appropriate, due to the high adsorption capacity of organic and inorganic compounds, despite that sometimes its use may be limited due to its high cost (Bhattacharya and Venkobachar 1984; Mckay et al. 1984; Nassar and El-Geundi 1994; Geundi 1997). Between this type of porous solids that can be used for decontamination of lakes and rivers are the activated carbons, carbon aerogels and carbon xerogeles.

6.4 Methods Used to Characterize Porous Solids

6.4.1 Textural Analysis

The physical adsorption of gases and vapors in solids is one of the most commonly used techniques for the study of the porous texture of various solids. In the characterization of the porous texture of solid, parameters to determine are the surface area, volume and distribution of pore size.

Surface area or apparent surface is determined normally through adsorption-desorption of a gas N_2 is obtained information of pores from 35 to 4000 Ǻ, CO_2 information is obtained from the micro porosity more closely 5–35 Ǻ in isothermal conditions. The adsorption isotherm was analyzed through the implementation of a given equation to determine the call volume of monolayer, from which it calculates the area apparent if you know the area occupied by each molecule (Rodriguez-Reinoso and Molina-Sabio 1998). Samples are first subjected to a degassing process by vacuuming at 0.5 militorr with a temperature ramp from room temperature to 80 °C at 2 $°C.min^{-1}$ with a residence time of 60 minutes, then the temperature is increased up to 120 °C at the same heating rate and with a residence time of 60 min, then the temperature is increased to 250 °C at a heating rate of 5 $°C.min^{-1}$ and left for 120 min, then sample is cooled to room temperature maintaining the vacuum until it is used for the realization of the nitrogen isotherm at 77 K.

The equation is often used to calculate the surface area is called the method of Brunauer-Emmett-Teller (BET). This is based on the measurement of successive volumes of a non-polar gas, usually nitrogen or noble gases, adsorbed on the inner surface of the pores of the solid to the time that the pressure is measured of the molecules which adsorb, until we achieve the saturation of the surface (Brunauer et al. 1938; Bansal and Goyal 2005). According to the type of surface and porosity is present different ways in the adsorption-desorption isotherm.

The linear form of the BET equation, putting in a practical way to your graphics application, is:

$$\frac{P}{V\left(P^0-P\right)}=\frac{1}{C.V_m}+\frac{C-1}{C.V_m}.\frac{p}{P^0} \tag{6.1}$$

Where the term P is equal to the vapor pressure of balance, P^o is the saturation vapor pressure of the gas that is adsorbed, V is the volume of gas adsorbed to the pressure P, there are two constants: Vm, which is the volume corresponding to the monolayer and C is a constant that is related to the heat of adsorption of the first monolayer (Brunauer et al. 1938).

Dubinin-Radushkevich equation, describes well many carbonaceous solids with low degree of burn-off. For carbonaceous solids resulting from a high degree of burn-off during activation, the degree of heterogeneity increases because of a wider pore size distribution, and for such cases the equation does not describe well the equilibrium data. To describe adsorption on wider range of microporous materials the Dubinin-Astakhov equation was proposed:

$$W=W_0\exp\left[-\left(\frac{-RT\ln\frac{P}{P^0}}{E}\right)^n\right] \tag{6.2}$$

where:

W = weight adsorbed at P/P^0 and T.
W_0 = total weight adsorbed.
E = characteristic energy.
n = non-integer value typically between 1 and 3.

is a generalized form of the Dubinin-Radushkevich equation $n = 2$ and has been found to fit adsorption data for heterogeneous micropores (Stoeckli 1990).

The Dubinin-Astakhov equation requires the parameters n and E to be calculated reiteratively by non-linear curve fitting to the adsorption isotherm in the low relative pressure, micropore region. The values of n and E obtained are then used in equation (Janssen and Van-Oorschot 1989):

$$\frac{d\left(\dfrac{w}{w_0}\right)}{dr} = 3n\left(\frac{K}{E}\right)^n r^{-(3n+1)} \exp\left[-\left(\frac{K}{E}\right)^n r^{-3r}\right] \tag{6.3}$$

where.

r = pore radius.
K = interaction constant = 2.96 kJ.nm^3.mol^{-1} (N_2).
= 2.34 kJ.nm^3.mol^{-1} (Ar).

A plot of [d(w/w_0)]/dr vs. r yields the method pore size distribution.

Since the degree of sharpness of the adsorption isotherm versus adsorption potential or the reduced pressure increases as the parameter n increases, this parameter could be used as an empirical parameter to characterize the heterogeneity of the system. Since it is an empirical parameter, it does not point to the source of the heterogeneity. However, it can be used as a macroscopic measure of the sharpness of the micropore size distribution. For solids having narrow micropore size distribution such as the molecular sieving carbon, the Dubinin-Astakhov equation with $n = 3$ is found to describe the data well. Therefore, if the parameter n of a given system is found to deviate from 3 usually smaller than 3, that system is said to be heterogeneous or has a broad micropore size distribution. Typical values of n for strongly activated carbon are between 1.2 and 1.8. For zeolite having extremely narrow micropore size distribution, the parameter n is found to lie between 3 and 6 (Do 1998).

Many methods for mesopore size analysis, which make use of the modified Kelvin equation, include those proposed by Barrett, Joyner and Halenda (BJH) and Broeckhoff and de Boer (Rouquerol et al. 2013). To account for the preadsorbed multilayer film, the Kelvin equation is combined with a standard isotherm the *t*-curve, which is determined on certain well-defined nonporous solids. However, for the size analysis of narrow mesopores, the standard t-curve is not entirely satisfactory, because the curvature and enhanced surface forces are not properly considered. Similarly, the validity of the Kelvin equation is questionable as the mesopore width is reduced because macroscopic concepts can no longer be safely applied.

This was clearly demonstrated with the aid of model mesoporous molecular sieves. Because of their high degree of order, the pore diameter of such model substances can be derived by independent methods X-ray-diffraction, high-resolution transmission electron microscopy. It was shown (Landers et al. 2013; Thommes and Cychosz 2014) that the Kelvin equation based procedures, such as the BJH method, significantly underestimate the pore size for narrow mesopores for pore diameter < ~ 10 nm the pore size will be underestimated by ~ 20–30%.

The limitations of the Kelvin equation can be avoided by applying microscopic methods based on molecular simulation or DFT.

DFT and Monte Carlo simulation have been developed into powerful methods for the description of the adsorption and phase behavior of fluids confined in well-defined pore structures (Monson 2012; Landers et al. 2013). These procedures are based on the fundamental principles of statistical mechanics as applied to the molecular behavior of confined fluids. They describe the distribution of adsorbed molecules in pores on a molecular level and thus provide detailed information about the local fluid structure near the adsorbent surface. The fluid–solid interaction potential is dependent on the pore model. Different pore shape models e.g., slit, cylinder and spherical geometries and hybrid shapes have been developed for various material classes such as carbons, silicas, zeolites.

These methods allow one to calculate for a particular adsorptive/adsorbent pair a series of theoretical isotherms, $N(p/p^0, W)$, in pores of different widths for a given pore shape. The series of theoretical isotherms is called the kernel, which can be regarded as a theoretical reference for a given class of adsorbent/adsorptive system. The calculation of the pore size distribution function $f(W)$ is based on a solution of the general adsorption isotherm (GAI) equation, which correlates the experimental adsorption isotherm $N(p/p^0)$ with the kernel of the theoretical adsorption or desorption isotherms $N(p/p^0, W)$. For this purpose, the GAI equation is expressed in the form:

$$N\left(\frac{p}{p^0}\right) = \int_{w_{\min}}^{w_{\max}} N\left(\frac{p}{p^0}, W\right) f\left(W\right) dW \tag{6.4}$$

Several approaches have been suggested to account for the heterogeneity of most adsorbents, which if not properly taken into account can lead to appreciable inaccuracy in the pore size analysis. Such methods include the development of complex 3D structural models of disordered porous solids by advanced molecular simulation techniques, but these are still too complex to be implemented for routine pore size analysis. The drawbacks of the conventional NLDFT model which assumes a smooth and homogenous carbon surface have been addressed by the introduction of two-dimensional DFT approaches. Quenched solid density functional theory (QSDFT) is another approach to quantitatively allow for the effects of surface heterogeneity in a practical way (Landers et al. 2013; Thommes and Cychosz 2014 ; Valladares et al. 1998). It has been demonstrated that taking into account surface heterogeneity significantly improves the reliability of the pore size analysis of heterogenous nanoporous carbons.

6.4.2 *Surface Chemistry*

Although the adsorption capacity of a porous solid depends on the porous texture and volume of pores there are other factors that determine their behavior in a process of adsorption. Therefore, solids with the same surface areas but prepared by different methods may show features different adsorbents. For this reason, it is necessary to characterize the surface chemistry of the materials by different techniques.

6.4.3 FTIR Spectroscopy

The characterization of the surface functional groups present in the porous solids by Fourier transform infrared spectroscopy (FTIR) is based on the same principles of traditional functional analysis of organic chemistry. Therefore, each group is associated with one or several bands features. However, the characteristic values of number of wave (cm^{-1}) of the functional groups of the activated carbons, which appears a certain band in the spectrum, can vary for the corresponding value presented isolated group. This is due to the high conjugation or matrix effect that occurs on the surface of these materials.

Another experimental aspect to be considered is the great absorption of radiation that present the materials based on carbon and which obliges a large dilution of the sample in the case more of traditional preparation of tablets with KBr. There is no doubt that this dilution produces a loss or minimizes the intensity of certain bands. By this is that it is reported the convenience of using non-traditional methodologies for the FTIR spectrum in carbonized, as are the techniques of diffuse reflectance (DRIFT), or the use of the detector photoacoustic (Martin Martinez 1988).

6.4.4 Total Acidity and Basicity

The knowledge of the surface chemistry, is of great importance since the physicochemical properties of the material are influenced by the presence of chemical species in the surface. Therefore, applications are conditioned by their chemical characteristics.

Many investigations have shown the role of the surface chemistry in the adsorption of compounds aromatic, dyes, heavy metals, drugs among others. For this reason, the nature and the concentration of groups vary depending of the precursor and its preparation. Boehm developed a selective titration method to identify the superficial oxygenated groups an acid nature. The method is based on the use of four bases of different forces. The bases are $NaHCO_3$; Na_2CO_3, NaOH; and $NaOC_2H_5$. Each of these bases neutralizes different groups and is posited the following relationships (Boehm 2002):

$NaHCO_3$ → Carboxyl
Na_2CO_3 → Lactones
NaOH → Phenols
$NaOC_2H_5$ → Carbonyl

Although the method has been criticized, its simplicity justifies the fact that, so much was used as the standard method.

About the basic oxygenated groups, it can be said that some structures that could neutralize HCl have been proposed; however, its existence is still questioned (Bandosz et al. 1993; García Lovera 2005).

6.4.5 Point of Zero Charge

The point of zero charge (PZC) refers to the pH in which the surface of the material is neutral and is used to predict the tendency of the particles. According to this value depends on the concentration of functional groups acids or basic. A material with a PZC should have a higher acid content of such groups among both a basic PZC will have less concentration of these groups (Babic et al. 1999; García Lovera 2005).

6.4.6 Scanning Electron Microscopy

The scanning electron microscope (SEM), has been used to examine the topology of the surface of the solid, morphology of the particles and crystals. In SEM, a beam of electrons from close to 5 nm minimum focused of the sample, moves over a small area by means of a set of deck coils, this is magnified and exposed in a cathode ray tube. By varying the orientation of the sample about the signal detector can produce an effect light-darkness forming a three-dimensional effect on the screen.

When adding a spectrophotometer energy dispersive X-rays (EDX) of lithium to a scanning electron microscope SEM, there is an instrument for the study of structures of micrometric scale, which provides a spectrum with the most probable elements located in the observed area, in addition to surface images allow to observe surface changes before and after treatment (Martin Martinez 1988).

6.4.7 X-Ray Diffraction

The measures of diffraction in solids are made by inducing an X-ray beam on a sample, prepared by measuring the angles at which is diffracted a wavelength λ of X-ray defined. The diffraction angle θ can relate to the interplanar spacing d, by means of the Bragg law. The forms of analysis that allows the development of methodology are:

- Qualitative analysis: The identification of phases present is performed by comparing the positions of the peaks with those of the standard patterns.
- Quantitative analysis: With calibration procedures can be obtain this type of analysis, determine the amount of a phase in a sample and the degree of crystallinity of the sample (Martin Martinez 1988).

6.4.8 Immersion Calorimetry

This technique is to determine the heat involved in the interaction of a liquid with a solid whose surface has been eliminated all species adsorbed. The heat is related to the intensity of the interaction and therefore a study of this type, it is possible to obtain information about the porous structure of the solid surface, the chemical nature and the adsorption capacity (Moreno and Giraldo 2000; Silvestre-Albero et al. 2001).

The immersion enthalpy ΔH_{inm} is defined as the transfer of heat to pressure and constant temperature that occurs when a solid is immersed in a liquid in which does not dissolve or react. The immersion enthalpy will be proportional to:

- The magnitude of the solid surface: For a solid-liquid, system given the immersion enthalpy increases with the surface area available.
- The chemical nature of the liquid and the surface of the solid:
- The porous texture of the solid: when the liquid has a molecular size very close to the dimensions of the pores, the forced interaction can increase the immersion enthalpy; in addition, larger molecules that some of the pores will not be able to access certain areas (Menéndez 1998; Blanco-Martinez et al. 2009; Navarrete et al. 2006).

6.5 Examples of Applications of Porous Solids in Water Purification: Chemical Characterization, Textural Analysis and Adsorption in Aqueous Phase

6.5.1 Aerogels Chemical Characterization

Type and concentration of surface functional groups in carbon aerogels have been studied using analysis methods such as Boehm titration, determination of the pH at the point of zero charge by mass titration and infrared spectroscopy with diffuse reflectance. As can be seen in Table 6.1.

Total acidity for the samples of carbon aerogels is greater than the total basicity. This may be due to the oxidation process that the polymer gel undergoes in the process of drying with supercritical CO_2, which induces the formation of more acidic oxygenated functional groups. Lactonic groups are found in smaller proportion with respect to the carboxylic groups. Phenolic groups are present, in low proportion in the samples AeW25, AeW200, AeW600, AeW800 and AeW1500. With respect to the number of acid surface groups, in each case no specific trend is observed with respect to the resorcinol/catalyst ratio. When the carboxylic, lactonic and phenolic groups predominate, the surface of the carbonaceous structure presents good characteristics for the exchange of cationic ions.

Table 6.1 Surface groups (mmol.g^{-1}) in carbon aerogels determined by Boehm titration and pH at the point of zero charge (pHpzc)

GROUP	Lactonic	Carboxylic	Phenolic	Carbonyl	Total acidity	Total basicity	Total groups	pHpzc
SAMPLE	mmol.g^{-1}	mmol.g^{-1}	mmol.g^{-1}	mmol.g^{-1}	mmol.g^{-1}	mmol.g^{-1}	mmol.g^{-1}	
AeW25	0.885	2.111	0.045	0.000	3.041	0.825	3.865	6.12
AeW50	0.936	2.133	0.000	0.000	3.069	0.491	3.560	5.97
AeW100	0.828	1.905	0.000	0.000	2.733	0.502	3.235	5.76
AeW200	0.902	2.064	0.042	0.000	3.009	0.975	3.984	5.70
AeW400	0.946	2.255	0.000	0.000	3.200	0.961	4.161	5.65
AeW600	0.940	2.829	0.044	0.000	3.813	0.864	4.677	5.41
AeW800	0.921	2.229	0.043	0.000	3.193	1.065	4.258	5.50
AeW1500	1.041	2.026	0.045	0.000	3.112	0.938	4.051	5.45

The presence of these groups may be due to the stability of these groups at a higher temperature than the acid groups and to the presence of π electrons delocalized on the surface of the carbonaceous structure of the carbon aerogels (Boehm 2002; Contescu et al. 1993).

The pH at the point of zero charge decreased in its value as the ratio increased resorcinol/catalyst, these values are associated with the adsorption capacity of aerogels of different compounds. For low pHpzc values the adsorption of metal cations is favored when the pH of the medium is higher than the pHpzc, since the surface charge on the carbon aerogel will be negatively charged having an affinity for exchanging positive charges of the cationic ions. Care must be taken not to exceed the pH of the medium above the pH of precipitation of the cation as hydroxide, since the phenomenon of adsorption will not occur.

In Fig. 6.9, the variation of the pHpzc with respect to the different ratios of resorcinol and resorcinol/catalyst catalyst is observed, where a clear trend is observed. When increasing the resorcinol/catalyst ratio decreases the pHpzc, the AeW600 sample has the lowest value of pHpzc.

Thus, finally the distribution of the functional groups is due to the pyrolysis process, where the final structure of the carbon aerogels is formed with the oxidation of the samples when subjected to air. The chemical composition in the aerogels was evaluated using the spectroscopy. Infrared with diffuse reflectance cell. The results obtained in the IR spectroscopy are presented in Fig. 6.10. where the characteristic bands are observed in the different wavelengths and which present an adequate correlation with the data obtained by Boehm titration.

All samples of carbon aerogels have a peak of low intensity and characteristic of C–O stretching around 780 cm^{-1}. This same group C–O, also generates the bands that are observed between the 989 cm^{-1} and 1150 cm^{-1}. These bands are quite broad in carbon aerogels at low resorcinol/catalyst ratios that become stronger or stronger and more defined in samples with high resorcinol/catalyst ratios: AeW600, AeW800 and AeW1500. Towards 1320 cm^{-1}. These bands can be associated with groups of carboxylic acids, lactones, anhydrides, esters, ethers and phenols. There is a

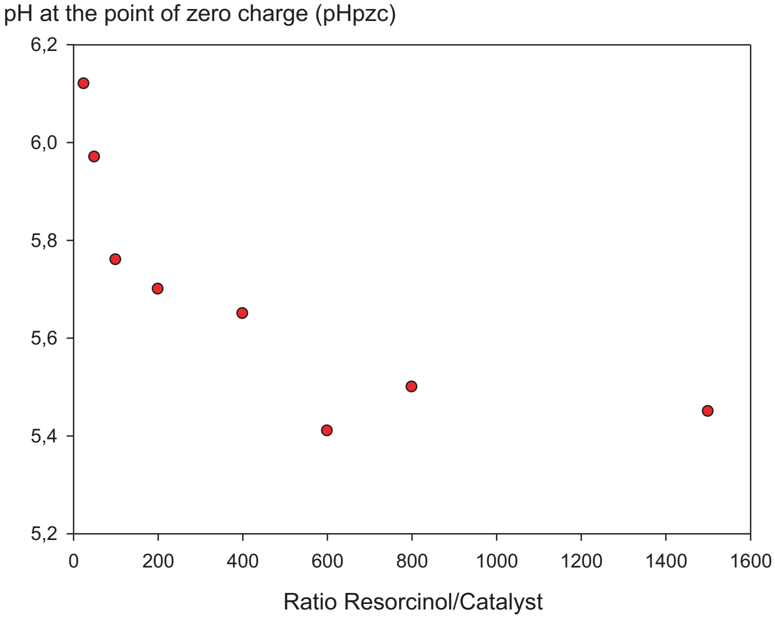

Fig. 6.9 Variation of pH at the point of zero charge (pHpzc) as a function of the change in the ratio Resorcinol/Catalyst for carbon aerogels

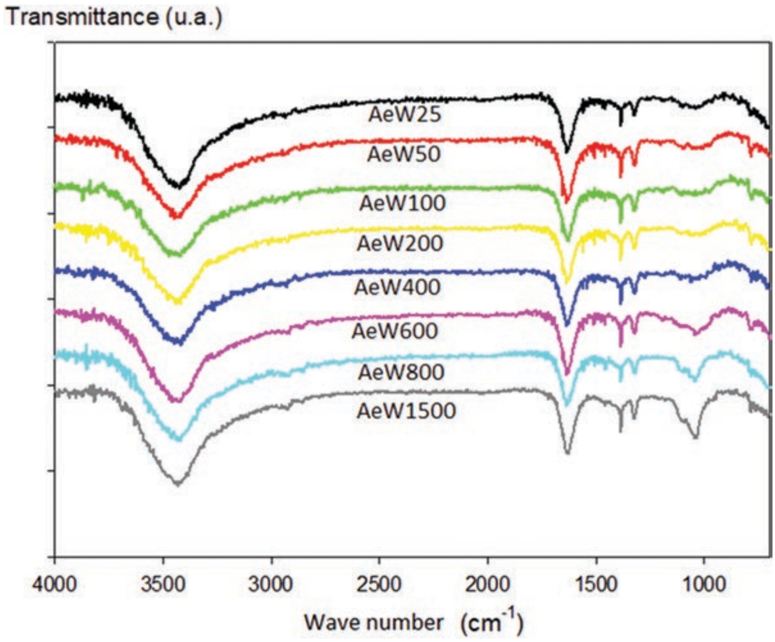

Fig. 6.10 Infrared spectrum with diffuse reflectance cell for the series of carbon aerogels. From AeW25 to AeW1500

well-defined band, although of low intensity that corresponds to C-H vibrations associated to alkanes and alkenes between 1290 and 1347 cm^{-1}. Towards 1384 cm^{-1} a well-defined peak is observed, associated in the same way to C–O vibrations of carboxyl groups, lactones, esters, ethers and phenols. The slightly wider but well-defined band that maintains its intensity in all samples between 1547 cm^{-1} and 1709 cm^{-1} corresponds to the C = O stretch in the aromatic rings of the carboxyl, ester, lactone and quinone groups, although in this region it is difficult to assign the bands since there is overlap of some groups and many peaks. Towards 1580 cm^{-1} there are stretches and vibrations of C = C groups in sp^2 hybridized carbons. The wide band observed between 3600 and 3200 cm^{-1} correspond to stretches and vibrations –OH of alcohols, carboxylic acids and phenolic groups (Dandekar et al. 1998; Mangun et al. 2001).

6.5.2 Adsorption Isotherms of N_2 on Bones

Adsorption of phenol and 2,4-dinitrophenol on bone charred was studied, like the adsorption of toxic ions such as the Ni^{2+} on carbon aerogel. The activated carbons were examined based on the results of the isotherms of N_2 to 77 K for both the AC's obtained from residues of bones and the carbon aerogel.

It is interesting before show the difference between the textural features that can be obtained in accordance with the starting material. For example, the characterization with the isotherms of adsorption of both N_2 and CO_2 for the case of the AC's from animal waste are very different, which shows that both the starting material as well as the method used to obtain them play an important role in the final characteristics.

In Fig. 6.11 shows the isotherms for chars obtained from bones of animals and the corresponding atmosphere under which were prepared by obtaining for all materials a Type IV isotherm with hysteresis cycle that it presents: a plateau relative pressures high, in the branch of adsorption is observed a slope high near the saturation and the desorption occurs at intermediate pressures. This type of characteristics corresponds to a cycle of hysteresis type H3 and is associated with the following geometries of capillaries (Sing et al. 1985; Thommes et al. 2015):

- Capillaries in the form of crack open with parallel walls.
- Capillaries with bodies' widths and short neck and narrow.

Apparent area is determined by the BET equation and the values of pore volume and average pore diameter can be calculated Barrett-Joyner-Halenda (BJH). Analysis method BJH using the branch of adsorption on where there is the blocking effect of pore.

The textural properties of the porous solids obtained (see Table 6.2) depend on different variables such as the nature of the precursor, atmosphere of carbonization, temperature and heating rate. It is noted that the chars obtained in atmosphere of N_2 shows a correlation between the value of the surface area and pore volume associ-

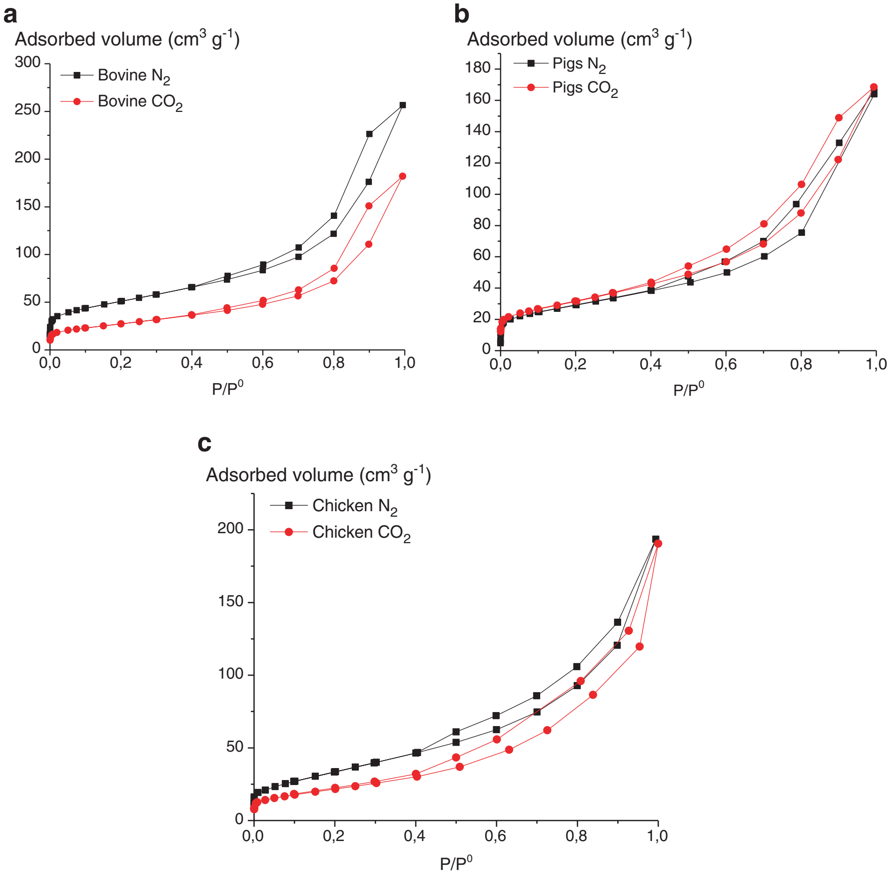

Fig. 6.11 Isotherms of N_2 (square black) and Isotherms of CO_2 (circles red) for charred: (**a**) bovine animals (**b**) pigs (**c**) chicken

Table 6.2 Textural properties of the chars

	N_2			CO_2		
	Bovine	Pigs	Chicken	Bovine	Pigs	Chicken
Surface area ($m^2.g^{-1}$)	180	104	127	99	114	81
Pore volume ($cm^3.g^{-1}$)	0.349	0.228	0.270	0.261	0.237	1.417
Average pore diameter (nm)	3.6	3.7	3.6	3.6	3.6	3.7

ated with the composition of the array between the different species. In the chars obtained in atmosphere of CO_2 notes that when increasing the area there is a decrease in the volume of pores, due to that atmosphere of CO_2 is removed part of the carbonaceous phase present in the matrix that contributes significantly in the surface area.

Comparing between the same species but obtained in different atmosphere, it is found that in the case of bovine and porcine the trend corresponds to the pore volume increases to the extent that makes the surface area. However, the opposite occurs in the species of chicken where decreases the area in CO_2 but increases the pore volume due to the presence of microporosity close, which is consistent with the performance value of 56,88%, lower than that which is presented for the other solids.

6.5.3 Adsorption Isotherms of N_2 on Carbon Aerogel

In Fig. 6.12a–f are shown the isotherms of adsorption-desorption corresponding to those obtained for the carbon aerogel and the corresponding distribution analysis studies of porosity. The structures of these compounds vary according to relations resorcinol/formaldehyde. The results are summarized in Table 6.3. It is noteworthy that the study by the isotherms of N_2 enable you to differentiate between two types of aerogels: a series of aerogels AeW25, AeW50, AeW100 and AeW200 called series I, and a second series of aerogels, let's call that hereinafter series II AeW400, AeW600, AeW800 and AeW1500, where the effect of the ratio resorcinol/catalyst is evident presenting appearance of mesoporous (Fonseca-Correa et al. 2017).

Isotherms of adsorption-desorption of N_2 to 77 K corresponding to the series I are shown in Fig. 6.12a; these isotherms correspond to Type I according to IUPAC (Sing et al. 1985; Thommes et al. 2015) that are characterized by a well-developed system that is porous and in a way with good presence of micropores.

Isotherms obtained for the latter synthesized aerogel to these relations resorcinol/catalysts in this investigation are reversible and do not possess hysteresis loop, characterized by present dish well defined and parallel to the axis corresponding to that of relative pressures. A slight separation occurs in the samples AeW100 and AeW200 without which these separations can be called loops. It is likely that some small gaps that are observed are due to the incipient development of mesoporosity, considering that has increased the ratio resorcinol/catalyst and are associated with the reaction between the resorcinol and Na_2CO_3, in a way in the first step corresponding to the addition reaction.

The parameters of Dubinin-Astakhov show that the volume of micropores is increasing in function of the growth of the ratio resorcinol/catalyst, while the radius of pore is maintained in each one of the samples to relations prepared series I and series II, this being around 7 Å, while "n" presents a value of approximately 2.0, which is associated and corresponds to carbonaceous materials, demonstrating in this case that the aerogels possess a porous network system that adjust to the that present the activated carbons. The values of the energy characteristic obtained are values of approximately 8.0 kJ.mol^{-1}, which allows lower, by the order of magnitude that aerogels synthesized have good potential of adsorption toward nitrogen molecules.

To complement the textural study of the aerogels, micrographs obtained by scanning electron microscopy images were evaluated (Fig. 6.13) to determine the morphology of the samples and X-ray diffraction analyzes were made (Fig. 6.14) to study the structural ordering achieved in carbon aerogels.

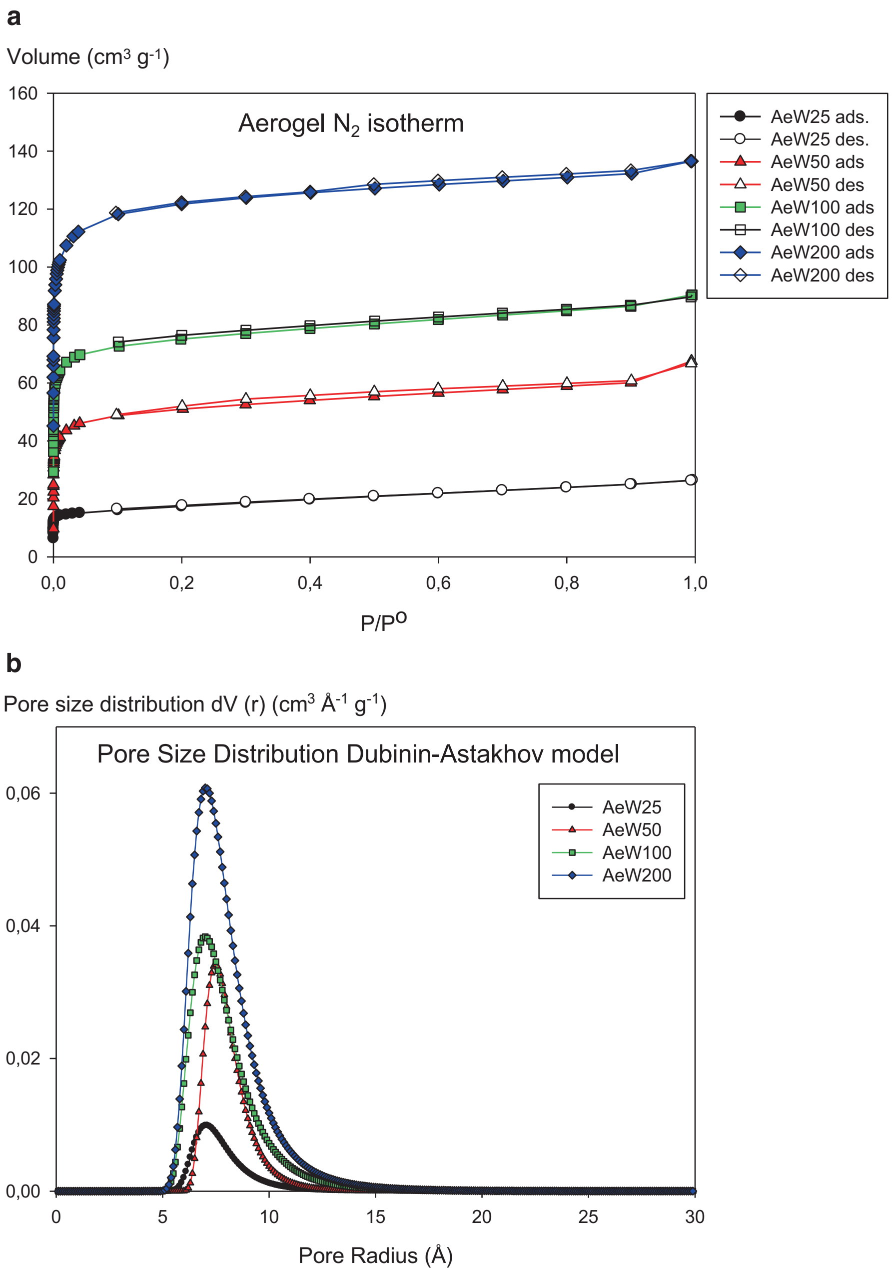

Fig. 6.12 Adsorption isotherms of nitrogen on carbon aerogels at 77 K and Pore Size Distribution QSDFT applied cylinder-slit model. (**a**) Isotherms AeW25, AeW50, AeW100, AeW200 with N_2 at 77 K; (**b**) Pore Size Distribution applied Dubinin-Astakhov model: AeW25, AeW50, AeW100, AeW200; (**c**) Pore Size Distribution applied QSDFT and cylinder-slit pore: AeW25, AeW50, AeW100, AeW200; (**d**) Isotherms AeW400, AeW600, AeW800, AeW1500 with N_2 at 77 K; (**e**) Pore Size Distribution applied Dubinin-Astakhov model: AeW400, AeW600, AeW800, AeW1500; (**f**) Pore Size Distribution applied QSDFT and cylinder-slit pore: AeW400, AeW600, AeW800, AeW1500. The numbers refer to the relationship resorcinol/catalytic converter

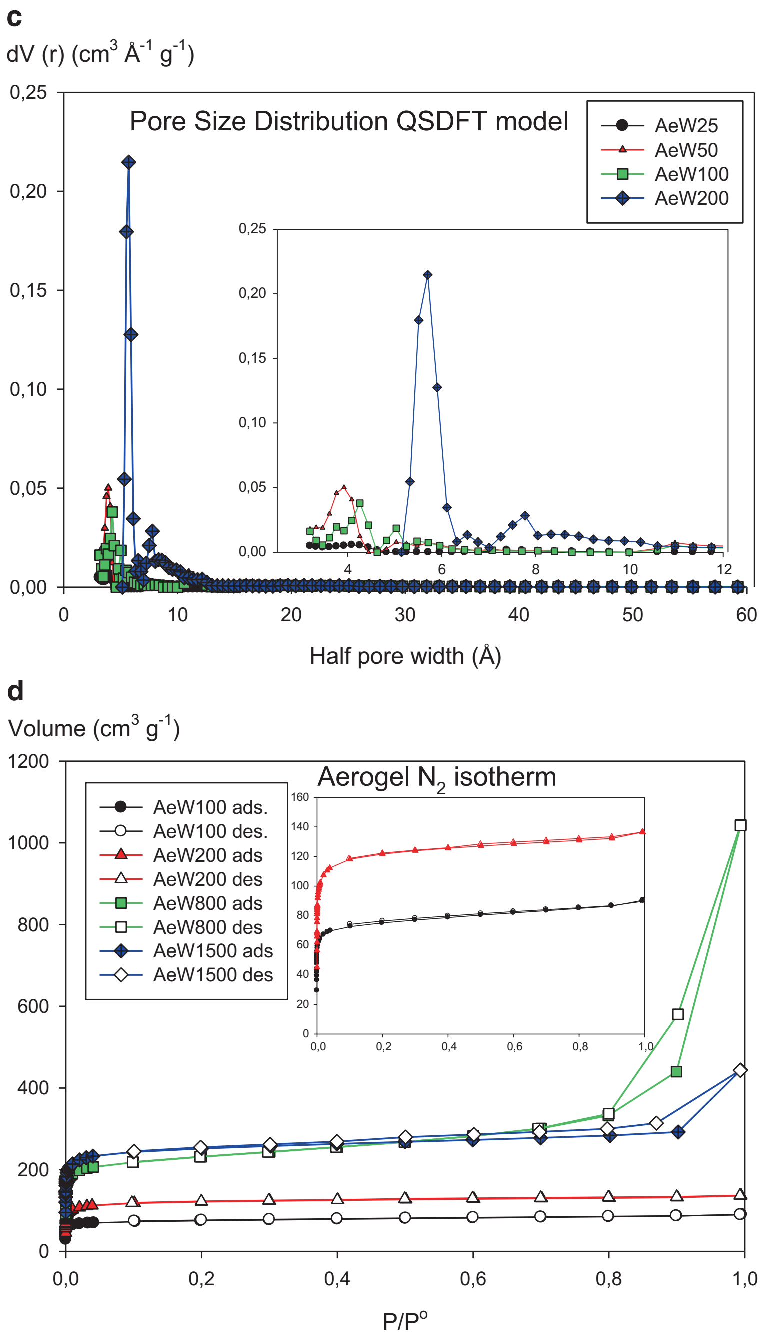

Fig. 6.12 (continued)

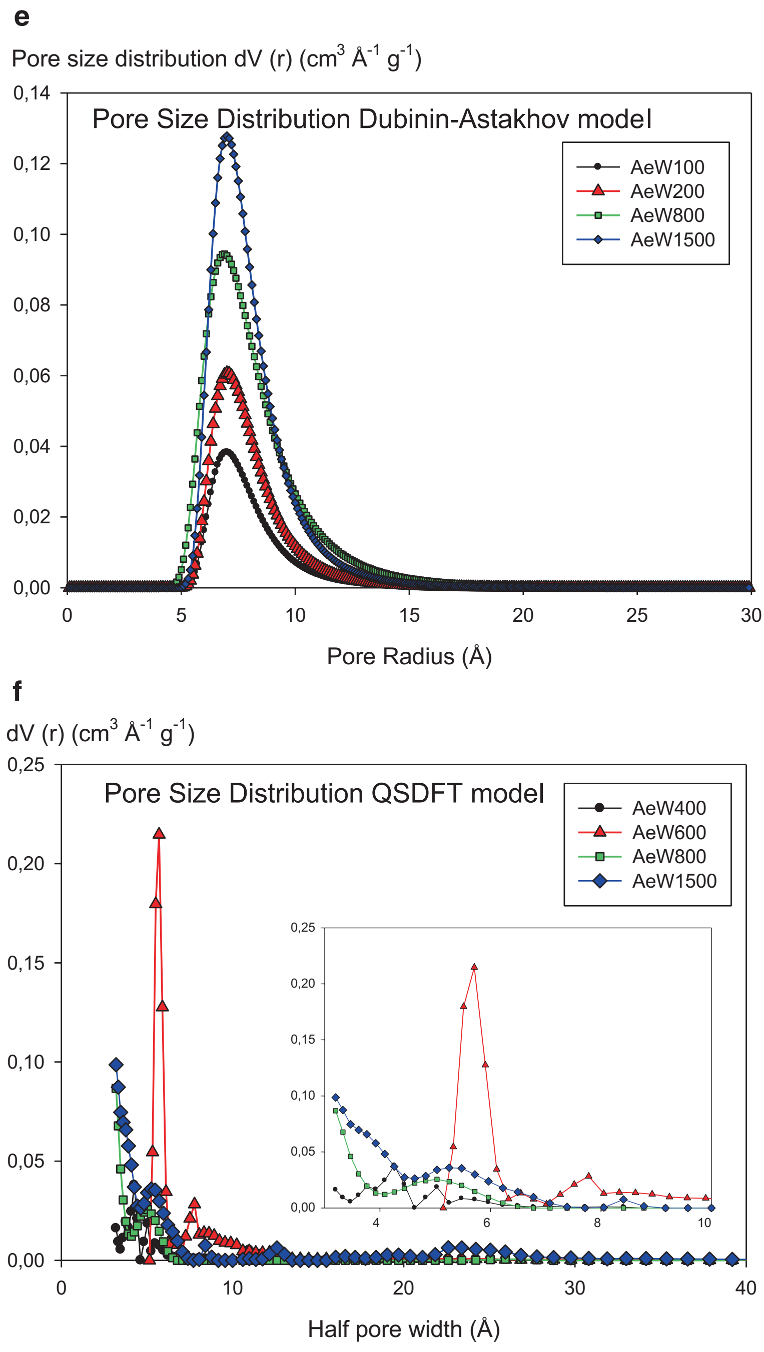

Fig. 6.12 (continued)

Table 6.3 Textural parameters of aerogels

Samples	S_{BET} $[m^2.g^{-1}]$	Dubinin-Astakhov $V_{micropore}$ $[cm^3.g^{-1}]$	E_0 [kJ. mol^{-1}]	n	Pore radio [Å]	B-J-H Vmeso $[cm^3.g^{-1}]$	Pore radio [Å]
AeW25	64	0.02	8.06	2.7	7.1	0.01	23.1
AeW50	196	0.07	6.89	3.4	7.5	0.02	18.2
AeW100	295	0.11	8.11	2.2	7.0	0.02	18.2
AeW200	478	0.18	8.00	2.2	7.0	0.02	18.1
AeW400	609	0.24	8.57	1.8	6.8	0.18	18.4
AeW600	849	0.33	8.15	1.8	6.9	1.23	79.3
AeW800	876	0.34	8.26	1.8	6.9	1.28	79.3
AeW1500	990	0.36	8.15	2.4	7.0	0.31	18.2

In Figs. 6.13a–h, scanning electron microscopy are presented for the surfaces of carbon aerogels. They are made at the same magnification to compare the effects in relation to changes in structure as the resorcinol/catalyst ratio changes.

It is evident that as the resorcinol/catalyst ratio increases, the formation of structural aggregates increases. In the samples of the series-I, the structures are simpler with flat and sharp shapes where there is an incipient formation of interconnected structures. It is possible to deduce that the greater amount of catalyst more monomer units are formed, resulting in the formation of some characteristics of the pearl necklace type for the samples of the series-II, proper for this type of materials (Pekala and Schaefer 1993; Moreno-Castilla and Maldonado-Hódar 2005).

The micropores and mesopores evaluated by the textural analysis models are not evident in the micrographs of carbon aerogels. Some formations of cavities in the surface of the materials are observed and as the resorcinol/catalyst ratio increases, there is an increase in the roughness of the samples without modifying the interconnected structure.

In Fig. 6.14 the X-ray diffractograms of the synthesized carbon aerogels are shown for the different resorcinol/catalyst ratios. The behavior shows that the materials present a disorganized nanocrystalline structure similar to activated carbons (Fairén-Jiménez et al. 2006).

Diffractograms obtained for the aerogels, show that the drying method, although it produces changes in the textural development and the morphological characteristics observed in the electron scanning microscopy, does not affect the formation of the crystalline structure. The diffractograms confirm the thesis of the formation of an amorphous structure, which correlates with the textural analysis, which says that carbon aerogels are heterogeneous materials with rough characteristics. No differentiating trend is observed in diffractograms as the resorcinol/catalyst ratio increases, which presupposes that this variable does not affect the organization of the structure in any way.

There are two broad characteristic bands between $2\theta = 19°$ and $2\theta = 21°$ for all samples and $2\theta = 38°$. The first of greater intensity and the second very light of less intensity. These two bands are associated with the formation of amorphous carbon, which are very characteristic of activated carbons.

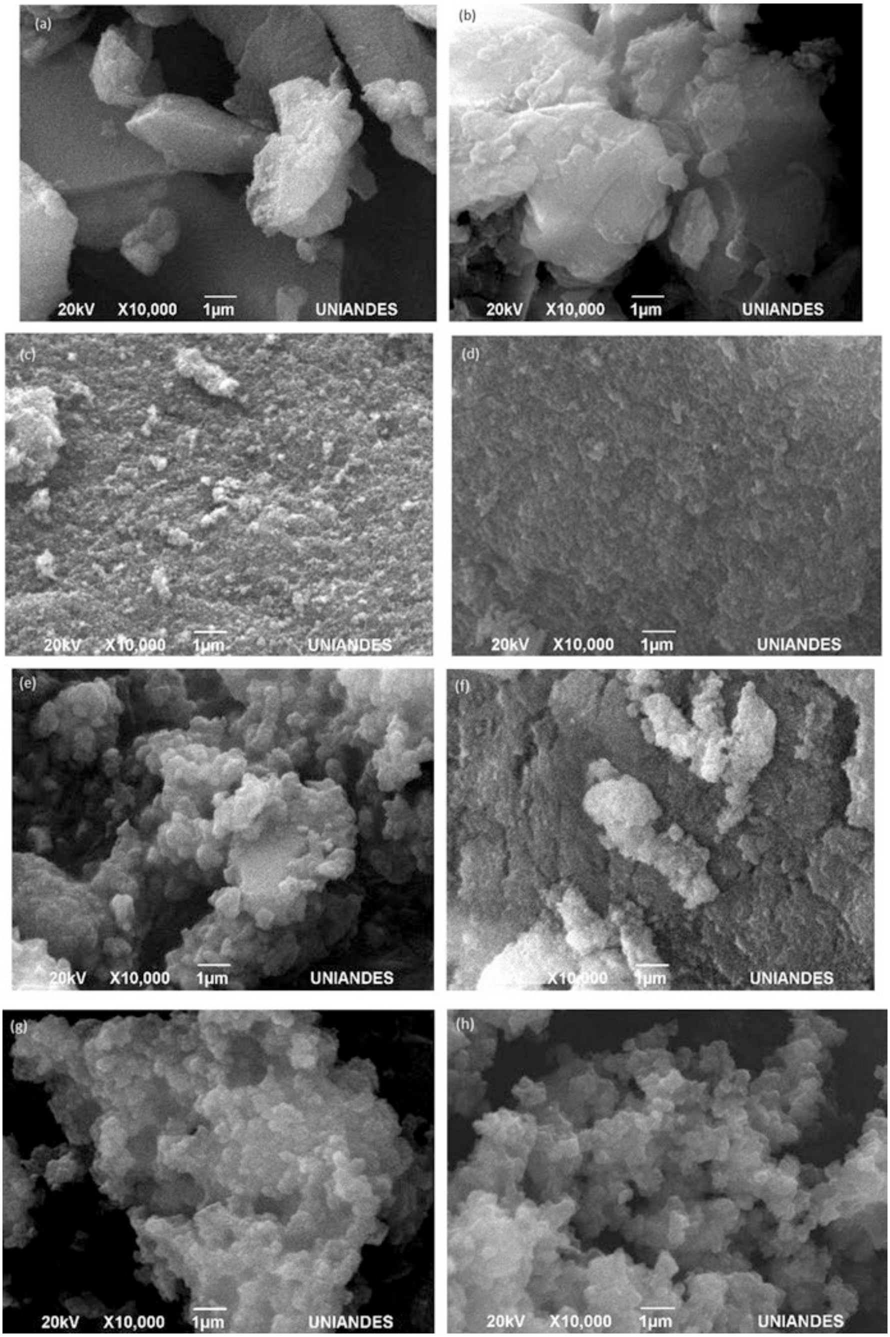

Fig. 6.13 Scanning electron microscopy micrographs at 10,000 magnifications for carbon aerogels. (**a**) AeW25, (**b**) AeW50, (**c**) AeW100, (**d**) AeW200, (**e**) AeW400, (**f**) AeW600, (**g**) AeW800 y (**h**) AeW1500

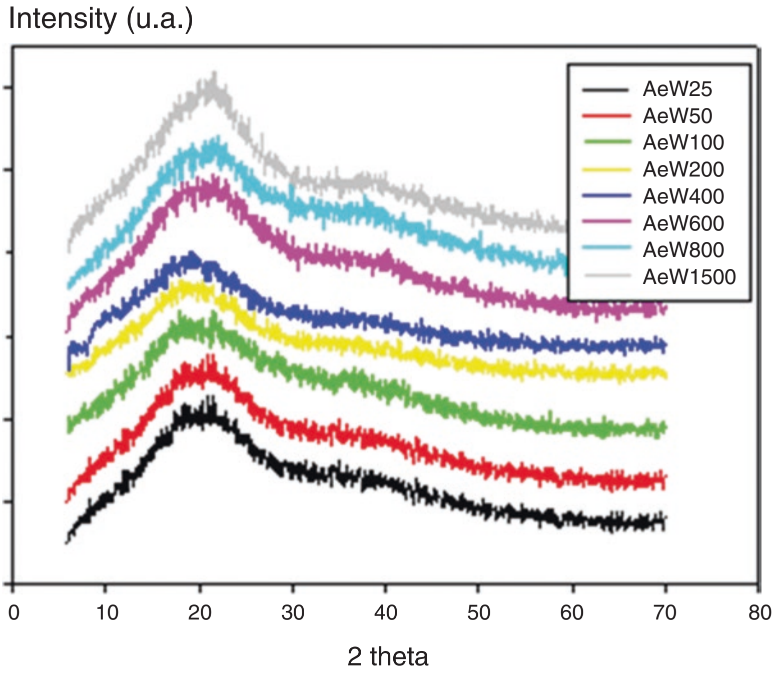

Fig. 6.14 X-ray diffractograms of carbon aerogels synthesized at different resorcinol/catalyst ratio for the series of carbon aerogels. From AeW25 to AeW1500

6.5.4 *Adsorption Isotherms of Phenol and 2,4-Dinitrophenol on Charred Bones*

Attempts to model adsorption phenomena, in the case of phenolic compounds in activated carbon, have focused mainly on the use of the Freundlich and Langmuir model. Although phenol adsorption has been adequately represented by both models, there is however, some disagreement in the literature about the applicability of one or the other model. The apparent inconsistency in the results can be attributed to the intrinsic nature of the activated carbon and the adsorbate / adsorbent ratios considered, whereas the statistical rigor applied to ensure adherence to a model differs in most cases.

It should also be noted that Freundlich's model, although it is an empirical equation, has the advantage of introducing the heterogeneity of the surface and giving good reproductions of the experimental data in liquid-solid systems. A finite limit when the concentration is sufficiently high, and therefore, in general, it is valid in low equilibrium concentration ranges. On the other hand, there is a proposal made by Sips (Do 1998; Hamdaoui and Naffrechoux 2007; Foo and Hameed 2010), which results from a combination of the Freundlich and Langmuir models, also known as the Langmuir-Freundlich model. At low concentrations of adsorbate, the model is

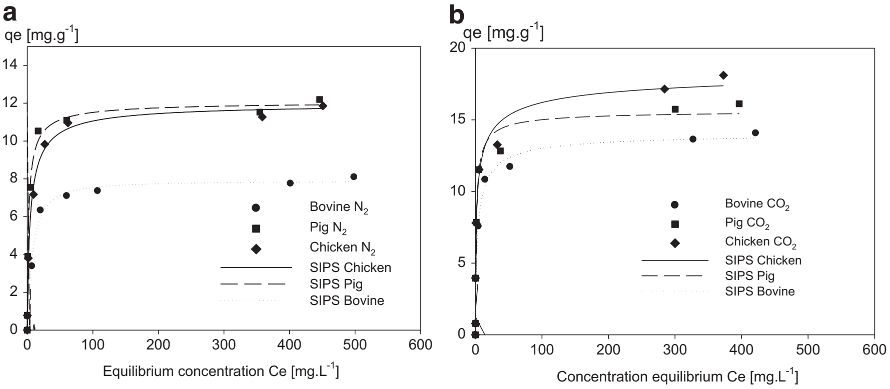

Fig. 6.15 2,4-dinitrophenol isotherms (**a**) in charred of N_2, (**b**) in charred of CO_2

Table. 6.4 Parameters of the Sips model of 2,4-dinitrophenol

Sample	q_m (mg.g^{-1})	1/n_s	K_s (L.mg^{-1})$^{1/n}$	R^2
Bovine N_2	7.89	1,22	0.12	0.99
Pig N_2	12.11	0.78	0.44	0.99
Chicken N_2	12.02	0.80	0.21	0.99
Bovine CO_2	14.16	0.72	0.28	0.99
Pig CO_2	15.69	0.72	0.72	0.98
Chicken CO_2	18.83	0.50	0.37	0.97

limited to that of Freundlich and at high, predicts the monolayer adsorption characteristic of the Langmuir isotherm.

In Fig. 6.15a, b show the adsorption isotherm from aqueous solution for 2,4-dinitrophenol. This is done using the models of Sips to adjust the experimental data of adsorption on the equilibrium of 2,4-dinitrophenol in the charred.

The variables and parameters of the model are: Ce (mg.L^{-1}) is the concentration of 2,4-dinitrophenol in the equilibrium, K_s (L.mg^{-1}) $^{1/n}$) and q_m (mg.g^{-1}) are the constants of Sips related with the energy of adsorption and maximum capacity of adsorption, respectively; q_e (mg.g^{-1}) amount adsorbed in equilibrium and 1/n_s the heterogeneity parameter (see Table 6.4.)

Sips model was assumed as the best model because it has good correlation coefficients R^2 as shown in Table 6.4, which will be denoted in the graph where the experimental points exhibit an asymptotic, behavior that is typical of this model. Although it has been found in other jobs that this type of materials best fit in the model of Freundlich, it is important to note that the conditions under which takes the heat treatment are determinant in the solid type that is obtained. In this case, the speed of heating with which took the heat treatment allows you to obtain a solid homogenous due to withdrew organized the matrix constituents.

On the other hand, the corresponding isotherms of adsorption of phenol (Fig. 6.16a, b) presented a similar behavior to the 2,4-dinitrophenol.

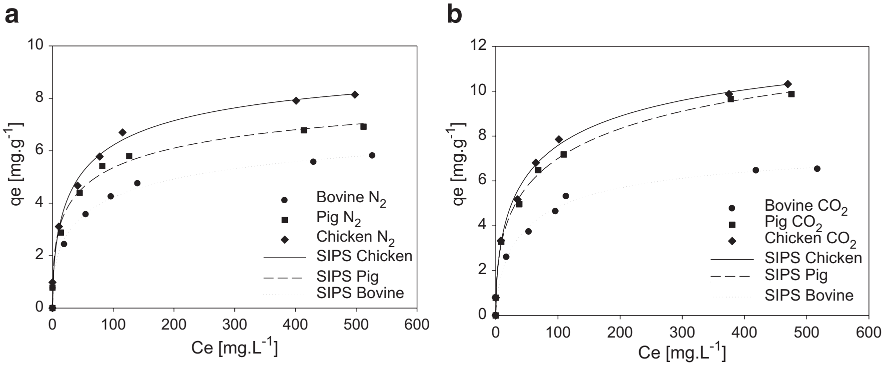

Fig. 6.16 Phenol isotherm (**a**) in carbonized of N_2, (**b**) in carbonized of CO_2

Table 6.5 Parameters of the Sips model of phenol

Sample	q_m (mg.g^{-1})	1/n_s	K_s (L.mg^{-1})$^{1/n}$	R^2
Bovine N_2	8.41	0.49	0.010	0.99
Pig N_2	10.03	0.44	0.014	0.99
Chicken N_2	10.27	0.58	0.021	0.98
Bovine CO_2	8.99	0.69	0.018	0.98
Pig CO_2	14.58	0.47	0.005	0.99
Chicken CO_2	14.99	0.56	0.014	0.99

Sips model was assumed as the best fit due to that has the values of correlation coefficients R^2 higher as can be seen in Table 6.5, which will be denoted in the graph where the experimental point exhibit an asymptotic behavior that is typical of this model.

Comparing the adsorbents used and using the Sips model it is noted that the q_m is lower for the phenol in comparison with the 2,4-dinitrophenol, due to the presence of substituents in the latter that affect the process of adsorption.

However, the charred to be basic character increase the pH of the solution to the case of 2,4-dinitrophenol increases the concentration of ionic species, while for phenol predominates the molecular form.

In addition, the results show that there is a correlation with surface chemistry i.e. the chars obtained in atmosphere of CO_2 with which they had been removed the acidity an increase is observed in the adsorption of both adsorbents. In the case of phenol, it is known that the adsorption occurs due to favor certain interactions that generate a change in the behavior of the system, the amount adsorbed is affected then by the presence of surface groups, specifically by reducing the acid groups the amount adsorbed increases, given that it interfere less with the electrons π layers graphenics the surface of the charred however the pH for the phenol solutions are in a range of 7.5–9 and 2,4-dinitrophenol 6.7–8, for the solution that allows to infer that there is a repulsion due to the surface of the carbonized is with a low density of negative surface charge and the Phenol molecule this mostly in its molecular state.

The presence of group nitro increases the acidity due to the partial positive charge on the nitrogen in the nitro group causes a deficiency in the aromatic ring, being greater the more groups nitro contains. The final pH of the solution allows the charred has a partially positive charge density, while the nitro groups cause a deficiency in the aromatic ring of the molecule of 2,4-dinitrophenol is in its ionic state which allows greater adsorption in comparison with the phenol.

6.5.5 Adsorption Isotherms of Ni^{2+} on Carbon Aerogels

Adsorption of the metal ion Ni^{2+} from aqueous solution is studied on the series II of the carbon aerogel synthesized, Aew400, AeW600, AeW800 and AeW1500, where the effect of the ratio resorcinol/catalyst on the modification of the structure is self-evident, due to this series is the one that presents more development of surface area and better development of the mesoporosity. This combination of pore distribution allows some materials with an adequate potential for the retention of metal ions in solution.

In Fig. 6.17 it is possible to observe the isotherms of adsorption for aerogels series II in which can be seen the experimental values and the adjusted with the Sips model, characteristic patterns of three parameters.

Isotherms show a trend characteristic in the adsorption of porous solids, in which it is observed that increasing the ratio resorcinol/catalyst increases slightly but so differentiable the amount adsorbed Ni^{2+}. This is in accordance with the development of the porosity that coincides with the increase in the surface area to the extent that it increases the relationship of resorcinol and the catalyst that is sodium carbonate. This can be explained in the measure that increasing the ratio resorcinol/catalyst the formation of enolate ion in the first step of the reaction is going to be greater and has more units of monomer formed, so that by the time that happens the polymerization interbreeding is going to be greater and is going to be reflected in the porous structure that is obtained.

Results in Table 6.6 show that the adsorption is adjusted in a better way because its correlation coefficient R^2 is close to one. When comparing the values obtained for the Sips model with the values reported for the different aerogels samples of the second series, it is observed that the adsorption capacities are higher for the samples that present greater development of mesoporosity according to the textural analysis of the series. The value of q_m is higher for samples AeW600 and AeW1500, this is explained by the fact that the volume of mesopores has a great influence on the amount of Ni^{2+} adsorbed, improving its adsorption capacity. This factor can be correlated with the fact that suggesting that the adsorbent has a finite adsorption capacity for the adsorbate and that the adsorption occurs in specific homogeneous sites.

To correlate the adsorption from aqueous solution of Ni^{2+} ions and the behavior of carbon aerogels when immersed in such solutions, it is necessary to use special techniques that provide direct information on the particular liquid-solid interactions and microcalorimetry is a useful technique for this purpose. The parameter that is

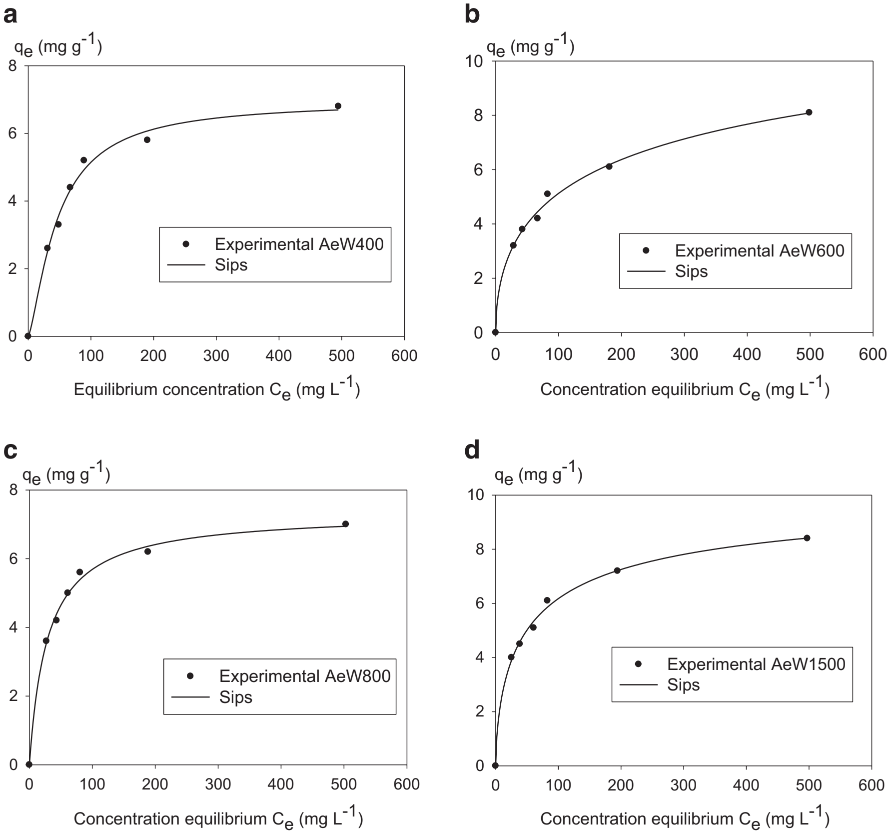

Fig. 6.17 Isotherms of Ni^{2+} in Carbon Aerogel, Series II adjusted by the Sips method (**a**) AeW400, (**b**) AeW600, (**c**) AeW800 and (**d**) AeW1500

Table 6.6 Parameters of the Sips model in Ni^{2+} adsorption

Sample	qm (mg.g–1)	1/ns	Ks (L.mg–1)1/n	R2
AeW400	6.954	1.38	0.021	0.992
AeW600	14.51	0.52	0.003	0.996
AeW800	7.350	1.00	0.034	0.996
AeW1500	10.05	0.64	0.017	0.997

evaluated by immersion microcalorimetry is the immersion enthalpy, Δ*Himm*. Figure 6.18 shows the correlation between the immersion enthalpies and the surface area of the solids synthesized for adsorbed ion.

When calculating the enthalpy of immersion would determine the degree and nature of the interaction in the solid-liquid interface, this information is useful because it allows to establish the magnitude of the interactions in the adsorption process. The most negative values correspond to the carbon aerogels for the highest

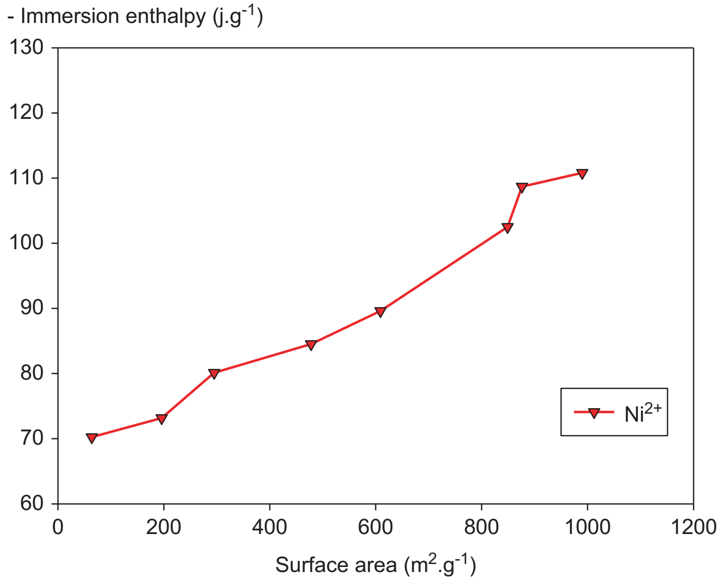

Fig. 6.18 Enthalpy ratio of immersion in Ni^{2+} solutions and surface area of carbon aerogels

resorcinol/catalyst ratios that are also those with the largest surface areas. The enthalpy value decreases as the ratio resorcinol/catalyst decreases, this indicates that the adsorption is directly related to the energy interactions of the ions with the active sites on the surface. As the surface area increases, the enthalpy of immersion increases.

6.6 Applications of Theoretical Numerical Calculations in Adsorption in Aqueous Solution

Theoretical studies based on molecular modeling and simulation tools are useful to obtain data that allow to correlate the structural characteristics of the solids to be obtained, the conditions of synthesis, the mechanisms involved and the applications in the adsorption of molecules of interest. Nowadays, with the increase in computing potential and the possibility of operating more complex calculations, the use of molecular dynamics simulations, unlike those using statistical data and probabilities like Monte Carlo, provides a “real time” representation of the physical process under study. This is highlighted when you want to explore the mechanisms involved. It is also possible from the simulation data to perform correlations with classical adsorption models Langmuir, Freundlich, Sips when trying to predict adsorption capacity in a solid study.

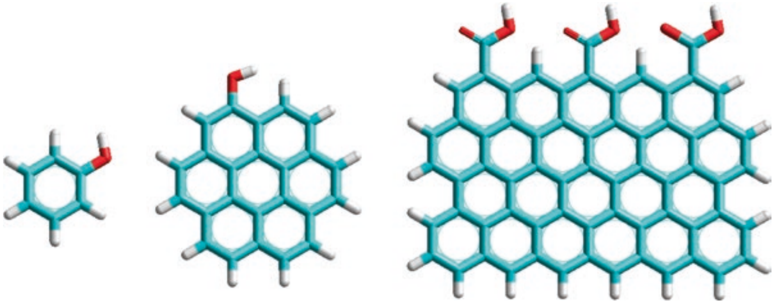

Fig. 6.19 Clusters used for the DFT calculations and the molecular dynamics simulations

It is possible using semi-empirical calculations of quantum mechanical; analyze the adsorption of aromatic compounds in general and of phenolic compounds, using three different approaches. In the first place, geometric aspects and energy of the adsorption of phenolic rigid molecules in the graphite surface can be studied by computer simulations, using the approach Gran Canonical Canon Monte-Carlo (GCMC). Secondly, by making use of quantum methods semi empiric com PM3, it is possible to describe the interaction between the different phenolic compounds and surfaces of graphene oxidized, controlling these results with the calculations of the Density Functional Theory (DFT). In this case, the substrate it is possible to simulate using a molecule type chromene. Finally, we can perform calculations by DFT and molecular dynamics, to analyze the presence of different solvents and evaluate their effect on adsorption of aromatic molecules (Figs. 6.19 and 6.20).

Despite the many arguments that have been presented on what is the role played by each one of the interactions that are involved in the mechanisms that govern the adsorption of aromatic compounds in activated carbons, the discussion about which is the main, continues until today in the debate. In the case of phenol, most researchers agree that in the adsorption can occur simultaneously different types of interactions surface-phenol, but the question about that prevalence assign each one, remains without a clear response.

When studying the adsorption of phenolic compounds in activated carbons, three types of interactions have been proposed: (1) effects of dispersion between the aromatic ring phenolic and electrons π the structure of graphene, (2) the interactions donor-acceptor between the aromatic ring phenolic and superficial groups with oxygen, and (3) electrostatic attractions and repulsions between the ions present. Although some researchers agree that the decrease in the quantity of phenol adsorbed (Terzyk 2003), after the oxidation of the carbon, is due to the passage oxidation of the carbonyl groups to carboxyl, and as a result does not allow the formation of complex electronic donor-acceptor; it is also thought that the mechanism donor - acceptor is not the main force in the adsorption of aromatic compounds on activated carbons (Salami and Bandosz 2003).

About point (1), we can say that if the phenol is adsorbed flat on the graphene layers, the forces that govern the adsorption must be interactions of dispersion π-π

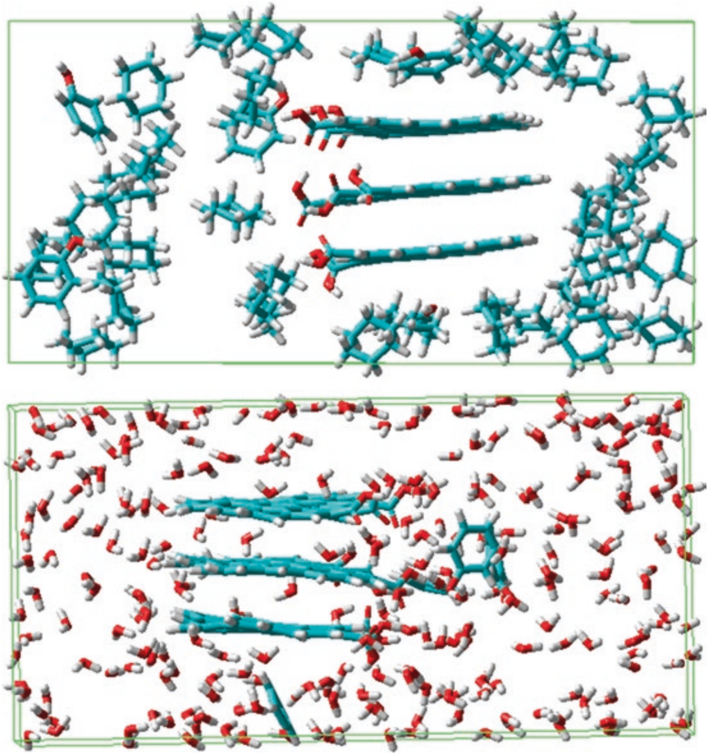

Fig. 6.20 Cells of molecular dynamics simulation employed in (for which the figures were clearer were removed from the cell some of the molecules of the solvent)

between the aromatic ring of phenol and the aromatic structure of the graphene layers. In this way, it was proposed that the acid groups, located at the edges of the basal planes, remove electrons to π the system, creating positive gaps in the conduction band p of the planes of the graphite. This would lead to a weakening of the interactions between electrons π of aromatic ring of phenol and the electrons π of basal level, thus reducing the amount of phenol adsorbed. However, these arguments have at least two weak points: first, it is assumed a priori that the phenol is adsorbed in flat form. Secondly, the proportion of atoms in the edges is very small compared to the atoms within the surface and thus the adsorption of oxygen would be very low.

Although this problem could be eased, arguing that, in the activated carbons not graphitizable, there is a high proportion of atoms at the edges and therefore the ability to adsorb oxygen should be higher, the hypothesis that molecules adsorb on flat on the surface also goes against the calculations quantum mechanical The importance of this point is confirmed through the crucial role that many researchers assigned, to the orientation of the molecules on the surface, when you want to study its adsorption (Salami and Bandosz 2003).

The importance of the presence of water in the process of adsorption, confirms that when the phenol is adsorbed, from an aqueous solution, with a polar solvent, the main form of adsorption should not be through interactions π-π, but by other mechanisms. Though the results do not tell us specifically what would be the main mechanism of adsorption, it is evident that the interactions π-π cannot play that role. It was thus proposed as mechanisms of adsorption, both to the interactions of dispersion π-π between the aromatic ring of phenol and the graphene layers, as the hydrogen bridge connections between the water and the carboxyl groups of the surface. The water molecules, adsorbed on these sites with oxygen, become secondary adsorption centers, to retain other molecules of water. Because of all this, were generating complexes formed with water that inhibits the migration of organic molecules in much of the surface with adsorption capacity.

To further explore this point, we analyze the residence times of the molecules of phenol near the carboxylic groups (see Fig. 6.21), to compare the water with other solvent less polar how cycle hexane.

Figure 6.21 shows the distance between two molecules of phenol and the surface as a function of time for the two solvents considered. We see that in the case of phenol in cyclohexane, mobility is higher than in the water and the residence times are relatively long, which tells us that the hydrogen bridge type interactions play an important role in the adsorption. This may be due to the large interaction of phenol with water, and would explain why the complexes formed from water, inhibition migration of organic molecules toward a large portion of the active surface.

We can say that when the phenol is adsorbed from an aqueous solution and a polar solvent, the main mechanism of adsorption would not be interactions π-π, but other mechanisms. Although these results did not respond specifically to the question of what is the mechanism of adsorption of phenol, the statement that they are the interactions π-π, should question seriously.

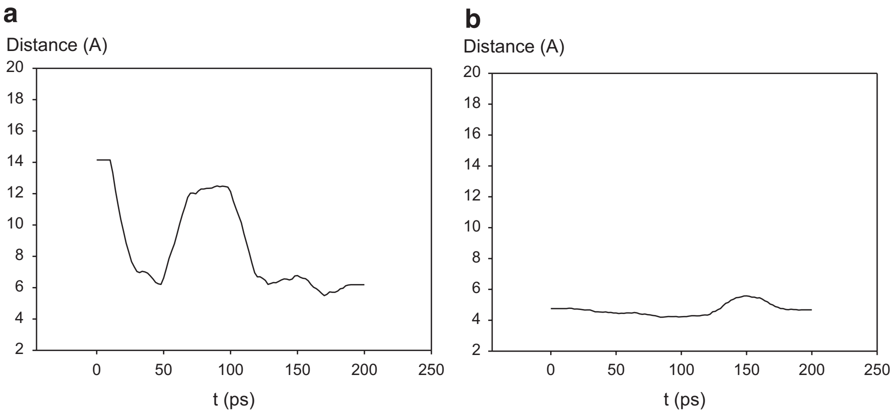

Fig. 6.21 Residence time of the molecule of phenol near the surface of an activated carbon. (**a**) Solvent Water, (**b**) solvent cyclohexane)

6.7 Conclusion

This chapter has shown that it is possible to obtain different types of porous materials from different sources and experimental conditions. These to be characterized by different methodologies is that have different chemical and textural characteristics which leads to its application in environmental protection the results will have a broad spectrum. Within this chapter, it is worth to emphasize that it is possible to use raw materials to prepare materials adsorbents waste as are the bones of animals, which are favorable in the synthesis of charred with application for the removal of organic compounds from aqueous phase. Its chemical composition and its subsequent heat treatment allows to obtain this type of materials with yields around 50%; the conditions under which were obtained allow to obtain materials with different chemical and textural properties. The studies of the adsorption isotherms in this case show that the chars obtained show a micropore volume between 0,228 and 1,417 $cm^3.g^{-1}$ and area values bet between 99 and 180 $m^2.g^{-1}$ depending of the precursor and atmosphere of carbonization, these results show that the materials obtained are mesoporous which is characteristic of this material. The chars of bone obtained under both atmospheres show a good capacity of adsorption of 2,4-dinitrophenol and phenol, the Langmuir isotherm properly adjusted to the experimental data obtained. The maximum capacities of adsorption of 2,4-dinitrophenol increase in the following order: Chicken CO_2 (17,90 $mg.g^{-1}$) > Pigs CO_2 (16.09 $mg.g^{-1}$) > Bovine CO_2 (14.03 $mg.g^{-1}$) > Pigs N_2 (11,99 $mg.g^{-1}$) > Chicken N_2 (11,74 $mg.g^{-1}$) > Bovine N_2 (8.08 $mg.g^{-1}$) and for phenol are Chicken CO_2 (10.52 $mg.g^{-1}$) > Pigs CO_2 (10.17 $mg.g^{-1}$) > Chicken N_2 (8,30 $mg.g^{-1}$) > Pigs N_2 (7.05 $mg.g^{-1}$) > Bovine CO_2 (6.75 $mg.g^{-1}$) > Bovine N_2 (5.92 $mg.g^{-1}$). The adsorption of phenol and 2,4-dinitrophenol from aqueous solution is affected by the content of superficial groups, pH of the solution and the presence of substituents in the aromatic ring. It is noted that the adsorption percentages are higher for the carbonized of CO_2 due to the interactions of the physical nature that occur for this reason its desorption efficiency is makes it a bit more difficult.

On the other hand, with the Carbon Aerogel is interesting to see that the ratio resorcinol/catalyst affects in a critical manner the textural properties of this type of materials. The results show that with the increase of the ratio resorcinol/catalyst are generated two series of aerogels: one in which are obtained microporosos materials and a second series where are characterized by the development of mesoporosity. Thus, in the series II of aerogels as you increase the ratio resorcinol/catalyst increases the adsorption capacity of the Ni^{2+} ions from aqueous solution, obtaining the greater capacity of adsorption of 14.51 mg g^{-1} of Ni^{2+} for AeW600 sample, which is the one with the most mesoporosity.

Finally, and based on the computational theoretical calculations, we can say that neither the oxidation of the surface, or the presence of a solvent polarizable, are compatible with the assumption that π-π interactions play a dominant role in the adsorption of phenolic compounds on carbonaceous materials.

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Chapter 7
Municipal Waste Biochar for Energy and Pollution Remediation

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Abstract Municipal solid waste has become a hassle in many developing countries due to haphazard disposing to open dumpsites, which has zero management. This way of disposing the waste has negative impacts in the environment that can directly contribute to the climate changes and atmospheric pollution through greenhouse gas and volatile organic compound emission and water and soil pollution via landfill leachate as well. Biochar, a carbonaceous material produced by limited or no oxygen pyrolysis of biomass is an emerging efficient substitute for activated carbon. Its production utilizes different feedstock including municipal solid wastes, which is the "greener" approach of transforming the existing municipal waste into a value added product that can be used in contaminant mitigation and resource recovery by using it as an adsorbent and as a hybrid with soil for better plant growth. The long term benefits of these biochar additions to soil and water can be manifold and potential as an improved nutrient retention and availability to plant growth; this gives the impetus of having the "greener transformation" from municipal wastes to biochar. This chapter outlines the ways of production of biochar derived from municipal solid waste, its significance as an adsorbents and its promising potential in landfill cover, leachate treatment and for permeable reactive barriers.

7.1 Introduction

Handling of municipal solid waste creates problems than opportunities to produce valuable products such as energy, heat or recyclable material (Portugal-Pereira and Lee 2016). According to the assessment of World Bank, current worldwide generation of waste exceeds 1.3 billion tonnes per year and it is estimated to increase up to 2.2 billion tonnes per year by 2025 (Hoornweg and Bhada-Tata 2012). The rapid increase of municipal waste is a result of an exponential increase of population, industrialization and a migration of population from rural to urban areas due to economic development (de Souza Melaré et al. 2017). Municipal solid waste management is complex and is a mammoth task for municipalities due to the substantial demands of human and financial resources (Sequeira and Chandrashekar 2015b). Municipalities have to deal with significant quantities of organic and compostable wastes that are generated daily (Sequeira and Chandrashekar 2015a) to provide adequate and effective waste management to the community. Generally, municipal solid wastes can be categorized into organic and inorganic wastes

(Ghanimeh et al. 2012). Many different methods such as source reduction, recycling, composting, incineration and disposal into landfill have been practiced to manage solid waste worldwide. The World Bank and United States Agency for International Development (USAID) reports that 20–50% of the budget of a municipal council in developing countries is spent on solid waste management and these funds originate from less than 50% of an urban population (Henry et al. 2006; Memon 2010). This highlights the need for cost effective management of municipal waste. Management of pollutants in water bodies by using municipal waste derived biochar is one method of effectively using municipal solid waste, without disposing them into landfills. Hence, this chapter focuses on producing biochar from municipal solid wastes. Biochar is a soil enhancer, it can improve water quality by retaining nutrients, it enables sustainable management of organic solid waste and by retaining carbon it also helps combat climate change. These aspects are further detailed in the later parts of the chapter. The disposal methods of municipal wastes and environmental concerns that arise from these disposal methods are discussed in the next sections.

7.1.1 Disposal of Municipal Solid Wastes

In most countries, the disposal of municipal solid waste are done by incineration, sanitary landfill or open dumping even though, more environmental friendly low cost technologies such as composting and vermicomposting exist (Sequeira and Chandrashekar 2015b). With minimum consideration towards environmental impact, most developing countries dispose solid waste in open dumps (Vithanage et al. 2014; Wijesekara et al. 2014). Incineration is commonly applied on non-biodegradable wastes containing relatively a less moisture content and use of incineration reduce solid waste that goes into landfill (Tan et al. 2014). Incineration has several advantages over landfill disposal (Eriksson et al. 2007). An estimated 80–95% volume reduction of solid waste with incineration is a significant advantage to greatly reduce landfill and also to manage the leachate produce by landfill. This benefit is of greater significance for urban areas where land is scarce. Other advantages include opportunities to extract energy (as electricity and heat) and its ability to immobilize and decompose toxic constituents enabling the ash produced to be used in the construction industry (Huai et al. 2008).

Today economically developed countries consider municipal solid waste as a resource and aims to convert solid waste to energy (e.g. fuels, electricity and heat) (Antizar-Ladislao and Turrion-Gomez 2010; Guerrero et al. 2013) mostly using technologies such as pyrolysis and gasification (Liu and Liu 2005) and these technologies are detailed in the later parts of the chapter.

The disposal of solid waste is largely dependent on the composition of municipal solid waste, availability of resources such as funds, technical knowhow, availability of land and/or man-power. The composition and the quantity of municipal solid waste produced largely differs from country to country or region to region, the economic development of a county, the industrial structure, consumption patterns, culture, climatic factors and the types of energy sources used (Moya et al. 2017). For instance, low income economies tend to produce a great amount of organic wastes while high to middle economies tend to produce more inorganic waste (Trang et al. 2017). Trang et al. (2017), provides a comprehensive study of the household municipal waste of a city in Vietnam, and demonstrates a correlation between generation of solid waste and the socio-economic status of the household. Less solid wastes were generated by high income households compared to low income households.

7.1.2 Environmental Pollution

The rate of municipal solid waste production far exceeds its natural decomposition and as a consequence there are severe implications on the environment (Tan et al. 2015). As a consequence the negative aspects of municipal solid waste, specifically the solid waste in landfills has become a critical point of discussion due to the detrimental impacts caused on health and the environment (Palmiotto et al. 2014).

Many developing countries still use open dumping as the most common method of municipal solid waste disposal (Menikpura and Basnayake 2009; Mor et al. 2006). According to the Tränkler et al. (2005), most of the South and Southeast Asian countries use non-engineered landfills for solid waste disposal. The negative impacts these landfill sites have on the environment are non- reversible at times and causes permanent damage to natural resources that are at close vicinity of the landfill sites. Specifically, release of hazardous chemical compounds into nearby water bodies and ground water, the release of toxic fumes and emission of odor impacting the health and the quality of life of neighboring communities (Downey and Van Willigen 2005; Ariyawansha et al. 2011).

7.1.2.1 Gaseous Emission

Landfill gas emissions are a major pollutant of our atmosphere. The landfill gases are comprised mainly of methane, water vapors, carbon dioxide and small amounts of other organic compounds, which are categorized as non-methane organic compounds (Soltani-Ahmadi 2000). The non-methane organic compounds primarily are consisted of hazardous gaseous pollutants, odorous compounds and volatile organic compounds (Davoli et al. 2003; Fang et al. 2012). Generation of methane in landfills is due to a prolonged accumulation of organic solid wastes and this methane is able to trigger explosions, open fires and global warming (Sridevi et al. 2012). Compared to carbon dioxide, methane is roughly 30 times more potent as a heat-trapping gas, and hence has the potential to expedite global warming.

The production of odorous compounds in landfills is elevated especially in summer periods due to high temperatures (Dasgupta et al. 2013) and these odorous compounds affect human settlements in the vicinity. Benzene, Ethyl Benzene, Xylene and Toluene are major volatile organic compounds that are regularly found in landfill sites (Harkov et al. 1985; Jayawardhana et al. 2016). Long term exposure to even very low concentrations (i.e., ppb or less) of these volatile organic compounds can cause adverse health effects (Leidinger et al. 2014). The exposure to these landfill gases are largely through respiration (Palmiotto et al. 2014) and hence the releases of these volatile organic compounds into the atmosphere should be well managed.

Even so called environmentally friendly technologies such as pyrolysis and gasification used to produce value added products (e.g. oil, char and syngas) from municipal solid wastes produce gaseous pollutants including polycyclic aromatic hydrocarbons and fine particulate matter (Hajizadeh et al. 2011; Rochman et al. 2013). Polycyclic aromatic hydrocarbons impact both the environment (Sun et al. 1998) and human health largely acting as teratogenic, carcinogenic or mutagenic compounds (Ionescu et al. 2012; Moeckel et al. 2013). Also fine particulate matter have possibilities to associated with polycyclic aromatic compounds (Richter and Howard 2000) and those with diameter of ≤2.5 μm cause lung cancers due to deep penetration into lung tissues (Buonanno et al. 2011; Ionescu et al. 2013).

7.1.2.2 Contaminants to Water and Soil

Landfill leachate has been recognized as one of the main causes of groundwater contamination (Fatta et al. 1999). Leachate originates with infiltration of rain water or with an underflow of groundwater through waste deposits. The decomposing solid waste results in a liquid rich in inorganic and organic substances and this liquid is referred to as landfill leachate. Normally, leachate collects at the bottom most part of the landfill and can percolate into groundwater (Mor et al. 2006). Rainfall is mainly responsible for leachate generation (Tränkler et al. 2005) and moisture content of the solid waste also have a significant influence on the volume of leachate produced (Wijesekara et al. 2014).

Landfill leachate mostly contain four main classes of compounds namely inorganic macro- components, trace metals, dissolved organic matter and xenobiotics (Christensen et al. 2001). These compounds are mainly responsible for the pollution of soil and groundwater impacting both the natural environment and neighboring communities. There are health risks that could arise with consumption of contaminated ground water or fruits and vegetables cultivated using contaminated soil and ground water (Palmiotto et al. 2014). In addition to humans, landfill leachate has been identified as extremely toxic to many other organisms such as algae, higher plants, invertebrates and fish (Langler 2004; Di Natale et al. 2008). Several studies reported that trace metals such as Cd, Ni, Hg, Cu, Mn, Pb and Zn are present in leachates at elevated concentrations and the ability of these to bind with dissolved organic carbon for instance, humic, fulvic and hydrophilic acid enhances their dispersion across ecosystems (Asadi 2008; Wijesekara et al. 2014). Furthermore, dissolved organic carbon particles are responsible for the characteristic dark brown color of the leachates. The xenobiotic compounds (e.g. chlorinated aliphatics, aromatics hydrocarbons, halogenated hydrocarbons and phenols) and inorganic ions (e.g. nitrate, nitrite, ammonium, sulphate and phosphate) on the other hand also can severely impact living organisms (Asadi 2008; Mor et al. 2006).

In the latter part of this chapter we discuss how production of biochar from municipal solid waste could reduce landfill. Additionally, we discuss how this biochar also could be used to sustainably treat landfill leachate produced at legacy sites.

Development of environmentally sustainable strategies to mitigate pollutants of municipal solid waste is one of the biggest challenges that humans have ever faced (Wijesekara et al. 2014). Ideally municipal solid waste management systems should be designed such to treat waste based on quality, quantity and composition (Kalantarifard and Yang 2011). However, development of such sustainable management systems are a challenge largely because of complexity, variability, quantitative assessment of waste, inadequate technological resources, limited information about pollutants and a lack of positive attitude towards waste management (Ionescu et al. 2013).

Today there are calls for development of technologies to convert municipal solids directly into value added products. This creates an avenue to re-utilize municipal solids specifically to facilitate various environmental solutions. Pyrolysis of municipal solid waste is one such technology that directly adds value with conversion of municipal solids into biogas and biochar as final end products.

The biochar, produced has proven to possess excellent adsorption capabilities to remove impurities from both water and soil (Glaser et al. 2000, 2002). Compared to technologies such as incineration, pyrolysis uses less energy and also helps sequest carbon reducing greenhouse gas emissions into the atmosphere. Therefore, pyrolysis has potential to facilitate management of municipal solid waste and the end products of pyrolysis could also become a revenue stream for municipalities.

7.2 Municipal Solid Waste- Biochar Production

7.2.1 Production Technologies

Biochar is generally produced by thermochemical decomposition of biomass (organic matter of living organisms (plants and animal) and their residues) at temperatures of 200–900 °C (Lehmann and Joseph 2009). Traditionally, biochar was produced in earthen charcoal kilns where pyrolysis, gasification, and combustion processes were carried out in parallel (Brown 2009; Duku et al. 2011). Traditional charcoal-making technologies emit considerable amount of smoke, soot and combustible gases to the environment and are energy inefficient (Brown 2009). Hence, there has been a development of cost effective and environmentally friendly thermochemical conversion processes. Pyrolysis, carbonization and gasification

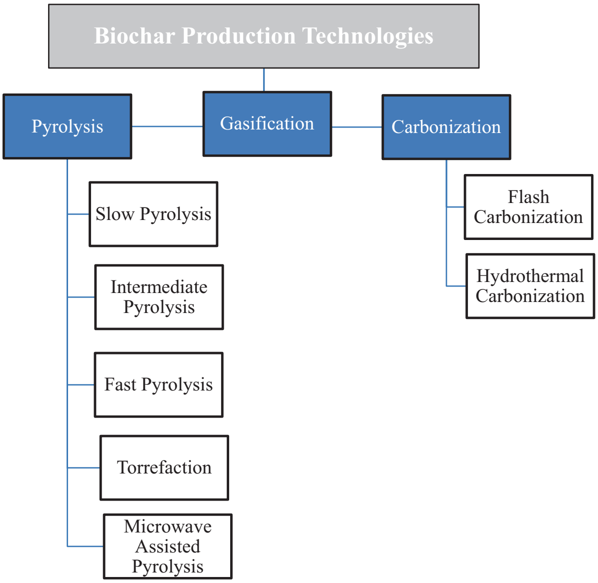

Fig. 7.1 Different technologies of biochar production: the "greener transformation" of municipal waste to a value- added products

processes are the main thermochemical processes that are used today to convert biomass to biofuels, gaseous products and other c-rich solid products (biochar) (Duku et al. 2011) (Fig. 7.1).

During pyrolysis, biomass is heated to a target temperature in the presence of little or no oxygen (Demirbas and Arin 2002). Due to the reductive atmosphere that prevails during formation of biochar, there is evaporation of Cd and Zn. However, Cu, Ni, and Cr are reduced to their elemental forms or sulfides (Dong et al. 2015). There are several pyrolysis technologies (e.g. fast pyrolysis, intermediate pyrolysis, slow pyrolysis, toreffaction, and microwave assisted pyrolysis) that can be used for thermochemical conversion of municipal solid waste into biochar (Mohan et al. 2014) and further details can be found in the later part of this chapter (Fig. 7.1).

Slow pyrolysis is carried out at a low rate of heating (lower than 10 °C/min) and a short residence time of few minutes to several hours is commonly applied to facilitate production of biochar. Fast pyrolysis is carried out at a higher rate of heating (~1000 °C/S) to produce bio-oils (as the major product (70%)) and biochar (Mohan et al. 2014). The yield of slow pyrolysis biochar is relatively high (35%) compared to fast pyrolysis (10%) and gasification (10%) (Sohi et al. 2009; Mohan et al. 2014). Torrefaction is a pyrolysis process, which is carried out at a low temperature (200–280 °C) to facilitate partial decomposition of biomass. There are numerous studies which has examined slow/moderate pyrolysis of municipal solid waste (Buah et al. 2007; Miskolczi et al. 2013; Kabir et al. 2015; Jayawardhana et al. 2017). But reports on the production of biochar via fast pyrolysis is limited (Wang et al. 2015).

Biochar yields from different studies have been summarized by Jayawardhana et al. (2018), and according to the study there is a huge variation in the observed yields (range between 14–66%). It has been further observed that the municipal solid waste biochar yields increase when rate of temperature increase is less and vice versa (Phan et al. 2008; Kabir et al. 2015; Zornoza et al. 2016; Jayawardhana et al. 2018).

Microwave assisted pyrolysis is a novel pyrolysis technique and may serve as an economically, and environmentally friendly biochar production process when comparing performance with conventional pyrolysis processes (Luque et al. 2012; Yu et al. 2017).

Hydrothermal carbonization is one of the most recently introduced carbonization processes and it reduces higher energy cost requirements of biochar production (Luque et al. 2012; Yu et al. 2017). The technology does not require a dry feedstocks and therefore has a reduced energy requirement (Lu et al. 2012b). The input energy requirements of hydrothermal carbonization is low due to the technology's ability to accommodate a feedstock with a high moisture content. During the carbonization process, the feedstock undergoes a series of simultaneous reactions, including hydrolysis, dehydration, decarboxylation, aromatization, and re-condensation (Libra et al. 2011). Flash carbonization converts biomass into gas at an elevated pressure (at about 1–2 MPa), a 30 min residence time and at a temperature range of 300–600 °C (Meyer et al. 2011).

Gasification converts biomass into a gaseous fuel as the primary product and liquid/solid as secondary products. This process requires a gasifying medium such as a steam of air, or oxygen to rearrange the molecular structures in solid or liquid biomass. Biomass is subjected to high temperatures in an aqueous media allowing transformation of carbon to a gaseous fuel (coal) (Lv et al. 2004). Pyrolysis process of municipal solid waste emits less toxic substances compared to combustion and gasification processes (Agarwal et al. 2015). To date majority of these municipal solid waste biochar production processes have been carried out in small scale or in laboratory scale. Designing a large scale municipal solid waste biochar production processes targeting a specific end product is challenging due to the complex and heterogeneous nature of municipal solid waste feed stocks.

7.2.2 Municipal Solid Waste Biochar Characteristics

The physicochemical characteristics (e.g. surface area, functional groups, particle/pore sizes, pH, ash content, moisture content, yield etc.) of biochar depends on the type, nature and origin of the feedstock and production conditions (Duku et al. 2011) (Table 7.1). It has already been shown that increasing pressure and decreasing peak temperatures increase biochar yields. Biochar produced at high temperatures has high aromatic content and high porosity (Table 7.1).

Table 7.1 Production processes of biochar at different temperatures with elemental contents

Origin of municipal solid waste	Thermochemical process	Pyrolysis temperature	Mobile matter	Fixed matter	Ash	C	H	O	N	Surface area	Pore volume	References
		°C	%	%	%	%	%	%	%	m²/g	cm³/g	
Sri Lanka	Slow pyrolysis	450	31.6	46.5	15.6	60.8	2.79	14.6	1.33	212.95	0.013	Jayawardhana et al. (2017)
Australia	Slow pyrolysis	450	11.9	13.0	72.7	68.6	4.33	20.1	6.09	–	–	Taherymoosavi et al. (2017)
		550	8.5	12.6	76.2	76.7	2.84	13.6	5.79	–	–	
		650	6.3	14.3	76.8	80.7	2.64	10.0	6.00	–	–	
USA (paper, textile, organic waste, plastic)	Slow pyrolysis	400	–	65.2	6.1	48.6	12.2	31.7	1.3	20.7	–	Jin et al. (2014))
		500	–	63.8	9.2	59.5	9.1	20.8	1.4	29.1	–	
		600	–	78.2	6.2	70.1	8.4	13.7	1.3	29.8	–	
China	Gasification	700	–	–	31.1	31.2	1.07	36.5	–	–	–	He et al. (2009)
		750	–	–	42.0	23.3	0.90	33.8	–	–	–	
		800	–	–	57.6	25.0	0.88	16.4	–	–	–	
		850	–	–	58.6	14.7	0.72	26.0	–	–	–	
		900	–	–	72.8	9.0	0.70	17.4	–	–	–	
		950	–	–	84.0	4.0	0.40	11.5	–	–	–	
	Slow pyrolysis	600	–	–	–	64.4	0.22	12.4	2.4	0.98	0.0003	Liu et al. (2017)
		700	–	–	–	64.1	0.21	12.8	2.8	28.4	0.01	
		800	–	–	–	64.8	0.23	12.6	2.7	112	0.04	
Korea	Hydrothermal carbonization	280	74.2	13.3	12.5	41.7	5.3	40.1	0.4			Kim et al. (2017)
Australia	Slow pyrolysis	450	11.9	13.0	72.7	68.6	4.33	20.1	6.1	–	–	Taherymoosavi et al. (2017)
		550	8.5	12.6	76.2	76.7	2.84	13.6	5.8	–	–	
		650	6.3	14.3	76.8	80.7	2.64	10.0	6.0	–	–	

7.3 Municipal Solid Waste Biochar As a Green Adsorbent for Contaminant Mitigation

Municipal solid waste derived biochar has been well studied for its ability to remove heavy metals, metalloids and organics (Agrafioti et al. 2014; Jin et al. 2014). Biochar has been examined to treat landfill leachate, as permeable reactive membranes and as landfill capping and results have shown promising outcomes. Several other studies have also shown its efficacy to retain nutrients in soil for plant uptake enabling the plants to tap into bioavailable nutrients over a longer periods of time (Milla et al. 2013; Liu et al. 2017).

The biochar from municipal solid waste is capable of removing two kinds of contaminants: organic and inorganic. The primary pathways for inorganic contaminant adsorption from aqueous media is via electrostatic interactions, ion exchange, chemical precipitation and complexation with functional groups. The most dominant route of entrapment is via surface reduction and adsorption on to surfaces of the biochar (Park et al. 2006). The schematic diagram of Fig. 7.2 illustrates the overall pollutant removal mechanisms of biochar.

The modes of removal of organic and inorganic contaminants using biochar from an aqueous medium tends to follow a certain pathway depending on the nature of the contaminant and its tendency to attach on to the surface of the carbonized and non-carbonized parts of the municipal waste biochar.

According to Chen et al. (2008), the adsorption of organic contaminant takes two pathways: i.e. by adsorption and partition onto carbonized and in non-carbonized fractions. Biochar derived from municipal solid wastes possess the same contaminant removal mechanisms that are detailed in Table 7.2.

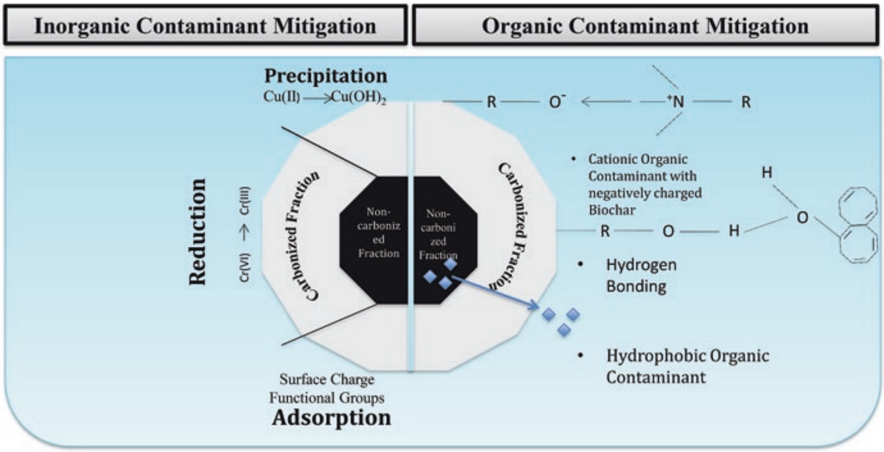

Fig. 7.2 Schematic representation of pollutant removal pathways observed in biochar produced using municipal solid waste

Table 7.2 Biochar pathways for contaminant removal

Biochar derived from different wastes	Trace metal(loid)	Mechanisms	Reference
Hardwood and corn straw	Cu, Zn	Adsorption	Chen et al. (2011)
Orchard punning biomass	Pb, Cr	Surface electrostatic interactions and surface complexation	Caporale et al. (2014)
Dairy manure	Cd, Cu, Zn	Precipitation and surface complexation	Xu et al. (2013)
Anaerobically digested garden waste	Cu, Zn	Chemisorption	Zhang and Luo (2014)
Sewage sludge	Pb	Adsorption due to cation release, functional groups complexation, and surface precipitation	Lu et al. (2012a)

7.3.1 Leachate Treatment

Removal of trace metals, for instance, Cd, Hg, Ni, Mn, Cu, Zn and Pb from leachates is important (Wijesekara et al. 2014). Most leachates have a blackish colored appearance and this is a result of dissolved organic carbon and trace metals. The degradation and release of dissolved organic and inorganic metals can cause leachate plumes in aquifers contaminating ground water (Christensen et al. 2001; Robinson 2005).

The heavy metals in landfill leachate are a hazard and new landfill management technologies aim to recovery these heavy metals as a secondary resource (Asadi 2008). The heavy metals are removed largely via sorption or precipitation from the landfill leachate. Biochar shows capacity to remove trace metals from both soil and aqueous media (Table 7.2). Due to high adsorption capacity of biochar derived from municipal solid wastes, it also has potential to remove trace metals from landfill leachate (Robinson 2005; Asadi 2008). Its ability to adsorb heavy metals arises from the electrostatic interactions between the carbonaceous surface and the positive metal ions. Biochar from municipal solid waste unlike other carbon based adsorbents contains metal oxide groups on the surface and few acidic oxygen groups as well that could make the adsorption more prominent with active sites of metal cations (Agrafioti et al. 2014).

In most developing countries, the municipal solid waste landfills are open dumps which makes leachate and gas management quite difficult at these sites (Vithanage et al. 2014). The gas emissions from municipal solid wastes are toxic and contains a wide range of volatile trace pollutants known as volatile organic compounds. The volatile organic compounds (VOCs) are the main reason for pungent odor that emits from these sites. These VOCs are highly carcinogenic as well as mutagenic when photo-oxidized (Srivastava and Mazumdar 2011; Jayawardhana et al. 2017). Benzene, toluene, xylene and ethyl benzene are the major constituents found in these volatile gases emited from these sites (Harkov et al. 1985; Robinson 2005).

The potential to use biochar derived from municipal solid waste to remediate these VOCs has been studied and proven promising (Jayawardhana et al. 2017). In this study, the municipal solid waste was made to pyrolyze at 450 °C and the biochar produced was analyzed for its behaviors with the gases pollutants. The adsorbents showed a low polarity index and high H/C ratios facilitating intermolecular interactions between the contaminant and the adsorbent surface. Hence, non- polar benzene was observed attaching onto the surface of municipal solid waste biochar effortlessly and as a consequence, a consistent removal of gaseous VOCs was feasible (Daifullah and Girgis 2003; Costa et al. 2012). A further analysis of the biochar revealed an insignificant amount of trace metals adsorbed onto the surface. Thus, the adsorbent showed promise towards removal of the hazardous gases from landfill sites (Jayawardhana et al. 2017).

7.3.2 Material for Permeable Reactive Barriers

Lot of studies have examined the suitability of different materials to use as permeable reactive membranes in landfills. Some of the materials examined include activated carbon, non- zero valent iron, etc. (Tratnyek et al. 2003; Turner et al. 2005). Understanding the characteristics of the above materials help to assess effectiveness of biochar produced from municipal solid waste as a PRB to remediate leachate from landfill. The main objective of these barriers are to intercept and remove contaminants as much as possible at the subsurface before the contaminants could reach groundwater (Thiruvenkatachari et al. 2008). The reactive barrier has to be a permanent permeable membrane placed across the path of a plume. At a natural gradient, the plume would pass though the reactive barrier and with entrapment of pollutants the contamination of ground water downstream can be minimized.

Materials that are used in these barriers, typically, have an adsorptive surface that demonstrate good hydrophobicity and they also are insoluble. As explained in the previous section biochar has these properties that enable entrapment of contaminants on its surface and this prevents any change of ground water quality parameters such as pH and dissolved oxygen (Panturu et al. 2009; Obiri-Nyarko et al. 2014).

Commercially, activated carbon has been the preferred choice for reactive barriers to adsorp contaminants from water. However, it has not been effective when scaled up to mitigate large plumes. At large scale, the associated cost of these reactive barriers are also significant (Ali and Gupta 2006). Biochar on the other hand is low cost and comparatively have shown to be more effective than activated carbon. Biochar produced sustainably using municipal solid waste on the other hand is not only cost effective it also helps better manage the disposal of organic solid waste. (Mor et al. 2016; Jayawardhana et al. 2017).

Agrafioti et al. (2014), studied removal of As (V), Cr (III) and Cr (VI) form wastewater using biochar derived from municipal solid waste. Similarly,

Table 7.3 Potential of municipal solid waste biochar for contaminant mitigation

Feedstock and contaminant type	Temperature attained at pyrolysis of MSW (°C)	Contaminants mitigated	Contaminant conc.	Adsorption capacity	Reference
MSW (inorganic contaminant mitigation)	400	As(V)	5–400 ppm	24.2 mg g^{-1}	Jin et al. (2014)
	500			24.49 mg g^{-1}	
	600			18.06 mg g^{-1}	
	500 (activated)			30.98 mg g^{-1}	
	300		0–100 ppb	–	Agrafioti et al. (2014)
	300	Cr(VI)	0–800 ppb	–	
	600	Hg	0.042 ppb	26.8 μg g^{-1}	Li et al. (2015)
	600 (chemically activated)			118.1 μg g^{-1}	
	600 (chemically and microwave activated)			157.7 μg g^{-1}	
MSW/urban food waste (organic contaminant mitigation)	250	Acridine Orange	10–100 ppm	60 mg g^{-1}	Parshetti et al. (2014)
				75 mg g^{-1}	
				79 mg g^{-1}	
		Rhodamine	10–100 ppm	51 mg g^{-1}	Parshetti et al. (2014)
				62 mg g^{-1}	
				71 mg g^{-1}	
	450	Benzene	30–300 ppb	576 μg g^{-1}	Jayawardhana et al. (2017)

Jayawardhana et al. (2017), examined removal of benzene using biochar derived from municipal solid waste. When effectiveness of biochar derived from husks was compared with biochar derived from municipal solid waste, the latter was found to be 1.3 times more effective at adsorbing pollutants. All of these studies were based on the adsorption mechanisms that were detailed in the previous sections.

From amongst the pathways mentioned in the previous sections, the plausible route of heavy metal adsorption onto municipal solid waste biochar is by electrostatic attractions. Due to the available pore volume and surface area, the metal cations are easily bound to the carbonaceous sites of the biochar (Li et al. 2015). As far as the inorganic contaminants are concerned, the forces involved are hydrogen bonding, along with electrostatic interactions and van der Waals forces and this has been explained examining adsorption of Acridine Orange and Rhodamine onto biochar produced from urban food waste (as in Table 7.3) (Parshetti et al. 2014).

7.3.3 Material for Landfill Capping

Some of the main challenges associated with sustainable management of landfills are the reduction of greenhouse gas emissions and mitigation of odor (Lamb et al. 2014). To reduce above impacts several technologies have been developed such as gas-collection systems, compacted clay covers and composite covers. However, due to lack of technical knowledge and economic complications, construction of effective gas-collection systems to manage methane emissions is still a difficult task for many landfills throughout the world (Yang et al. 2017). Also, the municipal solid wastes of many developing countries is mainly consisted of organic matter. Specifically there is a great amounts of food waste and the high moisture content that is associated with food waste creates a conducive environment for production of methane (Hui et al. 2006; Zhang et al. 2010). Under such conditions, collection of methane is a big challenge even for the landfills that are fitted with gas-extraction systems (Yang et al. 2017).

Landfill covers are one the most promising methods to control emission of gases from landfills (Yuen et al. 2013). Impermeable barriers made from compacted clay layers are most suitable for the construction of landfill caps (Yuen et al. 2013). However, shorter life spans, difficulties to prevent percolation of water through cracks and the reduced interaction of methane with oxygen preventing oxidation of methane are main disadvantages of clay clapping (Albrecht and Benson 2001; Vasudevan et al. 2003; Abichou et al. 2004). Hence, biologically active covers or filters are considered vital to mitigate landfill gases emissions (Bogner et al. 2008; Yang et al. 2017).

The mechanism behind the use of biologically active barriers is oxidation of methane to carbon dioxide by facilitating an environment for methanotraphic microorganisms (Karthikeyan et al. 2015). Many types of biologically active materials such as sewage sludge, compost and mechanical biological treatment residues have been examined in previous studies (Einola et al. 2008; Mei et al. 2016; Lee et al. 2017). Lately biochar has also been examined and found to be a promising material to mitigate methane emissions from landfills. Biochar is efficient as a biologically active material due to its distinctive physicochemical characteristics. The large specific surface area and the reduced particle size of biochar enhances contact between methane, oxygen and methanogenic microorganisms, increasing the rate of methane oxidation (Yang et al. 2017). The biochar derived from municipal solid waste is not only cost effective it also enables re- utilization of a secondary resource, in this instance to mitigate pollution.

Phytocapping is another technique utilized to mitigate landfill gas emissions. That practice employs the growth of dense vegetation on a layer of soil that acts as a top cover for landfills. Studies have shown that phytocapping can also be enhanced by mixing biochar with the soil layer (Lamb et al. 2014).

7.4 Municipal Solid Waste Biochar for Resource Recovery

7.4.1 Waste to Energy

Fossil fuel combustion and industrial processes are responsible for 65% of CO_2 and many other toxic gaseous (e.g. volatile organic compounds, carbon monoxide (CO), Nitrogen oxides (NO, NO_2), particulate matter etc.) emissions into atmosphere (Hossain et al. 2008). Due to increase of global warming, there is worldwide effort to control release of these greenhouse gases into the atmosphere. Accordingly, there are stringent regulations being enforced to mitigate greenhouse gas emissions from environments such as landfills. Therefore, there is much interest to generate energy from municipal solid waste to minimize its discharge into landfill.

There are four main pathways to convert municipal solid wastes into energy. They are thermal conversion, thermochemical conversion, biochemical conversion and physio-chemical conversion (Gumisiriza et al. 2017). Thermochemical conversion technologies directly produce heat and energy while thermochemical, biochemical and physiochemical technologies first produce secondary energy carriers which can be used for the production of energy as heat or as electricity (Gumisiriza et al. 2017) (Table 7.4).

Direct conversion of biomass to heat via burning is referred to as direct combustion (Clini et al. 2008). The most primitive way of using direct combustion is burning dry biomass for the generation of heat for cooking. Direct combustion of biomass in furnaces is also carried out by industries to generate thermal energy requirements for boilers (Gumisiriza et al. 2017). The steam generated by boilers can then be used to drive turbines to generate electricity (Chambers 2004).

Gasification is the partial combustion of solid waste materials at higher temperatures (700–1500 °C) and pressures exposed to a low oxygen environment for a few seconds to minutes (Mohan et al. 2014). The end product of gasification is syngas, a mixture of H_2, CO and CO_2. Temperature, heating rate, pressure, and the gas

Table 7.4 Conversion pathways of municipal solid wastes

Conversion pathway	Method	End product	Reference
Thermal conversion	Incineration	Heat and electricity	Gumisiriza et al. (2017)
	Direct combustion		
Thermochemical conversion	Gasification	Syngas	Matsakas et al. (2017)
	Pyrolysis	Biochar, bio oil	
	Torrefaction	Stabilized friable biomass	
Biochemical conversion	Anaerobic digestion	Biogas	Gumisiriza et al. (2017)
	Anaerobic fermentation	Ethanol	
Physio-chemical conversion	Transesterification	Biodiesel	

Table 7.5 Pyrolysis classification

Thermal conversion process	Temperature range (°C)	Heating rate (°C/min)	Residence time	Product
Slow pyrolysis	350–800	Slow,	Minutes–hours	Biochar
		(<10 °C/min)		
Intermediate pyrolysis	350–800	Medium	Minutes–hours	Biochar
Fast pyrolysis	400–600	Very fast	Few seconds	Bio oil
		(1000 °C/s)		

composition under which feedstocks are treated determine the composition of the resulting gas mixture (Mohan et al. 2014). Syngas can be used in fuel cells, as a synthetic fuel and as a chemical feedstocks (Verma et al. 2012). However, there is still only a handful of gasification plants worldwide (Arena 2012). Flue gas released by gasification plants consist of acidic gases (e.g., NO_x and hydrogen chloride), organic pollutants (dioxins) and particulate matter (Matsakas et al. 2017). Emission of these are controlled by use of electrostatic precipitation, bag filters and slaked lime (Arena 2012). One major draw backs of gasification is the additional cost associated with cleaning the syngas. There are also additional operational costs associated with cleaning the tar that gets formed which is responsible for corrosion, blocking and fouling of gasifies (Matsakas et al. 2017). Fluidized bed gasifiers, cyclone gasifiers, entrained flow gasifiers and packed-bed gasifiers are widely used in gasification (Klinghoffer and Castaldi 2013).

Pyrolysis is the thermochemical conversion of MSW biomass at 200–900 °C exposed to a no/limited oxygen environment (Lehmann and Joseph 2009). Depending on the rate of heating, pyrolysis is divided into three main categories; namely fast pyrolysis, intermediate pyrolysis and slow pyrolysis (Mohan et al. 2006) (Table 7.5).

Characteristics and yield of pyrolysis products vary with the properties of feedstock, pyrolysis temperature and heating rate (Ahmad et al. 2014). Reactors used in large scale MSW pyrolysis are rotary kilns and tubular reactors. Lab-scale studies, however, have been carried out in fixed-bed and fluid bed reactors. Efficiency of pyrolysis can be improved by sorting and drying of MSW prior to pyrolysis.

Torrefaction is a thermochemical process carried out at a 200–300 °C temperature range with a low rate of heating (Mohan et al. 2014). Residence time of torrefaction vary from few minutes to several hours (Matsakas et al. 2017). Based on applied temperature, torrefaction can be categorized as a light (below 240 °C) or a severe (above 270 °C) torrefaction process (Bilgic et al. 2016). The major product of the process is char and it is able to retain up to 96% of its chemical energy (Gumisiriza et al. 2017). Hence, char can be used as a substitute for coal/charcoal and utilized in power plants, entrained-flow gasifiers and in small scale combustion facilities as a high quality fuel (Uslu et al. 2008).

Biodiesel produced by transesterification of tryglyceride oil with monohydric alcohols is another alternative fuel. It is nontoxic and can be produced using different waste cooking oils such as palm, soybean, canola, rice bran, sunflower, coconut, corn oil, fish oil, chicken fat, etc. (Hossain et al. 2008).

7.4.2 Nutrient Retention and Recovery

Because of the high carbonaceous constituents and its unique properties, municipal solid waste derived biochar serves as a better soil amendment than commercial activated carbon.

Municipal solid waste derived biochar and its priming effects on soil have been investigated to understand its impact on seed germination. Different biochar have varying fertilizer properties and the influence on the growth rates of plants also differ. Biochar can induced either a positive or a negative priming effect on soil (Milla et al. 2013; Liu et al. 2017).

Biochar derived from municipal solid wastes also improves soil pH and cation exchange capacity and as a consequence there is direct implications on plant growth. The increase of carbon content that results in with application of biochar also increases the water holding capacity in soil. As a result, there is retention of water and this has impact on heavy metal retention and release reducing its bioavailability (Glaser et al. 2002; Ahmad et al. 2014). Research shows that there are significant improvements to plant growth and seed germination when soil is amended with biochar and its impact is further enhanced when mixed with organic or inorganic fertilizers (Lehmann et al. 2011; Zhou et al. 2017).

7.4.3 Hybrid Composting and Land Application

Table 7.6 shows the concentrations of available trace metals in biochar derived from municipal solid wastes (Chen et al. 2014; Jin et al. 2014). Insignificant trace metal content of MSW-BC facilitates the use of it as an adsorbent without having further constrain to the environment (Jayawardhana et al. 2018). At the same time, this encourages MSW-BC use in compost and agriculture. However, it is indeed important to assess the trace metal concentrations frequently since there might be chances to have high metal concentrations which is not suitable for composting and/or agriculture use (Chen et al. 2014). Furthermore, it has been reported that MSW-BC stimulates Soil Organic Carbon (SOC) mineralization but rates decreased with time

Table 7.6 Trace element analysis for biochar derived from MSW

Study	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
	mg/kg								
Jin et al. (2014)	12	5	64	101	–	–	143	10	213
Chen et al. (2014)	–	3.37	100.3	202.4	31,000	749	–	51.5	–
Jayawardhana et al. (2018)	–	–	9.27	10.9	1810	305	1.8	2.5	82.8
Taherymoosavi et al. (2017)	8	3	35	163	–	–	45	192	987
450 °C									
550 °C	9	<1	29	187	–	–	23	193	791
650 °C	7	2	29	160	–	–	18	160	735

in dry land. Since, priming direction varies from positive to negative in the longer term, biochar amendment may suppress SOC mineralization (Liu et al. 2017). Hence, MSW-BC has been proposed as an appropriate management tool for increasing soil organic C storage, which is beneficial for fertilizing soil and fighting climate change.

Biochar addition increase soil pH, cation exchange capacity, electric conductivity, nutrients and water retention. Municipal solid waste derived biochar is capable of bring about positive outcomes for acidic arid soils. The properties of municipal solid waste derived biochar vary with production temperature, technology and application rate (Ahmad et al. 2014). Agronomic research reveal that biochar application overall improves crop productivity and has shown to support crop growth even under stress conditions (Seneviratne et al. 2017). The biochars ability to promote soil microbial activities growth and water retention (Bandara et al. 2017) is encouraging and future research should further examine the potential of biochar derived from municipal solid waste. Biochar also has excellent solute adsorption capacities. However, only few studies have investigated its applicability as a nutrient carrier to extend its use as a slow-release fertilizers. Few studies have shown that biochar is a nutrient-impregnated material, which has slow releasing properties similar to a slow releasing chemical fertilizer (Gwenzi et al. 2017). Biochars' ability to slowly release nitrate suggests a potential mechanism to deliver nitrate to plants facilitating better retention of nitrate in agronomic systems (Hagemann et al. 2017). To date, there is however, little evidence on biochars' impact on compost and on crop growth and future studies should particularly examine the potential of MSW-BC to enhance properties of compost.

7.5 Remarks

Biochar production, from municipal solid waste, undoubtedly reduces biomass wastage particularly municipal solid wastes that are otherwise a challenge to dispose. It is one of the greener approaches to sustainably dispose and recover nutrients that are present in municipal solid waste. Biochar derived from municipal solid waste provides opportunities to better manage landfills for instance, by facilitating treatment of leachate, by enabling its use as a material suitable for capping, permeable reactive barrier and as a green adsorbent to reduce greenhouse gas emissions. In addition to its ability to reduce greenhouse gas emissions, biochar is able to adsorb volatile organic compounds, organic pollutants (pharmaceuticals, polycyclic aromatic hydrocarbons, pesticides etc.), trace metals and nutrients. A further improvement of biochars' adsorption capacity may enhance its contaminant remediation potential. This can be approached by modifying the properties of biochar, specifically varying the pyrolysis temperatures and by segregating different organic solids present in the municipal solid waste feedstock.

In addition to making use of municipal solid waste to remediate the environment, research should focus on also identifying other possible beneficial applications to maximize reuse of municipal solid wastes. This would necessitate development of technology to facilitate for example chemical modifications of the biochar or nanoparticle impregnation to further improve its adsorption capacity.

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Chapter 8
Dye Removal Using Microbial Biosorbents

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Abstract Due to the rapid urbanization and industrialization, huge amounts of toxic sludge are being disposed into the environment. Improper management of this toxic sludge contaminates all components of the environment. Dyes are being used from very ancient period of time as colouring substances for almost every commodity. Some dyes are toxic to living organisms. Dyes may initiate cancer, mutation in the genetic sequences and suppress enzyme activities.

The review presents physical and chemical dye decolourizing methods. Complete removal of dyes pollution is not easy owing to the diversity and complex molecular structure of the dyes coupled with the associated toxicological aspects. The review also discuss the use of microbial species for dye removal. Many microbes of different taxonomic group of bacteria, fungi, and algae have been reported to enzymatically degrade dye molecules. In addition, these types of biomasses have very high dye sorption capacity. Thus complete dye removal from the polluted water can be done by combining the bio-adsorption and bio-degradation processes.

8.1 Introduction

High rate of population growth, urbanization, industrialization enhanced the demands for freshwater resources. It is estimated that by 2030, the world would face around 40% global water deficits (http://www.2030wrg.org/wp-content/uploads/2014/08/2030-WRG-Annual-Report-English.pdf). In India, the water scarcity is already a burning issue. Although, it needs food for around 16% of the total global population living on the earth, have only 4% of world’s fresh water resources. It is clear that proper use of fresh water, reuse, recycling and reclamation of wastewater would improve the situation (Kaur et al. 2012).

It is estimated that around 38,354 million litres per day domestic sewage is generated in major cities of India. However, only 11,786 million litres per day sewage is treated properly. In addition, it is reported that only 60% of industrial wastewater generated from large scale industries, is treated (Kaur et al. 2012). These data indicated that huge amount of domestic and industrial wastewater is being disposed into the environment without proper treatment. These activities enhanced the water pollution with different types of toxic chemicals which could pose chronic health hazards to living organisms (Ahalya et al. 2003). Dye is one of the major pollutants found in wastewater and it is known to be teratogenic, carcinogenic and mutagenic to human and marine organisms (Satapathy and Das 2013). It is estimated that around 7105 tons of 10,000 different dyes and pigments are produced worldwide annually (Manna et al. 2017). Also it is reported that during dyeing process almost 1–15% of the dye is lost and discarded with the effluent (Manna et al. 2017). This untreated dye-containing effluent introduces aesthetic concerns, promotes eutrophication and adversely affects the environmental health of the region. In addition, it is also known that this type of pollutants can create health issue even in very minute concentration (Vijayaraghavan and Yun 2008). The toxicological sides of dyes can cause acute or chronic toxicity to living creatures (Burgeron et al. 2015). Dyes may impart toxicity to aquatic life and may be mutagenic, carcinogenic, teratogenic, genotoxic and cause severe health hazards to human beings, such as dysfunction of the kidneys, digestive tract system, liver, brain, skin and central nervous system (Satapathy and Das 2013). It decreases food intake capacity, growth and fertility rates in mammalian cells. The accumulation of these dyes from industries into lakes, and rivers decreases concentration of dissolved oxygen causing anoxic conditions, which brings many severe effects on aquatic organisms (Vijayaraghavan and Yun 2008). The biological oxygen demand (BOD), chemical oxygen demand (COD), dissolved and suspended solids of water are enhanced by the presence of varieties of dye molecules in water body (Doi et al. 2013). They are widely used in different industries such as textile, cosmetics, food, pigment, pharmaceutical, solvents, acrylic, leather tanning, printing, paint, paper and pulp. These industries are increasing in number with increase in human population (Chowdhury and Saha 2011). These industries are therefore challenged by the requirement to satisfy the demands of increasingly stringent legislation and controls introduced by governments and regulatory agencies (Satapathy et al. 2015). Azo dyes make up almost 70% by weight of all the different types of dyes utilized worldwide (Panitchagul et al. 2014).

The physical methods such as sedimentation, flocculation, coagulation, ultra filtration as well as the chemical methods, such as neutralization, electrolysis, ion-exchange, have been used by many researchers for dye removal from water. Some of these processes are found to be very efficient in dye removal. But complete removal was not achieved till now due to the diversity and complex molecular structure of the dyes coupled with the associated toxicological aspects. The problem with most of the chemical and physical methods is that these are expensive and also related to the use of hazardous chemicals. Biological treatment methods have often been visualized as an economically viable option utilizing culture of different microbial strains. In this context biological treatment has proven to be advantageous (Chowdhury and Saha 2011; Chowdhury et al. 2012). Bio-sorption can be described as the removal of dye compounds, particulates, metals from solution by various natural materials of biological origin, which includes bacteria, fungi, algae, yeast (Wang and Chen 2009).

8.2 Dyes

8.2.1 Fundamentals of Dyes and Its Fate

Dyes, organic compounds with complex aromatic structures, are being used in various substrates such as leather, drugs, foods, cosmetics, fur, hair, waxes, greases, plastics and textile materials to impart colour. Each dye preferentially absorbs certain wavelengths of light which makes them colourful. They have two key components (a) chromophores–unsaturated functional groups responsible for appearance of colour, such as –N=N–, –C=C–, –C=N–, –C=O, and (b) auxochromes–supplement the chromophore by intensifying colour and make the molecule soluble in water, such as –OH, $-NH_2$, –NHR, $-NR_2$, $-NO_2$, –OR, –COOH, –CHO, $-SO_3$, –SH. Based on the chemical structure and application, dyes are broadly categorized as cationic, anionic and non-ionic dyes (Gupta and Suhas 2009). The classification of dyes based on applications is presented in Table 8.1.

Dyes are known to be used since the dawn of human civilization. However, the colorants and dyes available at that time were mainly from natural origin such as plants, animals, and minerals. In modern times almost all dyes and colorants are synthesized in large scale in industrial set up. The synthetic dyes are known to be resistant to heat, light, water, oxidizing agents and microbial attack for their stable molecular structure. In recent times more than 10,000 synthetic dyes and pigments are commercially available. Moreover the dye manufacturing industries worldwide produce over 7 × 105 tons of dyes annually (Crini 2006). The dye consuming industries such as, textile, dyeing, paper and pulp, tannery, paint and printing, cosmetics, rubber, plastic, food and pharmaceutical, along with the dye manufacturing industries generate huge amount of dye containing liquid spent. This liquid spent is drained to local water resources which ultimately contaminate the surrounding environment. Though exact data of residual dye charge to the water resources is not available, it is assumed that every year textile industries alone release about 146,000 tons of residual dyes in their effluent (Onal 2006). The dyes deteriorate aesthetic properties of water by imparting significant color changes. The presence of dyes in water could alter the COD, BOD, dissolved and suspended solids. In addition, it interferes with the normal photosynthesis water-borne plants and biological metabolism processes, and cause micro-toxicity to fish and other organisms.

8.2.2 Environmental Impacts and Toxicity

Hunger extensively studied the impact and toxicity of the synthetic dyes to the living being. The report indicated synthetic dyes could cause acute (harmful short-term effects) and chronic (adverse, irreversible, long-term effects) toxic effects.

Table 8.1 Classification of dyes as per application (Toor 2010)

Class	Structural unit	Application	Examples
Acid dyes	Azo, anthraquinone, triphenylmethane, azine, xanthene, nitro, and nitroso	Nylon, wool, silk, modified acrylics, paper, leather, inkjet printing, food, and cosmetics	Congo red, methyl orange, methyl red, orange I, orange II
Azo dyes	Azo	Cotton, rayon, cellulose acetate and polyester	Aniline yellow, disperse orange 1, butter yellow
Basic dyes (cationic)	Cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, thiazine, xanthene, acridine, and, oxazine	Paper, polyacrylonitrile, modified nylons, modified polyesters, polyethylene terephthalate, medicine	Methylene blue, malachite green, amine yellow, butter yellow
Direct dyes (anionic)	Polyazo, stilbene, oxazine, phthalocyanine	Cotton, rayon, wool, silk, paper, leather, nylon	Congo red, direct black, violet 51
Disperse dyes (nonionic)	Azo, anthraquinone, styryl, nitro, and benzodifuranone	Polyester, synthetic polyamide, nylon and polyacrylonitriles	Disperse blue 3, violet 1, celliton fast pink B
Fluorescent brighteners	Stilbene, pyrazoles, coumarin, imidazole, naphthalimides, 1,3-diphenyl-2-pyrazolin, benzoxazole, and heteroaromatics	Thermoplastics, detergents, plastic films, fibers, papers, adhesives and leathers soaps, oils, paints	Tinopal, calcofluor white, benetex
Mordant dyes	Azo and anthraquinone	Wools and silks	Alizarin
Reactive dyes	Azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine	Cotton and other cellulosics, silk, wool and nylon	Procion red, remazol brilliant blue, drimarene red
Solvent dyes	Azo, triphenylmethane, anthraquinone, and phthalocyanine	Plastics, varnishes, lacquers, gasoline, stains, inks, fats, oils, and waxes	
Sulfur dyes	Disulfide or sodium sulphide	Cotton, rayon, polyamide fibers, silk, leather, paper, and wood	Sulfur black 1, sulfur brown 12, sulfur green 12
Vat dyes	Anthraquinone (including polycyclic quinones), and indigoids	Cotton, rayon and wool	Indigo blue, Tyrian purple, Bezanthrone, Indigo white

8.2.2.1 Acute Toxicity

Skin and eye irritation, and skin sensitization is very common acute toxic response of dyes upon contact. Many reactive dyes could also initiate severe health effects such as dermatitis, allergic conjunctivitis, rhinitis, asthma or other allergic reactions. Single or multiple contacts of dyes sometimes are problematic. Upon contact reactive dyes could combine with human serum albumin (HSA). The dye-HSA conjugate often acts as antigen producing specific immunoglobulin E and initiate histamine release which eventually cause allergic reactions. Reactive Yellow 25, Reactive Orange 14, Reactive Red 65, Reactive Violet 33, Reactive Blue 114, Reactive Blue 204, Reactive Black 5 are the examples of human respiratory/skin sensitizing reactive dyes which could initiate allergic reaction.

8.2.2.2 Chronic Toxicity of Dyes

Dyes with azo, anthraquinone, tri-phenylmethane, tri-phenylamine, ketonimine, di-phenylmethane, tri-arylmethane, nitrosamines, and aromatic amino and nitro groups cause chronic toxicity. They initiate geneo-toxicity, carcinogenicity and mutagenicity to human being. Dyes containing azo, amine, nitrosamine, and hydroxylamine, hydrazine, or amine precursors chemically react with nucleophilic DNA and produce a common carcinogen called nitrenium ion and causes mutations and subsequent adverse effects on the cell. Among all dyes, the azo dyes are more lethal as it inducts mutagenicity and carcinogenicity in human and animals. The water soluble dyes, such as Congo red, Evans blue develop cancer in liver, urinary bladder and intestines after alteration by metabolic processes. These types of water soluble dyes are being used in industries widely. Thus the resultant liquid spent generated also contains very large amount of water soluble dyes. The discharge from these industries comes into the surface water resources and contaminate surrounding environment. Some of this water soluble dyes get accumulated into food chains and eventually reach the human body. The aromatic ring generated during the metabolic reduction of azo dyes is bio-activated as mutagens. Some of the anthraquinone dyes contain one or more primary amino or methylamino groups induces mutation into DNA helix by inserting the planar portion of the dye between adjacent DNA base pairs (Gregory and Gerig 1991).

Cationic dyes such as Basic Violet 14, Basic Yellow 2, Acid Violet 49, and Basic Red 9 are known to be carcinogenic. While fluorescent red dyes, e.g., Pyronine B and azo pigments like dinitroaniline orange, ortho-nitroaniline orange, pigment orange 1, 2, and 5 are known to be potential mutagens. Some dyes form complex with heavy metal ions to improve the light fastness of dyes. These dyes are one of the major sources of metal pollution and related health hazards. Acid violet 56 and Acid blue 158 form complex with several heavy metal ions.

8.2.3 Law and Permissible Limit

Dyes are one of the most strictly regulated chemicals worldwide. However the legislation varies with countries. Dyes is permitted in one countries are not acceptable in others. The Regulation and specifications of safety assessment of many chemicals by the European Commission (EC) in the European Union (EU), the Food and Drug Administration (FDA) in the United States, as well as Ministry of Health, Labour and Welfare in Japan and Government of Canada in Canada are taken as standard by many countries. In many regions, same colouring agent has been permitted or banned for any specific application. For example, some countries permitted one dye for use in drug and food product, the same dye sometimes are banned to be used in other. However, the name may vary, but the colour index of any specific chemical is same. For example, Quinoline Yellow in Europe is named as D&C Yellow10 in the United States. But they have same Color Index and listed for different uses. Also this colouring agent is banned in Japan for use in food or drugs.

8.2.3.1 Dye Regulation in the European Union

Most European countries follow the directives of the European Union that enlisted the dyes and there specifications for use in foods, drugs and other uses. Currently the European Directive of 94/36/EC passed in 1994 are being used in all over the European Union. In 2007 few modifications has been introduced to this directive. The European Union commission assigned "E" number to all the dyes are being used as food additives. European Commission approved a common authorization procedure for food additives, food enzymes and food flavourings vide by the regulation No 1331/2008 of the European Parliament and the Council of16 December 2008. Table 8.2 enlisted the dyes approved by the European Union.

8.2.3.2 Dye Regulation in the United States

For the United States, FDA regulates the list of dyes to be used in different applications. For approval the dyes must comply with chemical specifications, uses, restrictions and labelling requirements as described in Title 21, parts 70–82 of the Code of Federal Regulations (CFR). The manufacturers are responsible to ensure that the dyes comply with the specifications as described in the CFR. Dyes and colouring agents permanently approved by FDA are enlisted in Table 8.2.

8.2.3.3 Dye Regulation in Canada

The Canadian regulations for dyes are found to be similar to the US regulations. Most of the colouring agent enlisted in the regulations of United States and Europe Union are listed in Canadian regulations. Also the dyeing agents that are approved or banned in United States are same in Canada and vice versa. All the approved dyes that are being used in Canada are listed in Table 8.2.

Table 8.2 List of dyes approved by European Union, United States, Canada and Japan (Pérez-Ibarbia et al. 2016)

Colour index number	Colour name	Approved in	E number	Name as per Food and Drug Administration	Japanese name
17200	Acid fuchsine	United States, Canada		D&C red #33	
45100	Acid red	Japan			Red #106
13058	Alba red	United States		D&C red #39	
61570	Alizarin cyanine green	United States, Canada		D&C green #5	
60730	Alizarin violet	United States		Ext. D&C violet #2	
60725	Alizurol purple SS	United States		D&C violet #2	
16035	Allura red AC	European Union, United States	E129	FD&C red #40	
16035:1	Allura red AC	European Union, United States		FD&C red #40 lake	
42090	Alphazurine FG	United States		D&C blue #4	
16185	Amaranth	European Union, Japan	E123		Red #2
28440	Brilliant black BN	European Union	E151		
42090	Brilliant blue FCF	European Union, United States, Canada	E133	FD&C blue #1	Blue #1
20285	Brown HT	European Union	E155		
14720	Carmoisine	European Union	E122		
12156		United States		Citrus red #2	
74160	Copper phthalocyanine	United States		[Phthalocyaninato (2-)] copper	
45370:1	Dibromofluorescein	United States		D&C orange #5	
45425:1	Diiodofluorescein	United States		D&C orange #10	
45380	Eosine	United States, Canada		D&C red #22	
45430	Erythrosine	European Union, US, CA, JP	E127	FD&C red #3	Red #3
42053	Fast green FCF	US, CA, JP		FD&C green #3	
12085	Flaming red	US, CA		D&C red #36	
45350:1	Fluorescein	United States		D&C yellow #7	
44090	Green S	European Union	E142		
73360	Helindone pink CN	United States, Canada		D&C red #30	

(continued)

Table 8.2 (continued)

Colour index number	Colour name	Approved in	E number	Name as per Food and Drug Administration	Japanese name
73000	Indigo	United States		D&C blue #6	
73015	Indigotine	European Union, United States, Canada, Japan	E132	FD&C blue #2	Blue #2
15850	Lithol rubin B	United States, Canada		D&C red #6	
15850:1	Lithol rubin B Ca	United States, Canada		D&C red #7	
10316	Napthol yellow S	United States		Ext. D&C yellow #7	
15510	Orange II	United States		D&C orange #4	
42051	Patent blue V	European Union	E131		
45410	Phloxine B	United States, Canada, Japan		D&C red #28	Red #104(1)
16255	Ponceau 4R	European Union, Canada, Japan	E124		Red #102
14700	Ponceau SX	United States, Canada		FD&C red #4	
59040	Pyranine concentrated	United States		D&C green #8	
19235		United States		Orange B	
61565	Quinizarine green SS	United States		D&C green #6	
47005	Quinoline yellow	European Union, United States	E104	D&C yellow #10	
20170	Resorcin brown	United States		D&C brown #1	
45440	Rose bengal	Japan			Red #105(1)
15985	Sunset yellow FCF	European Union, United States, Canada, Japan	E110	FD&C yellow #6	Yellow #5
19140	Tartrazine	European Union, United States, Canada, Japan	E102	FD&C yellow #5	Yellow #4
45380:2	Tetrabromo fluorescein	United States		D&C red #21	
45410:1	Tetrachlorotetra-bromofluorescein	United States		D&C red #27	
26100	Toney red	United States		D&C red #17	
45350	Uranine	United States		D&C yellow #8	

8.2.3.4 Dye Regulation in Japan

The Japanese Ministry of Health, Labour and Welfare (MHLW) of Japan is the authority for approving the specifications and safety issues of colour additives in different applications. Synthetic dyes permitted in Canada and US approved Japan. All the dyes approved in Japan are shown in Table 8.2.

8.2.3.5 Dye Regulation in India

In India, the Ministry of Environment and Forests, Ministry of Drugs and Fertilizer, and the Food Safety and Standards Authority of India (FSSAI), Government of India is the authority that maintains the regulation related to colouring agents used in different applications such as in drugs, foods and cosmetics products. The colouring agents used in food are regulated by the section 92 of the Food Safety and Standards Act, 2006 amended in 2009. The colouring agents used in cosmetic product are regulated by the Drugs and cosmetics Act 1940 and Rules1945. Also, the Ministry of Environment and Forests and Ministry of Drugs and Fertilizer, Government of India monitored the use of colouring agents in India and periodically banned the toxic colouring agents.

8.3 Dye Removal Techniques

India is the second largest producer of dyes and intermediates in Asia. Around 700 varieties dyes and dye intermediaries approx. 64,000 tonnes are being produced annually in India. Almost 2% of these dyes (7040 tonnes) are directly discharged into the environment during production and usage. Only one third of the dyes producing industries are identified as organized sector. Thus untold amount of dyes are discharged into water. Recently the Bureau of Indian Standards, IS 10500, has set some regulation for controlling the colouring agents in water. With stringent industrial effluent discharge regulations for aquatic environment protection, the development of advanced technological processes are needed to minimize concentration of dyes and their break down products in wastewater.

Over the last few decades, different types of techniques have been tried for removal of dyes from water. The conventional techniques for colour removal from aqueous streams include photo-catalytic decolourization and oxidation techniques, biological degradation, coagulation and precipitation, ion exchange, membrane filtration and adsorption.

8.3.1 Photo-Catalytic Decolourization and Oxidation Techniques

Photo-catalytic decolourization and oxidation is very common chemical technology that changes the chemical composition of the adsorbates and remove the pollutants by oxidation with oxidizing agents. Bromate, hydrogen peroxide, ozone, molecular oxygen, periodate, permanganate, persulfate, sodium hypochlorite are few examples of oxidizing agents frequently used. Due to limitations like low oxidizing power, inefficiency at low pH, inefficacy for removal of dispersed and vat dyes and production of color the conventional oxidation process is replaced by advanced oxidation processes (AOP). In AOP highly reactive hydroxyl radicals have been generated using one or more primary oxidants such as O_3, H_2O_2, O_2, UV light, Fenton reactants, metal catalysts, metal oxides, graphite and/or activated carbon.

Advanced electro-oxidation with electro-generated H_2O_2/Fe^{2+}, photolysis with UV, peroxidation with H_2O_2, peroxidation combined with UV/H_2O_2, and the photo-Fenton process with H_2O_2/Fe_{2+}/UV were tried for decolourization of textiles wastewater containing several dyes (El-Desoky et al. 2010; Ghoneim et al. 2011; Guimaraes et al. 2012). Review of Martinez-Huitel and Brillas (2009) indicated that electrochemical anodic oxidation were also one of the most extensively used techniques for degradations of dyes. For this type of oxidation several types of anodes including Fe, steel, Al, granular activated carbon, activated carbon fibre, glassy carbon, graphite, polypyrrole, and boron-doped diamond deposited on Si/Ti/Nb, and mixtures of Ti, Ir, Ru, Sn, Pb and/or Sb oxides, Pt or Ti supported Pt had been used. The catalytic wet peroxide oxidation process also used previously for decomposition of Congo red, Direct Brown 2 with the help of Fe exchanged commercial Y zeolite and Copper hydroxyl phosphate (Kondru et al. 2009; Zhan et al. 2010). Although advance oxidation processes are rapid and efficient in dye removal they also suffer from various limitations like high energy consumption, very short life of the generated radicals and variation of type of constituents present in the textile wastewaters, create technical constraints that hinder its large scale application in wastewater treatment (Verma et al. 2012).

8.3.2 Chemical Coagulation-Precipitation and Electrocoagulation

Coagulation has been one of the oldest known waste water treatment process due to its simplicity and low capital cost. Large numbers of reports are available on dye removal using coagulation from synthetic and real textile wastewater. Different types chemicals such as magnesium chloride, lime, alum (El-Gohary and Tawfik 2009), poly-aluminium chloride (Moghaddam et al. 2011), aluminium sulphate (Khayet et al. 2011), ferric chloride sludge (Anouzla et al. 2009; Moghaddam et al. 2010). Biopolymers, e.g., extract of *Moringa oleifera* seed and crude tannin also used as natural coagulants for colour removal (Prasad 2009; Beltran-Heredia et al. 2011). Although it is one of the popular methods, it also has limitations. This process consume huge amount of chemical reagents and as a results generate huge amount of highly toxic sludge difficult to handle and dispose. In addition, this method is not suitable for large water purification unit (Verma et al. 2012).

8.3.3 Ion Exchange

Synthetic resins have been used previously for removal of dyes from the aqueous medium by ion exchange method. Commercially available synthetic macro-porous basic anion exchange resin such as Purolite A-520E, polystyrene Amberlyst A-21, Amberlite IRA-958 (Greluk and Hubicki 2011; Wawrzkiewicz 2011) had been used previously for removal of Acid Orange 7, Acid Blue 29, Direct Red 75. Poly (glycidyl-methacrylate) cross-linked acrylate resin had also been tried to remove Crystal Violet and Basic Fuchsine. Though regeneration efficacy of this method is very high, it suffers from drawbacks like high operational cost, poor efficiency in presence of commonly present ions in textile effluents. In addition, this process is not suitable for all types of dyes (Verma et al. 2012).

8.3.4 Membrane Filtration

The dye separation by ultrafiltraion and nanofiltration are known to remove all kinds of dyes along with all ions. Unlike other separation methods, membrane based processes have special features like resisting temperature, chemical, and microbial attack. However, main drawback of this process is frequent clogging of membrane pores by the dye molecules. In addition, high working pressure is required for pollutants removal by this process. Moreover the process needs high initial investment and operational cost and significant energy consumption (Gupta and Suhas 2009).

8.3.5 Adsorption

Adsorption is a mass transfer phenomenon where adsorbate is accumulated at the fluid-solid interface by physical and/or chemical attractive forces. This process is operable independently and effectively for the dye removal from wastewater. Also adsorption process is easy to design and no skilled manpower is needed. It consumes very less energy and does not produce sludge daily. Though there are some issues like presence of competing ions might decrease the removal efficacy of adsorbent, it is not as drastic as it is observed for ion exchange method. Till date different types of adsorbent already have been tried for dye removal from water (Maiti 2010).

8.4 Biosorption of Dyes

Biological treatment of dyes containing wastewater through aerobic, anaerobic or combined aerobic–anaerobic biodegradation methods is commonly practice as it is relatively economical and does not produce any toxic end products. Large number different microbes such as bacteria, fungi, and algae were used to decolorize and mineralize various dyes. Dye removal by different types of microbes has been discussed in the following sub sections.

8.4.1 Bacterial Biosorbents

A numbers of microorganisms have been reported that they can be utilized as potential biosorbents for removal of dyes, metals, aromatic compounds, pesticides etc. They have low operating cost, non-hazardous ability, regeneration capacity, and high capability for pollutant intake. Pure and mixed cultures of bacterial species can utilize many dye particles, metals, and many other pollutants as their carbon source or nitrogen source (Pathak and Dikshit 2013). Different groups of bacteria have been reported for their ability to degrade azo dye molecules such as *Bacillus subtilis, Clostridium perfringens*, *Proteus vulgaris, Pseudomonas aeruginosa, Dietzia* sp., *Halomonas* sp. and many other bacterial species can degrade the Congo Red dye at their corresponding optimized conditions. Few ideas on biosorption of dye compounds by dead bacterial biomass have also been reported. Presence of hydroxyl, carboxyl, amino, and phosphate groups in peptidoglycan layer of bacterial cell wall assists bacterial biomass for binding dye particles. As biosorption is metabolism-independent approach, there is no need of supply of nutrients for the growth of bacterial cells (Saha et al. 2013).

8.4.1.1 Mechanisms

Dye molecules can usually be described as a colouring agent with an affinity to the molecules to which it is coloured. The effluents emanating from textile, paper, leather, plastic, and many other industries contain higher amount of dye wastes. Presence of dye in wastewater has many toxicological aspects such as, dye molecules can cause many abnormalities in reproductive system, respiratory system, skin irritation etc. In recent years the search for cost effective, efficient, environment friendly methods, especially biological methods for the treatment of dye containing wastewater have been initiated. Degree of dye molecule uptake by biosorbent is very high. Few biomasses are reported to adsorb an amount of toxicant almost as high as their dry weight (Vijayaraghavan and Yun 2008). Biosorption mechanism is usually complex process including chelation, ion exchange, adsorption, and entrapment in intra and inter-fibriller capillaries and spaces of the bacterial polysaccharide structure (Ahalya et al. 2003). Inactive microbial biomass can passively be attached with various ions present in dye molecules by different physicochemical mechanisms. Various research reports have been published that sorption using biosorbents depends not only on the chemical constituents of the biomass but also on the external solution chemistry and physicochemical factors. Many researchers have understood and explained that the mechanism of biosorption may be separated or together with the processes of electrostatic interaction, chelation, micro-precipitation, ion exchange, complexation. At acidic pH maximum biosorption has been occurred in case of metallic cations due to the involvement of carboxyl functional group present in bacterial cell wall, which are responsible for binding metal ion via different mechanisms. The fidelity of biosorption not only depends on the kind of ions but also on the type of bacterial species because of variation in bacterial cell wall compositions. Basically, metal-bacterial biomass steady state is attained within very short period of contact time due to mass transfer resistances are negligible because of usage of biomass is either in the form of fine powder or wet cell. Short contact time may be advantageous for the wastewater treatment systems. Researchers explained that anionic functional groups present in peptidoglycan, phospholipids, and lipopolysaccharides of Gram-negative bacteria and the peptidoglycan, teichoic acids of Gram-positive bacteria were the constituents responsible for the metal binding capacity of the bacterial cell wall. Extracellular polysaccharides have also ability to bind ions. Though, they can easily be detached from each other through mechanical friction or chemical washing. In case of bacterial biosorption the ions or solutes can either be attached on the bacterial cell surface or deposited within the cell wall structure. Different dye molecules, which dissociates as cations in solutions, are also attracted towards negatively charged groups especially carboxyl group. Amine groups present in cell wall can efficiently remove metal ions due to its chelating properties and also adsorbing capacity towards anionic dyes through hydrogen bonding or electrostatic interaction. However, negative charge of bacterial cell surface is increased and all relevant functional groups are deprotonated with the increase of pH. Thus, electrostatic attraction and adsorption of cations are favoured. At low pH, all the relevant functional groups are protonated and thus, anions would be expected to attract towards the cells due to increasing positive charges. Dye molecules dissociate in solution to form metal ions by hydrolysis at high pH value of the solution. During hydrolysis at first hydroxylated monomeric species are produced, then polymeric species are formed, and finally precipitates of crystalline oxides are generated after aging (Vijayaraghavan and Yun 2008). On the basis of principle of hard and soft acid base Na^+, Mg^{2+}, Ca^{2+} could bind with OH^-, CO_3^{2+}, R–COO–, HPO_4^{2-}, and other oxygen containing ligands. Heavy metal ions form stable bonds with CN-, R-S-, NH_2-, -SH-, and other nitrogen and sulfur atoms containing groups (Wang and Chen 2009). Recombinant bacteria are capable of removing of certain metals from wastewater. Recombinant *E. Coliwas* able to specifically accumulate 8 µmole Hg^{2+}/g cell dry weight exhibiting Hg^{2+} transport system and metallothionein (Ahalya et al. 2003).

8.4.1.2 Kinetics

The adsorption dynamics of dyes on biosorbent were investigated utilizing kinetic models, viz., pseudo-first-order, pseudo-second-order, model of liquid film diffusion and intraparticle diffusion. Adsorption process includes four consecutive steps-migration of dye particles from bulk solution through liquid film to the external surface of adsorbent, diffusion of solute across liquid film boundary covering the adsorbent surface, intraparticle diffusion into the internal surface of the adsorbent, and adsorption on active sites of the adsorbent. The linearized form of the pseudo-first-order rate equation is given by Lagergren:

$$\log\left(q_e - q_t\right) = log q_e - \left(\frac{k_1}{2.303}\right)t \tag{8.1}$$

Where q_t is the amount of adsorbed dye at time t, k_1 is the rate constant of pseudo-first-order adsorption and t is the contact time. The linear plot of Log ($q_e - q_t$) Vst indicated that the first-order-model had very few application on the adsorption kinetics because R^2 value is very poor and χ^2 value is large.

The linear form of pseudo-second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + t / q_e \tag{8.2}$$

Where k_2 is the rate constant of the second order adsorption. The straight line generated by plotting t/q_tVst provides R^2 values close to unity and negligible χ^2 values. Comparing both the models pseudo-second-order kinetic model provided a better fit to the experimental data for adsorption of dyes on adsorbents (Oladoja and Akinlabi 2009).

8.4.1.3 Thermodynamics

Adsorption is basically temperature dependent though most of the researchers have reported that temperature seems to make a difference on biosorption performance only within the temperature range of 20–400 °C. The relation Gibbs free energy change (ΔG), standard Gibbs free energy change (ΔG^0), and equilibrium constant (K) at constant temperature is expressed by Van't Hoff equation

$$\Delta G = \Delta G^{\circ} + RT \ln K \tag{8.3}$$

Where, R is universal gas constant. As Gibbs free energy change (ΔG) is equal to zero at equilibrium, then

$$\Delta G^{\circ} = -RT \ln K \tag{8.4}$$

Equilibrium can be determined from the biosorption experiments. Adsorption rate is equal to the rate of desorption at equilibrium. Therefore, the concentration ratio of absorbed particles on the biosorbent to the solution is basically constant. Equilibrium constant can be expressed as

$$\mathrm{K} = C_a / C_e \tag{8.5}$$

Where, C_a is the equilibrium concentration of adsorbed materials onto adsorbent surface and C_e is the equilibrium concentration of liquid solution. When the value of ΔG° is negative sorption process occurs spontaneously. Hence, the standard Gibb's free energy change is the indicator of spontaneity of the process. The standard free energy change (ΔG°) is correlated to standard enthalpy change (ΔH°) and standard entropy change (ΔS°) at a fixed temperature according to thermodynamic approach. The relation is expressed as

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{8.6}$$

Therefore, Eq. (8.4) can be rewritten as

$$\ln K = \left(-\Delta H^{\circ} / RT\right) + \left(\Delta S^{\circ} / R\right) \tag{8.7}$$

The linear relationship between ln K and $1/T$ is shown by the Eq. (8.7). The value of ΔH° for the biosorption process is deduced from the slope of a plot of the both parameters of ln K and $1/T$ and from the same plot the value of ΔS° for this process is determined from the intercept. Negative slope related to sorption experiments interpreted that the reaction is endothermic. The negative value of ΔG° implied that the adsorbent have higher sorption capacity. The value of ΔS° reflects the affinity of biosorbent toward the adsorbed particles. If the value of ΔS° is positive that means increased randomness at biosorbent surface then more ions are adsorbed at the surface of biosorbent. On the other hand, the negative value of ΔS° implied a decreased of disorder at biosorbent surface or liquid or solid interface (Panitchagul et al. 2014). The biosorption equilibrium data or biosorption isotherms imply how pollutants attached with biosorbent surface and so are difficult for optimizing the use of biosorbents. Experimental equilibrium data are represented by different models including Langmuir and Freundlich models. Langmuir isotherm is suited for uniform surface with finite identical sites and monolayer adsorption of the adsorbate. The Langmuir isotherm is expressed as

$$q_e = q_m k_L C_e / \left(1 + k_L C_e\right) \tag{8.8}$$

Where, q_m is the maximum biosorption of monolayer (mg g^{-1}) and k_L is the Langmuir constant (L mg^{-1}). Langmuir isotherm can be shown by equilibrium factor or separation factor (R_L) in the following Eq. (8.9)

$$R_L = 1 / \left(1 + k_L C_0\right) \tag{8.9}$$

From the Freundlich adsorption isotherm relation between q_e and C_e is obtained. The Freundlich isotherm is given by

$$q_e = k_F C_e^{1/n} \tag{8.10}$$

Where, k_F is the Freundlich constant ((mg g^{-1}) (mg L^{-1}) $1/n$) and n is the biosorption intensity (Dotto et al. 2013).

8.4.1.4 Statistical Modeling

Dye biosorption experiments were conducted at specific combinations of parameters using sequential statistically modeling experiments Plackett-Burman design (PBD), path of steepest ascent (PSA), and central composite design (CCD). Generally, a 12-run PBD along with three runs at zero level was used to screen the different parameters that affected biosorption. Variables like pH, dye concentration, temperature, biosorbent dosage, agitation speed, and contact time were chosen as the independent input variables and the efficacy of dye removal was used as the dependent response variable. Each variable was examined at two levels: −1 as the low level and +1 for the high level. The effect of each variable on biosorption was determined by the following equation

$$\mathrm{E}(\mathrm{Xi}) = 2\left(\sum \mathrm{M}+1-\mathrm{M}-1\right)/\mathrm{N} \tag{8.11}$$

Where, E (Xi) is the effect of tested variable (Xi) and M + 1 and M − 1 are responses (biosorption) of trials at which variable is at its high or low level, respectively. N is the total number of trials. According to regression analysis, significant factors responsible for biosorption were determined based on the t value.

To get the more accurate optimum results screened (using the PBD) factors were further optimized using the PSA. According to the sign of the main effects concentrations of variables were increased or decreased using stepwise units to improve biosorption. The zero level of PBD was detected as the base point of PSA and, for each point in the PSA, an experimental run was performed. The step along the path was obtained by practical experience. Experiments were performed along the steepest ascent path until no further increase of the response.

The optimal levels of the significant factors and interactions of these variables on biosorption were analyzed by CCD. The factors were coded according to the following equation

$$\mathrm{Xi} = \left(\mathrm{Xi}-\mathrm{X0}\right)/\Delta X, \quad \mathrm{i}=1,2,\ldots\ldots,\mathrm{k} \tag{8.12}$$

Where, Xi is coded independent factor, Xi is real independent factor, X0 is the value of Xi at the centre point. ΔX is the step change value. A second order polynomial equation was proposed to correlate the dependent and independent variables:

$$\mathrm{Y} = \beta 0 + \sum \beta \mathrm{ixi} + \sum \beta \mathrm{iixi2} + \sum \beta \mathrm{ijxixj}, \quad \mathrm{i}=1,2,3,4,\ldots..,\mathrm{k} \tag{8.13}$$

Where, Y is the predicted response, β0 is the intercept, xi and xj are the coded independent factors, βi is the linear coefficient and βii is the quadratic coefficient and βij is the interaction coefficient.

Determination coefficient (R2) decides the quality of polynomial equation. Statistical significance was checked by Fischer's F test. Analysis of variance (ANOVA) was conducted to determine the significance of the model (Yadav and Srivastava 2009).

8.4.2 Fungi

Fungi are a group of eukaryotic organisms classified as kingdom fungi. Fungi differ from plants, bacteria and some other protist by the possession of chitin in their cell walls. They acquire food by secreting digestive enzymes and dissolving molecules for absorption. They are incapable of photosynthesis. Extensive research has been carried out to determine the role of fungi in the treatment of wastewater (Sengupta et al. 2017). They have been proved to be efficient in the treatment of textile effluent and dye removal. The mode of nutrition of fungus by solubilising insoluble substrates by producing extacellular enzymes results in an increased cell to surface ratio and greater contact with the physical environment through their released enzymes. This nature of fungal enzymes also makes them tolerant to high concentrations of the toxicants. Thus many species of fungus have been employed in dye decolourization either in living or in dead form. (Azmi et al. 1998; Kaushik and Malik 2009). Fungal biomass has been used as low cost adsorbents for dye removal (Crini 2006). Waste fungal biomasses are a byproduct of fermentation industries which can be used as cheap sources of biosorbent (Gazsó 2001). The phosphate, amino, thiol and carboxyl groups present in the fungal cell wall binds onto the dye molecules and results in their biosorption into the cell surface in few hours (Mou et al. 1991).

8.4.2.1 Mechanisms

The mechanisms of dye removal by fungus can be divided into three types i.e. biosorption, biodegradation and bioaccumulation. Biosorption could be defined as the processes of binding of solutes on to the biomass through processes that does not involve any metabolic energy or transport, however simultaneously processes may take place where live biomass has been used. Thus this process can take place in both dead and living biomasses (Tobin et al. 1994) and is the most sought after process. Again, biodegradation is an energy consuming process which involves breakdown of the dye molecules by enzymatic actions. On the other hand bioaccumulation involves accumulation of pollutants by growing cells by metabolism (Aksu and Donmez 2005).

Dye removal by fungus involves three different types of mechanisms biosorption, bioaccumulation and biodegradation. A few fungal species and the dye they remove employing various in given in Table 8.3:

Table 8.3 Application of fungus for dye removal (Kaushik and Malik 2009)

Strain	Dye	Mechanism
Coriolus versicolor	Everzolturquoise Blue G	Biodegradation
Aspergillus foetidus	Drimarene red, drimarene blue	Biosorption
Aspergillus niger	Congo red	Biosorption
Irpex lacteus, Pleurotus ostreatus	Azo, diazo, anthraquinone-based, triphenylmethane, phthalocyanine, heterocyclic dyes	Biodegradation
Funalia trogii	Astrazon red	Biosorption and biodegradation
Thelephora sp.	Orange G, congo red, amido black 10B	Biodegradation
Saccharomyces cerevisiae	Remazol blue, remazol black B, Remazol red RB	Bioaccumulation
Saccharomyces cerevisiae, Schizosaccharomyces pombe, Kluyveromyces marxianus, Candida spp.	Remazol blue	Biosorption
Candida tropicalis	Remazol blue, Remazol black B	Bioaccumulation
Fomes sclerodermeus	Malachite green	Biodegradation
Trametes versicolor	Amaranth, reactive black 5, cibacron brillian yellow, remazol brilliant blue R	Biodegradation
Phanerochaete chrysosporium	Directblue15	Enzymatic degradation, bio-sorption playing a minor role
Rhizopus arrhizus	Gemazol turquoise blue-G	Biosorption
Fomes sclerodermus, Phanerochaete chrysosporium	Malachite green	Biosorption
Aspergillus ochraceus	Reactive blue 25	Biosorption and biodegradation
Rhizopus stolonifer	Bromophenol blue	Biosorption
Trametes versicolor	Remazol black B	Biodegradation
Trametes versicolor	Directblue1, direct red 128	Biosorption
Trametes versicolor	Grey lanaset G	Biodegradation
Ganodermaap planatum	Olive mill wastewater	Biodegradation
Perenniporia tephropora	Remazol brilliant blue R, neolane blue, neolane pink	Biodegradation
Pleurotus ostreatus	Disperse orange 3, disperse yellow 3	Biodegradation
Aspergillus níger, Rhizopus arrhizus, Trametes versicolor	Gryfalan black RL	Biosorption
Schizophyllum commune, Ganoderma lucidum	Solar golden yellow R	Biodegradation
Aspergillus niger	Synazol red HF6BN, synazol yellow HF2GR	Biosorption

Thus, researches so far have concentrated mainly on wood rot fungi for biodegradation studies but biosorption have been applied on wide variety of species (Kaushik and Malik 2009).

Further analysing fungal biosorption mechanism it is known that the fungi cell wall is represent by a very complex macromolecular structure containing chitin, mannans, proteins, glucans along with lipids, polysaccharides and pigments like melanin. The different components of the fungal cell wall results in the presence of functional groups of varying degrees which ensures biosorption (Crini and Badot 2008). Of all the components chitin is the effective biosorbent as are chitosan and other chitin derivatives. For example in *Rhizopus arrhizus*, biosorption involved coordination to the amine N of chitin and adsorption in the cell wall chitin. In comparison to chitin, chitosan is low cost. It is derived by deacetylation of fungal chitin which strongly complexes pollutants. Since chitin is predominant fermentation approach to cultivate fungi for subsequent chitosan preparation could be done but economics do not appear favourable along with generation of wastes. Chitosan has been widely assessed for dye removal studies (Banerjee et al. 2017). Fungal phenolic polymers and melanin possess many groups such as carboxyl, phenolic and alcoholic hydroxyl, carbonyl and methoxyl groups which assist in biosorption (Crini and Badot 2008).

8.4.2.2 Kinetics

It is well known that the adsorption of a substance from a phase onto the surface of another in a system leads to a distribution of thermodynamically defined substance between the phases at equilibrium. This distribution is expressed as the amount of substance adsorbed per unit weight of adsorbent, qe, as a function of the residual equilibrium concentration, Ce, of substance remaining in the “solution” phase. This expression is known as adsorption isotherm. The experimental isotherms are used to describe adsorption capacity and facilitates in the evaluation of the feasibility of the process (Kaushik and Malik 2009). This also helps in selecting the appropriate adsorbent and its dosage. Selecting fungal biomasses used biosorbent have undergone kinetic studies, preferably Langmuir and Freundlich isotherms have been widely used (Weber Jr 2008). Temkin and Radke Prausnitz isotherms were used for fitting the data. It has been reported that biosorption of congo red by *Aspergillus niger*, methylene blue and rhodamine B by *Phellinus igniarius, Fomesfomentarius*, Bromophenol blue by *Rhizopus stolonifera*, fitted the Langmuir and Freundlich isotherms (Fu and Viraraghavan 2002; Maurya et al. 2006; Zeroual et al. 2006).

8.4.2.3 Thermodynamics

The thermodynamic parameters are known to reflect the spontaneous nature and feasibility of the process. The equilibrium constants varying with temperature are used to estimate the thermodynamic parameters of free energy, enthalpy and entropy changes. The sorption of dye can be summarized by the following reversible process which represents a heterogeneous equilibrium (Aksu and Karabayir 2008).

Dye ion in solution ↔ Dye ion – Biosorbent

It has been reported by Aksu and Karabayir (2008), *R. arrhizus*, T. versicolor and A. niger, respectively at 25 °C were used to find the ΔG° value of each dye–sorbent system where standard Gibbs free energy were found to 5.79, 2.47 and 0.66 kJ mol^{-1} for dried *R. arrhizus*, *T. versicolor* and *A. Niger* biosorbents, respectively. The negative values of DG confirm the feasibility and spontaneous nature of the biosorption processes at 25 °C by the fungus having a high degree of affinity for the dye ions for each biosorbent surface (Aksu and Karabayir 2008).

8.4.2.4 Statistical Modelling

Fungal biomass based dye removal process have been optimized using softwares like central composite design (CCD). Sharma et al. (2009) have reported optimization of decolourization of fungal isolate *Aspergillus fumigatus fresenius* of azo dye acid red 151 (AR 151). The central composite design matrix and response surface methodology (RSM) was applied to design the experiments in order to evaluate the interactive effects of three variables i.e. temperature, initial dye concentration and pH. High regression coefficient between the variables and the response ($R^2 = 0.9934$) indicated good evaluation of the experimentally derived data by second order polynomial regression model (Sharma et al. 2009).

8.4.3 Algae

Algae are group of photosynthetic organisms living both marine and freshwater environments. This divers group ranges from phytoplanktonic to filamentous in nature and could convert sunlight, water and CO_2 to a wide range of metabolites and chemicals (Demirbas 2010; Bharathiraja et al. 2015; Sambusiti et al. 2015). Till date more than 55,000 algae species living in marine, brackish, fresh water and terrestrial environment have been identified (Ullah et al. 2015; Raslavicius et al. 2014). Macroalgae are comparatively large, multicellular and photoauxotrophic organisms (Bharathiraja et al. 2015; Sambusiti et al. 2015). While Microalgae are unicellular or simple-multicellular photosynthetic microorganisms and have size of less than 400 μm (Ullah et al. 2015; Demirbas 2010; Bharathiraja et al. 2015; Sambusiti et al. 2015). Like other biomasses, algal biomass also composed of complex heterogeneous mixture of organic matter and inorganic matter. Organic matter includes hemicellulose, cellulose, lignin, proteins, lipids and others. While inorganic matter includes silicates, oxyhydroxides, sulphates, phosphates, carbonates, chlorides, nitrates and others (Vassilev and Vassileva 2016).

Recently algae are being used for different industrial applications such biodiesel and secondary metabolites production in many countries. This produces large volume of waste algal biomass. Management and proper disposal of this waste algal biomass is needed proper attention. Researchers started to use this biomass for production of bioethanol, biogas, biofertilizer and fodder for animal/poultry/fish. Use of this biomass for wastewater remediation could be a promising management strategy. Till date different types of algae has been used for dye removal from water (Maurya et al. 2014). Algal biomass is known to have high sorption efficiency as they have large surface area and different types of active functional groups (Pathak et al. 2015).

This sorption is mainly driven by the active sites present on the algal cell wall (Sari and Tuzen 2008). Dead biomass of Spirogyra had been used for removal of reactive dye from textile wastewater (Khalaf 2008). Microalgal biomass of *Caulerpa lentillifera* and *Caulerpa scalpelliform* is also showed potential for removal of basic dye from wastewater (Marungrueng and Pavasant 2006). In addition to sorption, algal biomass also had been used for bioconversion of dye removal. *Chlorella vulgaris* biomass shown efficient removal of tectilon yellow 2G by converting it to aniline (Acuner and Dilek 2004). In addition to this dry and wet biomass of Chlorella pyrenoidosa and Chlorella vulgaris had been tried for separation of coloring agents from textile wastewater (Pathak et al. 2015; El-Kassas and Mohamed 2014).

8.4.3.1 Mechanisms

Live microalgae are known to remove dyes through a series of events firstly bioadsorption, biodegradation and then bioconversion of the dye in to less toxic or nontoxic end products. Generally microalgae take the dye as food supplements for nitrogen phosphorus, and carbon source. Thus, they control the eutrophication in the aquatic environment (Olguı’n 2003; Ruiz et al. 2011) and purify water that is unfit for human consumption (Mata et al. 2010, 2011).

Algal biomass is composed of different types of organic and inorganic matter which includes hemicellulose, cellulose, lignin, proteins, lipids, and salts of silicates, oxyhydroxides, sulphates, phosphates, carbonates, chlorides and nitrates (Vassilev and Vassileva 2016). This indicating that, algal biomass has different types of surface functional groups like hydroxyl, carbonyl, epoxy, amine, nitrate and sulphate which could be useful for capturing different types of pollutants. Due to this uniqueness algal biomasses are being used rapidly for separating multiple pollutants from water. Hydrogen bonding, van der Waals force and electrostatic interactions between the dye and the surface functional groups are the major physical attraction force which helps the dye to adhere on any kind of surface. This type of physical attraction force dependent dye adsorption is known to be physisorption. The dye molecules adsorbed on surface could be desorbed very easily. The dye molecules also could chemically bound on the surface of the algal biomass. This type of adsorption is called chemisorption. The chemisorbed dye could not be desorbed fully. There are various isothermic models like Langmuir, Freundlich which often used by various researchers for understanding the physisorptive or chemisorptive nature of any dye removal process (El Jamal and Ncibi 2012). Apart from these types of mechanisms, diffusion also play major role in dye removal from water. Inter or intra particle diffusion and film diffusion of dyes within the adsorbent is reported by previous researchers (Rubı'n et al. 2010; Mohan et al. 2008). Details of this kinetic have described in the following sub section 8.4.1.2. Researchers tried to understand the dye adsorption processes through thermodynamic analysis (El Jamal and Ncibi 2012). Details of the thermodynamic analysis have described in the following subsection 8.4.1.3.

8.4.3.2 Kinetics

As described in section 8.4.1.2, in general previous researchers had used pseudo-first-order, pseudo-second-order, model of liquid film diffusion and intraparticle diffusion model equations to understand the kinetic nature of bacterial dye adsorption process. Likewise for algal biomass based dye removal process these four types of kinetic equations were used to understand the algal dye removal process (Rubı'n et al. 2010; Mohan et al. 2008; El Jamal and Ncibi 2012; Marungrueng and Pavasant 2006). The pseudo-first-order and pseudo-second-order indicate the rate of adsorption process. Also the variation in dye adsorption rate is determined by the kinetic studies.

8.4.3.3 Thermodynamics

In subsection 8.4.1.3, all the thermodynamic equations are described elaborately. Similar types of equations were also used for dye removal using algal biomass (Rubı'n et al. 2010; El Jamal and Ncibi 2012; Marungrueng and Pavasant 2006). The Gibb's free energy change ($\Delta G°$), changes in entropy ($\Delta S°$) and enthalpy change ($\Delta H°$) in Eqs. 8.1, 8.2, 8.3, 8.4, and 8.5 in subsection 8.4.1.3 describe the nature of dye adsorption process. Negative values of $\Delta G°$ indicate that the dye adsorption process was spontaneous in nature. Furthermore, positive change in the enthalpy ($\Delta H°$) is indicative of endothermic nature of dye removal process. In addition, the positive value of $\Delta S°$ indicates increased randomness at the solid-solution interface during dye adsorption by algae (Gürses et al. 2004; Liang et al. 2017).

8.4.3.4 Statistical Modelling

Alike bacterial biomass based dye removal process, algal biomass based dye removal processes also could be optimized by using Plackett Burman design (PBD), path of steepest ascent (PSA), and central composite design (CCD) statistical software. Details of this analysis are described in the subsection 8.4.1.3. Apart from this statistical analysis, many researchers used Artificial Neural Network (ANN) models for identifying complex input-output relationship and developing a model to predict the output of dependent variables for given set of independent variables. Performance of various parameters for dye adsorption was evaluated from mean square error and regression derived from ANN model through MATLAB R2013a software. In addition, the validity of used models (e.g., isothers, kinetic) was determined by the sum of error squares (SSE, %) test by following equation (Hameed et al. 2006):

$$SSE\left(\%\right) = \sqrt{\Sigma\left[\left(q_e\right)\exp - \left(q_e\right)cal\right]^2 / N} \tag{8.14}$$

Where, q_e *exp* is the amount of dye adsorbed obtained experimentally and q_e Cal is the amount of dye adsorbed obtained from models. N is the number of data points. The SSE (%) along with the regression coefficient (r^2) indicated the validity and best fitted model.

8.5 Conclusions

This chapter describes about dye chemistry, its use in different aspects and toxic effects to the living being. Moreover it briefly summarized recent dye removal techniques especially by using bacterial, fungal and algal biomasses. This indicated that both live and dead biomasses had been used to separate dye stuffs from wastewater. The bacteria are mainly used for bioconversion of colouring agents into a less toxic by-product. The fungal and algal biomass is mainly used as adsorbent for dye removal from wastewater. Mechanisms, kinetics and thermodynamics of these types' biosorption processes have also been discussed in this chapter. Statistical models used for biosorption data analysis also discussed. It is evident that bacterial, fungal and algal biomass based dye removal process could be an eco-friendly and promising alternative to the available processes.

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Chapter 9
Mushroom Biomass and Spent Mushroom Substrate As Adsorbent to Remove Pollutants

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Abstract The edible and non-edible varieties of mushroom can be used as a green adsorbent and can be used in modified and natural form for the adsorption of dyes, pollutants and heavy metals. However, the use of edible mushroom varieties in the adsorption of pollutants is not judicious because edible mushrooms have good nutritive and medicinal properties and can be used for consumption. Recent research is thus focused on the utilization of spent mushrooms. Spent mushroom substrate, generated as waste by mushroom industries after the harvesting of mushroom, and hence, is the source of immobilized mushroom mycelium. The species of mushroom *Agaricus, Pleurotus, Lentinus, Calocybe* are efficient adsorbents with 70–90% removal of pollutants in laboratory conditions. Spent mushroom substrates can also remove pollutants such as dyes, heavy metals, pesticides and fungicides in laboratory conditions with comparable efficiency as mushroom. Chemisorption and physisorption processes are involved in the adsorption. The data of adsorption are well fitted to Langmuir isotherm, revealing the involvement of monolayer adsorption irrespective of the use of mushroom fruit bodies or spent mushroom substrate. Fourier-transform infrared spectroscopic analysis reveal the presence of carboxyl, hydroxyl, amino group in the adsorption of pollutants, dyes and heavy metals.

9.1 Introduction

Globally, the production and per capita consumption of mushroom has increased at a rapid rate for last five decades. According to the United Nations Food and Agriculture Organization statistics, the average annual growth rate of edible fungi is 5.6% worldwide. During 1997–2012, annual per capita consumption of mushrooms increased from about 1 kg to over 4 kg. The main producer and consumer of mushroom is China (Royse 2014). In India, more than 40,600 tons of mushrooms produced annually (Pandey et al. 2014). Mushroom cultivation is one of the environmental friendly ways to recycle agricultural and agro-industrial wastes for the production of mushroom fruit bodies or mycelium with good nutritive and medicinal properties. In 2016, market value of cultivated edible mushroom species is about 30–34 billion dollars and medicinal mushroom species is 10–12 billion dollars. Therefore, it is billion dollar agribusiness which cannot be shut down.

The problem related to mushroom cultivation industries is the disposal of waste generated after the harvesting of mushrooms. The mushroom substrate, left over after harvesting of mushroom fruit bodies, is called as spent mushroom substrate. This spent mushroom substrate creates the problem of disposal in environment-friendly way. In Iran, there is an increase in the mushroom production industries which are generating more than 50,000 tons of spent mushroom substrate annually. The generation of spent mushroom substrate was, generally two times higher than the mushroom harvested. According to Oei (1991), two tons of spent mushroom substrate remains from each ton of mushroom harvested. Now, efforts have been made to increase the mushroom production like the use of different substrate combinations and optimization of processes, which not only increased the biological efficiency and production capacity of mushroom but also reduced the generation of spent mushroom substrate. According to Pandey et al. (2014), amount of spent mushroom substrate generated from each ton of mushroom is approximately equal to the amount of generated mushroom.

Besides nutritional and medicinal properties, mushrooms are also known for their potential as adsorbent for the adsorption of pollutants from the industrial effluent and soil (Table 9.1). However, there are critics in using nutritive and medicinal species of mushroom in the adsorption of pollutants. To solve this issue, either non-edible varieties of mushroom or spent mushroom substrate of edible mushroom varieties have been used.

Spent mushroom substrate possesses leftover mycelium of the mushroom which can be utilized as a source of immobilized mushroom mycelium. Burning and landfill are the most adopted techniques for the disposal of spent mushroom substrate but are not environment friendly. Many researchers have analyzed the efficiency of mushrooms (Damodaran et al. 2014; Kan et al. 2015; Kariuki et al. 2017) and spent mushroom substrate (Kamarudzaman et al. 2015; Siasar and Sargazi 2015; Md-Desa et al. 2016) as adsorbent of pollutants, dyes and heavy metals along with evaluating the environmental impacts. This chapter describes the potential of mushroom and spent mushroom substrate in the adsorption of pollutants.

9.2 Mushroom As Green Adsorbent

Mushrooms can be served as green adsorbent which can accumulate pollutants from the surroundings and reduce their concentration (Udochukwu et al. 2014). The role of mushroom in adsorption of pollutants, dyes and heavy metals has been assessed by many researchers (Table 9.1). The mushroom mycelium can be used in the live or dead form. Live form of mycelium requires the maintenance of appropriate condition in order to maintain the viability. However, dead biomass can be used in a variety of conditions like high temperature, low temperature, acidic solution basic

Table 9.1 Removal of pollutants by biomass of mushroom using adsorption process

S. no	Mushroom spp.	Accumulated pollutants	Remarks	Reference
1.	*Pleurotus ostreatus*	Mercury	Mushroom adsorbs mercury and bioaccumulate it in fruit bodies	Bressa et al. (1988)
2.	*A. bisporus*	Silver	Higher bioconcentration rate was recorded even when the fruit bodies were grown in a low silver contaminated substrate	Falandysz et al. (1994)
3.	*Agaricus* sp.	Mercury	Potential candidate for mercury biosorption	Falandysz and Danisiewicz (1995) and Falandysz et al. (1995)
4.	*Ganoderma lucidum*	Copper	Highest uptake capacity in mushroom for copper	Muraleedharan et al. (1995)
5.	*Pycnoporus sanguineus*	Heavy metals	Removal of heavy metals lead, copper and cadmium from aqueous solution was investigated in fixed-bed column studies. Besides the removal of heavy metals, column can be used even after a number of adsorption and desorption cycles	Zulfadhly et al. (2001)
6.	*Agaricus bisporus* and *Lentinus edodes*	Cadmium	Adsorption of cadmium from aqueous solutions by these edible mushrooms	Mathialagan et al. (2003)
7.	*Phanerochaete chrysosporium*	Cadmium	Used in two ways: (i) immobilized on loofa sponge disc and, (ii) free fungal biomass. Immobilized biomass could be regenerated and metal recovery can be done and reused in ten biosorption-desorption cycles without significant loss of capacity	Iqbal and Edyvean (2005)
8.	*Agaricus macrosporus*	Zinc, copper, mercury, cadmium or lead	In supplemented and non-supplemented acid medium, the greatest differences in biosorption capacity were seen for living biomass	Melgar et al. (2007)

(continued)

Table 9.1 (continued)

S. no	Mushroom spp.	Accumulated pollutants	Remarks	Reference
9.	*Inonotus hispidus*	Arsenic	*I. hispidus* biomass was feasible, spontaneous and exothermic under examined conditions and therefore, can be used for arsenic adsorption	Sarı and Tuzen (2009)
10.	*Pleurotus platypus*, *Agaricus bisporus* and *Calocybe indica*	Cadmium and lead	*P. platypus* showed the highest metal uptake potential for cadmium whereas *A. bisporus* exhibited maximum potential for lead. Milky mushroom showed the lowest metal uptake capacity for both the metals	Vimala and Das (2009)
11.	*Tremella fuciformis* and *Auricularia polytricha*	Cd, Cu, Pb, and Zn	The humid *T. fuciformis* biomass is able to reduce heavy metals concentration as compared to dry biomass	Pan et al. (2010)
12.	*Mushroom*	Crude oil	These have ability to adsorb crude oil and heavy metals	Emuh (2010)
13.	*Pycnoporus sanguineus*	Oil removal	Oil removal from water using mushroom	Srinivasan and Viraraghavan (2010)
14.	*Pleurotus ostreatus*	Cadmium	*P. ostreatus* has good biosorption capacity	Tay et al. (2011)
15.	*Agrocybe aegerita; Pleurotus ostreatus; Hericium erinaceus*	Copper	Adsorption affected by the initial concentration of Cu^{2+}, adsorption time and concentration of mushroom powder	Huo et al. (2011)
16.	*Pleurotus sajor-caju*	Heavy metal Zn	Mushroom fruit body is effective in reducing the concentration of heavy metals and zinc	Jibran and Milsee Mol (2011)
17.	*Boletus edulis, Macrolepiota procera* and *Xerocomus badius*	Mercury	Data obtained by gas chromatography and atomic absorption spectrometry and inductively coupled plasma atomic emission spectroscopy, were highly biased for mercury adsorption	Jarzynska and Falandysz (2011)
18.	*Trichoderma* sp.	Mancozeb pesticide	*Trichoderma* sp. remove mancozeb from soil	Ahlawat et al. (2010)

(continued)

Table 9.1 (continued)

S. no	Mushroom spp.	Accumulated pollutants	Remarks	Reference
19.	*Tricholoma lobayense*	Congo red dye	Langmuir isotherm was fitted to the sorption equilibrium data and the maximum adsorption capacity was 147.1 mg/g at 25 °C.	Tian et al. (2011)
20.	*Pleurotus tuber-regium*	Heavy metals	Biosorption potential of *Pleurotus tuber-regium* in contaminated with some heavy metals and the effect of such heavy metals on the pileus development of *Pleurotus tuber-regium* were investigated and found good	Oyetayo et al. (2012)
21.	*Galerina vittiformis*	Cadmium, chromium, copper, lead, zinc	This mushroom adsorbs the heavy metals and possesses various cellular mechanisms that may detoxify heavy metals	Damodaran et al. (2013), Damodaran et al. (2014)
22.	*Auricularia polytricha*	Emulsified oil	*A. polytricha* fruit body was a fast, film-diffusion-controlled physical process for oil biosorption as depicted by multifactor effectiveness study, kinetic study, and scanning electron micrographs	Yang et al. (2014)
23.	*Pleurotus ostreatus*	Malachite green	The highest percent removal of dyes was 89.58% and the biosorption capacity reached 32.33 mg/g.	Chen et al., (2014)
24.	*Pleurotus eryngii*	Copper	*Efficient in removing copper from the solution*	Kan et al. (2015)
25.	*Agaricus campestris, A mellea, C. inversa, C. nebularis, M. procera, B. aestivalis, B. edulis, L. deterrimus, T. portentosum, T. terreum*	Nickel, chromium, lead, cadmium, mercury	Heavy metal contents in the mushrooms are mainly affected by species and their lifestyle. All mushrooms species were bioexclusors of nickel, chromium, and lead	Širić et al. (2016)
26.	*Pleurotus ostreatus*	Dyes	It is able to decolorize dyes	Skariyachan et al. (2016)
27.	*Lepiota hystrix*	Copper and lead	This mushroom biomass has a good potential to be used in removal of metal ions and can be used up to three adsorption/desorption cycles without losing efficiency	Kariuki et al. (2017)

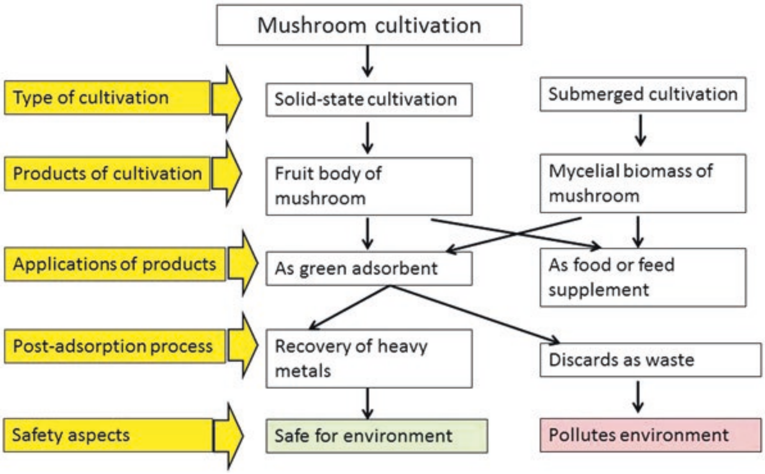

Fig. 9.1 Solid state and submerged cultivation of mushroom and the effect of different products on environment

solution as it is not affected by pH, temperature, salinity (Kulshreshtha et al. 2014). Mushroom possesses chitin, a negative charge compound in the cell wall, which provides negative charge to the surface of mushroom mycelium. Heavy metals and pollutants possess positive charge and therefore, these can adsorb on the surface of spent mushroom substrate due to ionic interaction. Thus, spent mushroom substrate can be a good candidate for adsorption of pollutants and heavy metals based on ionic interaction.

9.2.1 Preparation of Mushroom and Its Mycelium As Adsorbent

Mushroom and its mycelium are required in bulk amount for the adsorption purpose. Therefore, mushrooms can be collected in bulk amount from the natural environment or can be cultured in the laboratory. In the laboratory, mushroom can be cultured by solid state fermentation process and submerged fermentation process in the fermenter or Erlenmeyer flask. In solid state fermentation, substrate is prepared from agricultural or agro-industrial wastes which lead to the formation of fruit bodies of mushroom. In contrast, mushroom culture in Erlenmeyer flask or fermenter leads to the production of mycelial biomass of mushroom (Fig. 9.1).

Mycelium of mushroom can be cultured in an Erlenmeyer flask containing malt extract medium, and incubated at 25 °C, 125 rpm in an incubator shaker for 21 days. For harvesting the mycelium, broth was separated by filtration technique and discarded. Adsorbent can be prepared from the harvested mycelium or collected mushrooms by autoclaving for 15 min at 121 °C, 18 psi pressure, which is followed by oven drying for overnight at 60 °C. It can be ground into fine particles and then sieved to get particles of uniform size, i.e. lesser than or equal to 150 μm. This adsorbent can be used immediately, or preserved for a longer time in silica filled desiccators (Abdul-Talib et al. 2013).

9.2.2 Modified Mushroom for Adsorption

Recently, Xu et al. (2016) produced an adsorbent by using *Pleurotus cornucopiae* and further, used for the adsorption of hexavalent chromium ions from the aqueous solution. To prepare adsorbent from the *Pleurotus cornucopiae*, it was washed with deionized water for several times, which was followed by drying at 50 °C for 3 d using air-blower-driven drying closet. This was followed by grinding in a pulverized mill and sieve through 40-mesh, 60-mesh, and 100-mesh in order to get uniform particles of specific sizes. The surface of this dried mycelium was modified by chemical treatment to increase its adsorption capacity. To modify the surface for adsorption, 30 g of *Pleurotus cornucopiae* was agitated in 500 ml of the dodecyl dimethyl benzyl ammonium bromide solution for 24 h. Further, these particles were filtered and washed with double distilled water. Washing was done repeatedly till the complete removal of bromide ions. The washed mushroom biomass was dried at 30 °C for 24 h for self-assembling of mushroom mycelium powder. The surface scanning of modified *Pleurotus cornucopiae* revealed the presence of uneven surface and polyporous structure due to self-assembling of the material. Fourier-transform infrared spectroscopy analysis revealed that amine, hydroxyl, and carboxyl groups provide binding sites for adsorbate. These groups played an important role in adsorption when modified *Pleurotus cornucopiae* was used for the adsorption of hexavalent chromium ion. The increased dosage of this adsorbent increased the efficiency of adsorption of chromium ions. Under the optimum controllable factors like pH, temperature; hexavalent chromium removal efficiency of 75.91% was achieved. This adsorption was best fit to the Freundlich isotherm model. This is a successful approach to remove hexavalent chromium ions from the solution (Xu et al. 2016*)*. A detailed study at pilot scale and industrial scale plant is required to assess the potential of modified *Pleurotus cornucopiae* biomass in the adsorption of chromium ions so that technology can be implemented for industrial effluents.

In another experiment conducted by Xie et al. (2015), *Lentinula edodes* was treated with a mixture of sodium hydroxide, ethanol, and magnesium chloride. The effect of this treatment was assessed on adsorption capacity. For this purpose, 20 g of powdered raw biomass of *L. edodes* was mixed with 400 ml of mixed solution containing 200 ml of ethanol, 100 ml of sodium hydroxide and 100 ml of magnesium chloride. The biomass of *L. edodes* was left in solution at 25 °C and 150 rpm for 24 h. This treated biomass was filtered and supernatant was discarded. This was followed by washing with deionized water several times till the pH of *L. edodes* biomass became neutral. This biomass was dried in oven at 40 °C for 24 h. After drying, biomass was ground into fine particles and filtered through 100 or 200-mesh to obtain uniform sized particles. In this study, initial concentration of heavy metals was 50 mg/L; adsorbent dosage was 5 g/L. This magnesium chloride modified *Lentinula edodes* was used to adsorb cadmium and copper ions from the aqueous solution with high adsorption capacities of 51.64 ± 0.65 and 59.03 ± 0.64 mg/g, respectively. This capacity of adsorption of magnesium chloride modified *Lentinula edodes* was reported to be greater than one order of magnitude higher than that of raw biomass. A huge number of binding sites were exposed after the treatment of *L. edodes* with magnesium chloride which helps in the adsorption of metals. In the adsorption of copper and cadmium ions, both physisorption and chemisorption were reported to involve. These processes are based on electrostatic interaction, ion exchange and complex formation. The study of thermodynamic parameters revealed that the process was endothermic and spontaneous. The data were fitted well to pseudo-second order kinetic model which revealed the involvement of chemisorption process. This study also focused on the recovery of heavy metals from real industrial effluent. The adsorption and heavy metal recovery efficiency was 90% and 80%, respectively (Xie et al. 2015). Therefore, magnesium chloride treated spent mushroom substrate was found to be better than raw culture of *Lentinula edodes* in effective adsorption and desorption of heavy metals from the real industrial effluent.

9.2.3 Limitations of Using Mushroom in Adsorption

Harvesting the mushroom mycelium for removal of pollutants is not a feasible option, especially in developing and undeveloped countries because the primary focus of mushroom cultivation is to provide protein rich food to the people. Secondly, mushrooms also have anti-mutagenic, anti-inflammatory, anti-carcinogenic, antioxidant properties and can be used for medicinal purposes. Therefore, mushroom cultivation for bioremediation of pollutants, heavy metals and dyes by adsorption is not encouraged in these countries.

When mushroom biomass or fruit bodies are used for the adsorption of pollutants, heavy metals and dyes, proper disposal practices are required if metals and pollutants are not recovered. On dumping in the environment, the adsorbed metals and pollutants can leach out and cause soil and water pollution (Fig. 9.1). Adsorption by mushroom biomass or fruit bodies is worthy to remove pollutants from the environment; nevertheless there is a need of safe disposal practices.

Another problem related to mushroom cultivation is the generation of spent mushroom substrate. Mushroom cultivation requires a substrate composed of agricultural waste fibers including wheat straw, rice straw, corn cobs, cottonseed hulls, sawdust; manures like horse manure, poultry manure, cottonseed meal; and a calcium source like calcium carbonate or gypsum. This substrate is incubated at suitable temperature and humidity condition, depending upon the species of mushroom. In the appropriate conditions, substrate supports the growth of mycelium and fruit

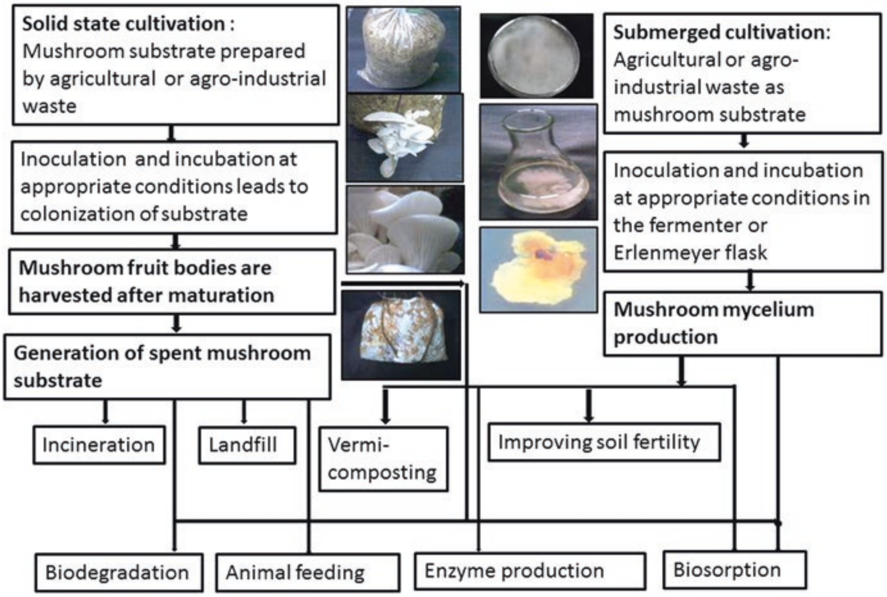

Fig. 9.2 Applications of the mushroom products and by-products generated by submerged and solid state cultivation of mushrooms

bodies. These fruit bodies are harvested on maturation. After the harvesting of mushroom fruit bodies, mushroom substrate is discarded as solid waste which is called as spent mushroom substrate, mushroom soil, recycled mushroom compost or spent mushroom compost (Fig. 9.1). This substrate is a byproduct of the mushroom industry, which give rise to the most significant environmental issues, and therefore need a strategy for its proper disposal.

9.3 Spent Mushroom Substrate As Adsorbent

In the earlier attempts, spent mushroom substrate was disposed by landfills or by burning in open fields. In the case of landfill, spent mushroom substrate is piled up on the land; however release of leachates from the pile due to the weathering of spent mushroom substrate may adversely affect the ground water quality (Kamarudzaman et al. 2014a) and adjacent land. Later, spent mushroom substrate was used for a variety of purposes like animal feed, production of enzymes, vermicomposting and soil quality improvement (Fig. 9.2).

The use of spent mushroom substrate in laccase, xylanase, lignin peroxidase, cellulase and other enzymes production is suggested by Phan and Sabaratnam (2012). Spent mushroom substrate contains 14% protein and lots of vitamins and microelements like iron, calcium, magnesium and zinc, and essential amino acids which are generally not present in animal feed. Therefore, spent mushroom substrate can be a good feedstuff for animals (Foluke et al. 2014).

The spent mushroom substrate was also used for improving the soil quality and crop yield. Ribas et al. (2009) reported the use of spent mushroom substrate as a growth supplement for lettuce, which not only promoted the growth of lettuce by improving microbial diversity of soil and related enzymatic activities, but also degraded biocides. Fidanza et al. (2010) reported that the supplementation of spent mushroom substrate to the soil improved the structure of clay soil, reduced the surface compaction and crusting, along with promoting the microbial growth and enzymatic activity in the soil. Improvement in soil quality led to turf establishment, improved turf density and colour, increased rooting, which further reduced the need of fertilizer and irrigation (Fidanza et al. 2010). Sendi et al. (2013) replaced the peat moss with spent mushroom substrate in the cultivation media of *Brassica oleracea* i.e. Kai-lan and reported the higher yield of *Brassica oleracea*. Lopes et al. (2015) reported that the use of spent mushroom substrate as compost provided higher yield of tomatoes as compared to green, organic and chemical fertilizers. Spent mushroom substrate is considered as a source of nutrient for the soil and hence, widely used as compost (Siasar and Sargazi 2015). Besides, spent mushroom substrate possesses high adsorption capacity which can be further utilized for the removal of heavy metals, dyes, pollutants from the soil. This ability was used by Tuhy et al. (2015) for converting spent mushroom substrate into biofertilizer by adsorbing some metals like zinc, manganese and copper for fulfilling the mineral requirement of the plant. In this way, spent mushroom substrate showed promising results towards improving the soil quality and crop productivity and greening of a shattered area or desert. In contrast to this, it is also reported in the literature that the high salt and nutrient content of spent mushroom substrate disturbs the nutrient balance of soil and therefore, limits their application in improving the soil quality. Any failure in utilization of spent mushroom substrate will lead to its accumulation in the environment.

To solve the aforesaid problems of waste accumulation, the spent mushroom substrate has also been used for adsorbing the toxic metals, dyes and pollutants from the environment. The spent mushroom substrate can act as a green adsorbent due to having immobilized mycelium and excellent abilities to adsorb or degrade organic compounds and pollutants, dyes present in soil and water (Ahlawat et al. 2010). They can play an important role in environmental cleanup. Further, they have the potential to adsorb metals which can be recovered on changing certain physiological conditions. These can be used for metal recovery from industrial effluent and soil. Ribas et al. (2009) reported the use of fresh spent mushroom substrate of *L. edodes* for soil remediation. The spent mushroom substrate also has potential to minimize the bioavailability of heavy metals (García-Delgado et al. 2013).

Application of spent mushroom substrate in the soil and water for the removal of dyes, pollutants and heavy metals may be a viable and acceptable option as it is a waste byproduct of mushroom industry. It is available in bulk amount at a lower price or sometimes free of cost; and efficient to use for adsorbing heavy metals and pollutants from the effluent and soil and thus, can improve the quality of environment.

The effective implementation of the adsorbent in environmental cleanup depends on its properties like cost-effectiveness, potential to adsorb pollutants. Besides, adsorbent should be amenable to any physical and chemical alterations which are required to enhance their adsorption properties (Ayangbenro and Babalola 2017). The most important aspect of using spent mushroom substrate as adsorbent is its cost and availability. The spent mushroom substrate is generated in high amount as the waste of mushroom production industries (Singh et al. 2003) and generally, discarded by burning in open field and disposed in municipal solid waste landfill. Hence, spent mushroom substrate can be available in bulk amount at a low price or free of cost for using as adsorbent. The use of spent mushroom substrate for adsorbing metals and pollutants will not only solve the problem of accumulation of spent mushroom substrate but also heavy metals and pollutants. Therefore, application of spent mushroom substrate will be a feasible technology to implement as far as availability of raw material is concerned.

Another parameter for choosing spent mushroom substrate is its properties. The lignocellulosic component of spent mushroom substrate possesses negative charged groups like hydroxyl, carboxylic acid and phenolic groups, which provide them ability to bind with metals. García-Delgado et al. (2013) compared the efficiency of spent mushroom substrate of *Pleurotus* and *Agaricus,* and reported that spent mushroom substrate of *Agaricus* has undergone an intense composting process due to which it produces higher amounts of fatty acid and humic acid and further, acquires the higher amount of alkyl and carboxyl group compare to spent mushroom substrate of *Pleurotus*. Therefore, the spent mushroom substrate of *Agaricus* can be a better substrate than *Pleurotus* spent mushroom substrate for adsorbing the positive charged metals and pollutants from the environment.

For practical application considerations, it is also important that adsorbent have the potential to adsorb heavy metals and further, helps in their recovery by desorption process (Javanbakht et al. 2014). In this way, spent mushroom substrate is generated as waste and can be revenue for the industries if utilized for the adsorption of heavy metals. This recovery based approach can be implemented in future due to having financial benefits along with environmental benefits.

9.3.1 Principle of Adsorption by Spent Mushroom Substrate

Adsorption is the ability of adsorbate to adhere or attach to the adsorbent. In case of spent mushroom substrate, the adsorption occurs mainly by two processes; coulombic interaction and intrinsic adsorption. Coulombic interaction is related to the electrostatic energy of interaction between ions. When surface of adsorbate and adsorbent possess opposite charge, they are attracted by coulombic interaction. Generally, spent mushroom substrate based adsorption phenomenon relies on the fact that surface of spent mushroom substrate possesses negative charge due to the presence of anions such hydroxyl, carboxyl, amide groups; and adsorbate like heavy metals or pollutants possesses positive charge ions. The active functional groups and charge on the spent mushroom substrate can be analyzed by Fourier-transform infrared spectroscopy analysis. This analysis revealed that the carboxyl, hydroxyl, phosphate, amide group of lignocelluloses and chitin, glucans, mannans of mushroom are involved in adsorption process (Tay et al. 2012). The ability of spent mushroom substrate to bind with the pollutants, dyes and metal ions depend upon the structural component of fungi and lignocellulosic agricultural residues. Chitin is an important component of spent mushroom substrate for the adsorption of heavy metals and radionuclides. Chitosan is a more effective alternative compared to chitin, to bind and form strong complexes with pollutants and metals. However, it cannot be used due to unfavourable economics, which need high cost to implement. Moreover, it is extracted by typical extraction procedure, which results in generation of toxic wastes (Gadd 2009). The intensity of interaction is based on charge of adsorbate and adsorbent; and strength of ions (Igwe and Abia 2006).

Intrinsic adsorption is associated with the surface area of adsorbent which can be observed by the effect of different sizes of adsorbent particle on the capacity of adsorption (Igwe and Abia 2006). This process is based on the Van der Waals attractions between the adsorbent and adsorbate.

9.3.2 Mechanism of Adsorption

Generally, binding of metals, pollutants and dyes to the mushrooms and spent mushroom substrate depends on the four mechanisms: (i) adsorption (ii) ion exchange (iii) complexation and (iv) precipitation. Physical adsorption is based on the electrostatic forces and van der Waals forces as mentioned in aforesaid section. Transport of cations across the microbial cell wall depends upon metabolism of mushroom and cell membrane permeability. This is required to maintain the ionic balance of metabolically important ions like sodium, potassium and magnesium. The metabolically independent transport mechanism involves transportation through cation transport systems. Occasionally, this system transports the metal ions bearing the same charge and ionic radius along with the other required ions. It has been reported that mushroom biomass develop mechanisms to resist the heavy metals through the secretion of chelating substances that are able to bind with metal ions. Further, metal ions accumulation is reduced due to the alterations in the metal transport system. Another mechanism to develop resistance includes the binding of metal ion to intracellular molecule such as metallothionein or accumulates in intracellular organelles like vacuole or mitochondria (Ayangbenro and Babalola 2017).

The principal mechanism of heavy metal binding is related to physical binding and chemical binding of metal ions to the spent mushroom substrate. However, ion exchange can be observed as an important phenomenon in adsorption. Occasionally, bivalent metal ions are exchanged with counter ions of polysaccharides.

As mentioned earlier, complexation plays an important role in the adsorption process. It is based on the surface charge of spent mushroom substrate and mushroom. Both possess negative charge due to the presence of carboxyl, amino, thiol, amide, imine, thioether, phosphate, which provide them ability to make complexes during metal-ligand and adsorbate-adsorbent interaction (Javanbakht et al. 2014).

Precipitation, a metabolically independent process, is a chemical reaction between the metal and cell surface of mushroom and spent mushroom substrate. This leads to the deposition of heavy metals into solution and on the surface of mushroom mycelium. Zhou et al. (2005) reported that lead ions form complex with the cellulose and precipitate the product of lead complex generated by hydrolysis. The precipitation of lead complex in the form of hydroxides has also increased with an increase in the pH.

In the living mushroom mycelium, adsorption process depends upon the metabolic processes while these are independent of metabolic processes if dead biomass of mushroom is used. Dead biomass of mushroom passively binds metal ions by various physicochemical mechanisms. Nevertheless, complete knowledge of metabolism dependent processes is required in order to optimize and maintain the adsorption in the living system. In the living biomass, metabolic activities are affected by rate of respiration, the products formed during metabolism and nutrient uptake which further affects adsorption, ion exchange, complexation and precipitation.

In the case of organic pollutants, adsorption is based on chemical structure such as molecular size, charge, solubility, hydrophobicity and reactivity. In addition to adsorption and complexation, permeation of spent mushroom substrate biomass may contribute to the adsorption process.

Hydrocarbons are hydrophobic compounds, insoluble in water, however, can be associated with non-polar environment. They can be adsorbed on the surface of organic substances and spent mushroom substrate biomass. Lipophilic, hydrophobic compounds can pass through cell membranes and adsorb into organic matrix of spent mushroom substrate (Javanbakht et al. 2014). In the case of dye adsorption, chitosan, extracted derivative of chitin, is better than naturally occurring mushroom chitin. Dyes adsorbed on the surface of chitosan by various mechanisms that include surface adsorption, chemisorption, film diffusion and pore diffusion; and chemical reactions like adsorption-complexation and ion exchange. The main group involve in the adsorption of dyes is amine group; however, hydroxyl group may also contribute in the process (Javanbakht et al. 2014). It is pertinent to note that effectiveness of the substrate in adsorbing the pollutants is more important than the mechanism involved in the adsorption.

9.3.3 Selection and Preparation of Spent Mushroom Substrate As Adsorbent

During the mushroom cultivation, cellulosic, lignocellulosic and hemicellulosic fibres are utilized by the mushroom for the growth. This leads to the gradual degradation of the substrate and pore formation. The pore size is increased with increase in time due to the continued substrate degradation process, which further increase adsorption properties of spent mushroom substrate.

The choice of spent mushroom substrate may vary as per availability in the local area (García-Delgado et al. 2013). Selection of appropriate spent mushroom substrate and its application in adsorption of pollutants seems to be a sustainable technology that will not only remove the pollutants, but also solve the problem of waste disposal (Prasad et al. 2013). The most popular mushroom species around the world is *Agaricus* species and *Pleurotus* species and therefore, cultivation of these species generates huge amount of waste which accumulates in the environment and causes ill effects. Therefore, spent mushroom substrate needs proper disposal practices (García-Delgado et al. 2013). The spent mushroom substrate of these mushrooms is readily available and inexpensive biomaterial with high capacity of pollutant adsorption.

Spent mushroom substrate for adsorption of pollutants, dyes and heavy metals have been prepared by different methods and analyzed. In one method, Siasar and Sargazi (2015) mixed 2 g of spent mushroom substrate in 20 ml of water and filtered the resultant solution through filter paper AK-01 blue. Spent mushroom substrate was retained by the filter which was collected and dried; and further, used in the adsorption experiment. In the method developed by Tay et al. (2011) the sample of spent mushroom substrate was prepared at 121 °C, 18 psi for 15 min and then dried in an oven at 60 °C. This was followed by grinding and sieving to obtain particle size lesser than 710 μm. This adsorbent was stored in dry cabinet. In another method, all conditions of preparing spent mushroom substrate adsorbent from *Pleurotus* species were kept same, except particle size which was lesser than 150 μm. This adsorbent was stored in silica filled desiccators and used in performing the experiment for lead and cadmium adsorption (Tay et al. 2011; Abdul-Talib et al. 2013).

A different preparation of spent mushroom substrate was also used by Gill (2014) for adsorbing an organic chemical spill. In this preparation, spent mushroom substrate was mixed with dry plant material, partially composted plant material, spent mushroom substrate, dry plant material, a petroleum hydrocarbon, ammonium nitrate, iron sulfate, mixture of iron sulfate and ammonium nitrate, and a clump preventing material like sawdust, vermiculite, diatomaceous earth. This mixture was supplemented with nutrient source such as raw sugar or sugar beet residue. When this substrate mixed with the spilled chemical and water, it can neutralize the hydrocarbon spill (Gill 2014). These studies revealed that all preparations of spent mushroom substrate are effective in removing the pollutants from the environment.

9.3.4 Characterization of Spent Mushroom Substrate Adsorbent

The adsorbent must be sufficiently porous to adsorb pollutants from the surrounding. The spent mushroom substrate is composed of different types of polymers such as lignin, cellulose and hemicellulose which are degraded by mushroom mycelia during its growth and utilized as carbon and energy sources. This degradation results in numerous pores in the spent mushroom substrate that makes it a suitable substrate for adsorption (Yan and Wang 2013). These pores can be classified as micropores if pore diameter is lesser than 2 nm, mesoporous if pore diameter is 2–50 nm and macropores if pore diameter is greater than 50 nm. The macroporous material has a great potential for adsorbing large sized adsorbates as compared to mesoporous or microporous adsorbent material. The structure of cell wall, micropores, mesopores and macropores must be evaluated in order to analyze the potential of adsorbent. The characterization of spent mushroom substrate for using it as adsorbent can be done by the following methods:

9.3.4.1 Brunauer Emmett Teller Analysis

The specific surface area and total pore volume of spent mushroom substrate can be measured by surface area analyzer, a fully automated analyzer which evaluates the material by nitrogen multilayer adsorption measured as a function of relative pressure. Nitrogen does not react chemically with the substrate and therefore, used in the analyzer. This technique determines the surface area and pore area and helps in acquiring important information for performing adsorption studies. Further, adsorbent categories can be defined on the basis of Brunauer Emmett Teller analysis, such as dispersed, nonporous, macroporous materials. Macroporous material have pore diameter greater than 50 nm is well-fitted to type II isotherm. Mesoporous materials have pore diameter between 2 nm and 50 nm is well fitted to type IV isotherm. Microporous material have diameter lesser than 2 nm and well fitted to type I isotherm.

9.3.4.2 Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy Analysis

It is an analytical technique used for the elemental analysis or chemical characterization of spent mushroom substrate. It is based on the interaction of X-ray and spent mushroom substrate. When X-rays are focused on the spent mushroom substrate, unique set of peaks can be observed on its electromagnetic emission spectrum according to the atomic structure of materials present in spent mushroom substrate.

9.3.4.3 Fourier-Transform Infrared Spectroscopy Analysis

This analysis provides an insight of adsorption process. The functional groups, involved in the adsorption process, can be determined by analyzing the peaks obtained by Fourier-transform infrared spectroscopy. Differences in the peaks of spent mushroom substrate before and after adsorption can be investigated by Fourier-transform infrared spectroscopy. These peaks reveal the important groups involved in the adsorption process (Kamarudzaman et al. 2014a).

9.3.4.4 Solid-State Cross-Polarization Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance

Solid-state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance is used to investigate the structural changes and interactions of cellulose (Larsson et al. 1999) with the pollutant during adsorption. It is also used to detect the presence of β-D-glucan and trace compounds present in dried powder of mushroom samples. For this purpose, the high- resolution solid-state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance spectra can be recorded at the resonance frequency of approximately 100 MHz with the use of 4 mm rotors and frequency of 12 kHz and pulse duration of 1.9 μs. A high-power proton-decoupling field of 92 kHz can be applied during data acquisition. The spectra can be obtained at room temperature averaging over 5000–33000 scans. Hydration of mushroom polysaccharide give rise to conformational stabilization, which is reflected in spectra by narrowing and splitting of resonance line (Fričová and Koval'aková 2013).

To evaluate the strategies for potential implementation, adsorption isotherms, adsorption kinetics, intra-particle diffusion ability can be used to explain the feasibility of adsorption process.

9.3.5 Adsorption of Heavy Metals by Spent Mushroom Substrate

Heavy metals are noxious products discharged by a number of industries after the completion of industrial processes and are major pollutants in the soil and water. These are discharged by electroplating and metal finishing and metallurgical industries, leather tanning, textile dyeing and printing based industries, fertilizer industries, acid mine drainages and landfill leachates. Besides, agricultural and domestic activities also discharge heavy metals in the environment.

These are recalcitrant and hence, accumulate in the environment and enter the food chain (Igwe and Abia 2006). After intake, heavy metals accumulate in the living tissue and disrupt biological processes due to their toxicity. Conventional methods for removing metal ions include a number of processes such as filtration, chemical precipitation and electrochemical treatment, ion-exchange, membrane technologies and activated carbon. Many of these processes are ineffective, especially when metal ion concentration in aqueous solution is 1–100 mg/L. Moreover, they produce huge amounts of toxic sludge which is difficult to dispose. Further, these cannot be implemented at large scale due to financial constraints. Nowadays, microbial adsorption based approaches are gaining much attention in removing the metals from the environment. The most popular microbial option for adsorbing metal is mushroom mycelium which can be obtained from mushroom industry or mushroom cultivation units. The spent mushroom substrate, as green adsorbent, presented as an alternative to traditional physicochemical means for removing heavy metals from soil and water. Spent mushroom substrate makes complex with heavy metals and increases its stability, however reduces its bioavailability, which in turn reduces the toxic effect of metal on living beings.

According to Wang and Chen (2009), there are two methods for the removal of heavy metals. The first method is related to the usage of living biomass of mushroom for metal adsorption and removal; while the other methods, rely on the immobilization technology and modification in the adsorbent for making a type of ion exchange resin to use in regeneration or reuse (Wang and Chen 2009). The use of spent mushroom substrate as green adsorbent is explained in the subsequent sections.

9.3.5.1 Spent Mushroom Substrate of *Lentinus edodes*

The spent mushroom substrate of *Lentinus edodes* is used as adsorbent for adsorbing cadmium, lead and chromium from solution. The effect of different parameters such as adsorbent concentration, initial pH, contact time and heavy metal concentration was evaluated by Tay et al. (2012). As the initial pH increase, active sites of spent mushroom substrate are deprotonated resulting in the increased adsorption of copper. In acidic condition, copper uptake is poor due to the protonation of the active sites of adsorbent. However, in basic condition, copper ions are precipitated as insoluble hydroxides resulting in decrease adsorption of copper. On increasing the adsorbent dosage, adsorption of heavy metals increased. Fourier-transform infrared spectroscopy analysis revealed that the carboxyl, phosphoryl, and phenolic groups are involved in adsorption (Tay et al. 2012). This study shows the potential of *Lentinula edodes* in removing heavy metals.

9.3.5.2 Spent Mushroom Substrate of *Pleurotus ostreatus*

Tay et al. (2012) used *Pleurotus ostreatus* and spent mushroom substrate for adsorbing heavy metals. The copper adsorption experiment, conducted by him, was based on the assessment of half saturation constant of adsorption so that results can be obtained with minimum adsorbent dosage and in shorter time. The findings revealed that optimum adsorption parameters were initial pH 5, contact time 10 min and initial copper concentration 50 mg/L. The adsorption co-efficient for *Pleurotus* mushroom and *Pleurotus* spent mushroom substrate was found 0.9598 and 0.9920, respectively. These values showed that both mushroom and spent mushroom substrate has same adsorption capacity. Fourier-transform infrared spectroscopy analysis revealed that carboxyl, hydroxyl and amide groups of lignocelluloses, chitin, and proteins were involved in the adsorption study. The kinetics of the study showed that chemisorption, complexation and ion exchange are the mechanisms involved in the adsorption of copper on spent mushroom substrate and mushroom fruit body.

Adsorption of Nickel

Nickel, a toxic metal, discharged with industrial effluent from mineral processing, electroplating and battery manufacturing industries. It is an essential micronutrient for some plant and microbes in minute amount, nevertheless toxic in high amount. It accumulates but not magnified along the food chain (Tay et al. 2011). Long term exposure to nickel causes serious health issues. Therefore, spent mushroom substrate was used to remove this metal from the environment.

Tay et al. (2011) studied the potential of *Pleurotus ostreatus* spent mushroom substrate as a green adsorbent for nickel adsorption. For this purpose, analytical grade of nickel nitrate hexahydrate salt was used to prepare nickel solution with ultrapure water. *Pleurotus ostreatus* spent mushroom substrate adsorbent was prepared using the protocol as mentioned by Tay et al. (2011) and particle size lesser than 710 μm was chosen for nickel adsorption study. Nickel adsorption was carried out in batch process. Erlenmeyer flasks were filled with 50 ml nickel solution and placed on incubator shaker at 125 rpm and 25 °C. The effect of different parameters such as adsorbent concentration, initial pH, and contact time and nickel concentration was evaluated. After withdrawal, samples were filtered and supernatants were analyzed by inductively coupled plasma optical emission spectrometry. Further, feasibility of technique in terms of effectiveness and cost was also compared. This was done by performing the same experiment with commercially available synthetic adsorbent, i.e. Amberlite IRC-86. Results of the study revealed that 50% of nickel adsorption was obtained at half saturation constant of 0.7 g adsorbent concentration, initial pH in range of 4–8, contact time of 10 min., 50 ml solution of nickel with initial nickel concentration 50 mg/L. In this way, maximum nickel adsorption was 3.04 mg/g and data was fitted to Langmuir isotherm model showing the occurrence of monolayer adsorption on the surface of adsorbent. Fourier-transform infrared spectroscopy analysis determined the involvement of alkyl, hydroxyl, amino, aliphatic, alcohol and carbonyl functional groups in the adsorption process. The mechanism of adsorption involves physisorption and chemisorption ion exchange process. Characterization of adsorbent indicates that *Pleurotus* spent mushroom substrate is weak ion exchanger and therefore, its ion exchange performance was evaluated against Amberlite IRC-86. It is reported that ion exchange capacity of spent mushroom substrate is comparable to Amberlite IRC-86 to remove nickel. Nevertheless, *Pleurotus* spent mushroom substrate was found to be six times cheaper than Amberlite IRC-86 in terms of cost per unit of metal removed (Tay et al. 2011). Therefore, a costly option Amberlite IRC-86 can be replaced with an economic option spent mushroom substrate.

Tay et al. (2016) also conducted the study on adsorption of bi-metal solution, containing copper and nickel by *Pleurotus* spent mushroom substrate. The maximum uptakes of copper and nickel were 3.54 mg/g and 1.85 mg/g, respectively. However, *Pleurotus* spent mushroom substrate has higher selectivity for nickel as compared to copper. To find out the possible mechanism involved in the adsorption, results were evaluated through isotherm, kinetic and thermodynamic studies. Data of adsorption study were in agreement with Langmuir and Freundlich isotherms. This confirms the involvement of chemisorption process. Further, the adsorption reaction is spontaneous and exothermic is elucidated by thermodynamic parameters. Inductively coupled plasma optical emission spectrometry technique of measuring metal concentration and differences in pH depicted the involvement of ion exchange mechanism.

The above mentioned findings indicate the effectiveness of *Pleurotus* spent mushroom substrate in adsorbing nickel from the effluents. After studying the detailed insight of the process and mechanism, in the future, this spent mushroom substrate will be a promising green adsorbent for removing the metals in environmental friendly manner.

Adsorption of Lead

Pleurotus spent mushroom substrate was assessed for its potential in adsorbing lead ions. In a study, conducted by Liew et al. (2010) the suitability of *Pleurotus* spent mushroom substrate for removal of lead was determined. The effect of pH of lead containing solution, contact time, initial lead concentration was analyzed. The percentage removal of lead from solution using different amount of *Pleurotus* spent mushroom substrate by keeping the constant contact time i.e. 60 mins, was also assessed. Results of the study revealed that Pb removal increased with an increase in the amount of *Pleurotus* spent mushroom substrate. However, a maximum of 88% lead removal was achieved by 0.5 g of *Pleurotus* spent mushroom substrate (Liew et al. 2010). The removal percentage of lead increased at the initial stage with increasing the amount of adsorbent which is possible due to the increase in binding sites in adsorbent. At saturation stage, the lead binding sites decreased and resulted in the reduced lead adsorption. This is possibly due to screening effect which can reduce the accessibility of binding sites (Liew et al. 2010) by previously bind lead ions. The study showed that *Pleurotus* spent mushroom substrate is an efficient adsorbent for lead ions.

Adsorption of Iron

Iron is a toxic heavy metal that is commonly found in various industrial effluents. The exposure of human causes respiratory diseases, heart attacks, tissue damage. Therefore, it is necessary to remove iron from the industrial effluents. Spent mushroom substrate has been used for adsorbing the iron from the industrial effluents.

Kamarudzaman et al. (2013) performed an experiment to adsorb iron from the solution by using spent mushroom substrate as adsorbent. Standard solution of iron i.e. 1000 mg/L was prepared by dissolving ferric nitrate in ultrapure water. It was further diluted to obtain different concentrations. The pH was adjusted by using 1 M hydrochloric acid or sodium hydroxide solutions. Scanning electron microscopy for the analysis of surface morphology of *Pleurotus ostreatus* spent mushroom substrate before adsorption, revealed the rough and porous surface of spent mushroom substrate, which was efficient enough to support the adsorption process due to large surface area. The optimum adsorption of iron by *Pleurotus* spent mushroom substrate was achieved at an initial pH ranging from 4 to 5, contact time 10 min. and initial iron concentration of 50 mg/L using half-saturation constant of 0.4 g adsorbent dosages. After adsorption, SEM analysis showed that the spent mushroom substrate surface appears to be fully covered with iron molecules due to the deposition of iron molecules in the pores. Further, energy-dispersive X-ray spectroscopic analysis confirmed the adsorption of iron molecule by rise in peaks of iron. Fourier-transform infrared spectroscopy spectra revealed the involvement of carboxyl, hydroxyl and amide functional groups. Physical and chemical characterization of spent mushroom substrate supports the use for the adsorption of iron (Kamarudzaman et al. 2014a).

Later, the potential of *Pleurotus* spent mushroom substrate for adsorbing iron in the fixed bed column reactor was also investigated to find out the influence of flow rate, bed depth, and initial concentration of iron. Results show that decrease in flow rate and initial iron concentration leads to increase in breakthrough time and exhaustion time. In contrast to this, the breakthrough and exhaustion time decreased with decrease in bed depth (Kamarudzaman et al. 2014b). The study of physical and chemical characterization revealed the suitability of spent mushroom substrate for the adsorption of iron.

Adsorption of Copper

Copper is used as anti-corrosive agent and also used to make a decorative coating on the metal alloys (Siasar and Sargazi 2015). It is used in electrical and electroplating industries. It reaches the water bodies with the industrial effluents. In natural environment, metal persist for a longer time due to their non-degradable nature. The most serious threat to the environment and living beings is the toxicity and bioaccumulation potential of heavy metals. Adsorption based approaches are the most promising option for removing copper from the industrial effluents.

Pleurotus ostreatus spent mushroom substrate was used to remove copper from the effluent. The copper adsorption on spent mushroom substrate was carried out in the batch experiment. The maximum adsorption of copper was reported to be 3.54 mg/g. To find out the mechanism of metal adsorption, isotherm, kinetic and thermodynamic studies were conducted. Copper adsorption can be explained by Langmuir and Freundich isotherms. The mean energy indicated the involvement of chemisorption process for copper adsorption.

The adsorption data fitted well to the pseudo-second order kinetic model which revealed the involvement of chemisorption process in the adsorption of copper ions on spent mushroom substrate. Another mechanism involved in copper adsorption was ion exchange mechanism which was confirmed by inductively coupled plasma optical emission spectrometry. Copper forms weaker and reversible bond after adsorption, revealing the involvement of ion-exchange mechanism in the copper adsorption (Tay et al. 2016). This study showed that copper can be adsorbed by using spent mushroom substrate, which is an economic and feasible option.

According to Sarioglu et al. (2009), copper removal efficiency has been affected by the formation of insoluble complexes between copper ions and anionic charges which is present on the surface of adsorbent such as hydroxide, carbonate and sulfate.

Adsorption of Manganese

Manganese in industry is used for rust and corrosion on steel. Ionized manganese provides different colours depending on the oxidation state of ions. Manganese is also used as cathode in zinc-carbon and alkaline batteries. Manganese compounds are less toxic than the other heavy metals like nickel and copper, however exposure to high doses even for short period produces toxic effects. Therefore, it is important to treat manganese containing effluent prior to discharge in water bodies.

Pleurotus spent mushroom substrate was selected as adsorbent to remove manganese ions in a batch experiment and effect of pH, contact time and initial manganese concentration were investigated by Kamarudzaman et al. (2015). The optimum adsorption of manganese ions was achieved at pH 6, contact time 20 min., 10 mg/L using 1 g dosage of *Pleurotus* spent mushroom substrate. The data of this study were fitted well to Langmuir isotherm model and pseudo-second order kinetic model. Again, this revealed the involvement of chemisorption process in manganese adsorption by spent mushroom substrate. This experiment indicates the suitability of spent mushroom substrate for adsorption of manganese (Kamarudzaman et al. 2015).

Thereafter, Kamarudzaman et al. (2015) conducted an experiment in a fixed-bed column for the removal of manganese by *Pleurotus* spent mushroom substrate. The effect of various parameters such as flow rate, bed height and initial concentration of manganese in the solution was studied. The results of breakthrough time, exhaustion time revealed the influence of flow rate, bed height and initial manganese concentration. The breakthrough time and exhaustion time increased with decreasing the flow rate and initial manganese concentration. In contrast to this, breakthrough time and exhaustion time increased with increasing the bed height. The process involved in the removal of manganese is confirmed as an adsorption process by energy-dispersive X-ray spectroscopic analysis. Fourier-transform infrared spectroscopy analysis revealed the involvement of carboxyl, hydroxyl and amide functional groups as the active binding sites for manganese ion adsorption (Kamarudzaman et al. 2015).

Adsorption of Zinc

The concentration of Zinc above the critical toxicity level, i.e. 200 mg per Kg is reported to be toxic for cotton crops. Excessive amount of zinc in the soil severely affects *Gossypium hirsutum* i.e. cotton plant and results in stunted growth. This toxicity can be reduced by increasing the pH of soil because this pH helps in binding the zinc to the soil organic matter and thus, reducing the bioavailability of zinc to the plant (Williams 1980). Therefore, increase in pH of soil results in eliminating the problem of zinc toxicity which is not practically feasible option.

Another method of ameliorating the zinc toxicity is the application of higher organic matter in the soil (Romney et al. 1977). Shuman and Li (1997) performed a study to find out the effect of lime and mushroom substrate in zinc adsorption from the soil in order to reduce the effect of zinc on cotton plant. A pot experiment was done by using spent mushroom substrate as adsorbent and zinc contaminated soil and results were compared with non-polluted soil. Lime was used as a supplement. In the pot, spent mushroom substrate alone and in combination with lime was reported to reduce the zinc toxicity. There was a steady decline in the zinc toxicity with increasing the lime supplementation. This experiment proved that lime and spent mushroom substrate supplementation is effective in reducing zinc toxicity from the soil where zinc concentration is very high. However, lime supplementation alone is sufficient to remove zinc, when it is present at low concentration.

9.3.5.3 Spent Mushroom Substrate of *Agaricus*

Agaricus species are widely cultivated mushroom on composted and non-composted autoclaved substrate. After harvesting mushroom fruit bodies, a huge amount of spent mushroom substrate is generated which discards as waste. Spent mushroom substrate has also been used as adsorbent in the adsorption of dyes, heavy metals and pollutants.

Adsorption of Lead
Agaricus spent mushroom substrate was used for removing the lead from aqueous solution by Huang et al. (2009) and further, lead removal conditions were optimized by Tagushi method (Taguchi and Konishi 1987). This was performed with four control factors, i.e. pH, contact time, adsorbent mass and initial lead concentration. Huang et al. (2009) investigated the adsorption capacity of spent mushroom substrate and percent removal of lead. The optimum adsorption capacity was reported to be at pH 5, time 5 h, adsorbent biomass 10 mg, initial lead concentration 50 mg/L. However, the optimum condition for removal of lead was reported to be pH 4, time 4 h, sorbent mass 0.010 g, initial lead concentration 50 mg/L. In these conditions, optimum lead adsorption capacity and percent removal was 60.76 mg/g and 80.50%, respectively.

Adsorption of Copper
Agaricus spent mushroom substrate was also used for the adsorption of copper. *Agaricus* spent mushroom substrate was mixed in 20 ml water and then filtered through filter paper. After filtration, mushroom mycelium was collected on filter paper. Prior to use in the adsorption studies, collected mycelium was dried. For adsorption studies, copper solution of 1 g/L, (w/v) was prepared by using copper sulphate penta-hydrate (Siasar and Sargazi 2015). Adsorption, at initial stage was faster compared to that occurred at later stage. The slow rate of adsorption at later stage is possibly due to the low number of available sites for binding with adsorbate or due to the shielding effect (Bishnoi et al. 2007).

The adsorption of copper is related to increase in pH of the solution from 2 to 6 due to the presence of negative charged ions on the surface of biomass. However, adsorption of copper decreases dramatically between pH 6–8 which is possibly due to the formation of anionic hydroxide complexes of the metal ions and their competition with the active sites. Adsorption of copper increases the density of positive charge on the surface of adsorbent at low pH values, which further leads to reduced rate of adsorption due to the repulsive forces. The maximum adsorption capacity of copper ions was reported to be present at pH 6. In this experiment, Langmuir model explained this as non-linear adsorption and suggested that uptake occurs on a homogenous surface by monolayer adsorption without interaction between adsorbed molecules. This experiment sheds a light on the fact that spent mushroom substrate has good efficiency of adsorbing copper ions from the aqueous solutions, especially with low metal concentrations.

9.3.5.4 Modified Spent Mushroom Substrate

The adsorption capacity of spent mushroom substrate can be modified by preparing activated carbon. Tay et al. (2015) prepared the spent mushroom substrate activated carbon by using central composite rotatable design-response surface methodology. In pre-carbonization stage, spent mushroom substrate was soaked in an activating agent i.e. potassium hydroxide. This was followed by drying at 80 °C for 24 h and further, carbonized in muffle furnace. Optimization of activated carbon percent yield can be described by central composite rotatable design-response surface methodology. This method helps in minimizing the use of chemicals and energy in the preparation of activated carbon, which is utmost important to implement the technology for achieving healthy environment in a sustainable way.

Adsorption of Nickel

The spent mushroom substrate was modified in the form of activated carbon by using Box-Nehnken design of response surface methodology. Md-Desa et al. (2016) prepared the activated carbon by spent mushroom substrate using potassium hydroxide as an activating agent. Potassium hydroxide forms the pores in activated carbon due to intercalation of metallic potassium ion in the carbon structure and increases the porosity of activated carbon. For the preparation of activated carbon, the spent mushroom substrate was soaked in 3 M potassium hydroxide for 24 h which was followed by drying at 80 °C for 24 h. This material was carbonized in the furnace at 500 °C with heating rate of 10 °C/min. The produced char was washed with hydrochloric acid and distilled water to remove residual potassium hydroxide and again, dried at 80 °C. The prepared activated carbon was sieved to 150 μm and kept at drying cabinet prior to use. A software generated experimental design was used to assess the effect of preparation parameters of impregnation ratio, and activation time. The potential of activated carbon derived from *Pleurotus ostreatus* spent mushroom substrate was assessed for the removal of nickel. The batch adsorption studies by varying adsorbent dosage, pH, contact time, metal concentration and temperature were determined. The samples were shaken at 125 rpm, filtered through filter paper and analyzed using inductively coupled plasma optical emission spectrometry. In this study, 50% nickel was adsorbed at 0.63 g adsorbent, pH 5–6, contact time 60 min, nickel concentration 50 mg/L and temperature 25 °C. Further, these results were also compared with Amberlite IRC86 resin and zeolite NK3. The result indicated that spent mushroom substrate derived activated carbon have a great potential (51.35%) to adsorb nickel from the water as compared to Amberlite IRC86 resin (39.31%) and zeolite NK3 (34.35%) (Md-Desa et al. 2016). The spent mushroom substrate is an economic alternative to adsorb nickel from waste water.

9.3.5.5 Super Adsorbent Preparation from Spent Mushroom Substrate

A super adsorbent was prepared by Ding and Gong (2013) using spent mushroom substrate. Spent mushroom substrate from the mushroom bed is, generally, obtained in the thick- slurried form with 80% water content. For the preparation of super-adsorbent, spent mushroom substrate was allowed to air-dry to reduce its moisture content up to 12%. This was followed by crushing into fine powder and passed through 100-mesh sieve in order to get particles of uniform size. Now, spent mushroom substrate along with ammonium persulfate, acrylic acid, N,N-methylene-bisacrylamide, water and solution of 40% sodium hydroxide were added into heat resistant bottles. This formed a suspension of 200 g in the bottle. After this, bottles were placed in a microwave oven. The whole mixture was heated for 8 min at low-grade-firepower till the porous hydrogel was formed. The gel was spread on an aluminum plate and dried in a vacuum oven to reduce the water content up to 9%. Again, the resin was passed through a 20-mesh screen. This material acted as a good quality adsorbent and further, adsorption strength and gel strength increased with an increase in the spent mushroom substrate ratio. The speed of adsorption was not much affected by ammonium persulphate dosage unlike spent mushroom substrate ratio. Scanning electron microscopy revealed the presence of multilayered and loose particles in the prepared super adsorbent because spent mushroom substrate particles interfere in the continuity of composite resin. The spent mushroom substrate particles distribute uniformly in the acrylic resin and form sub-microscopically homogenous composites (Ding and Gong 2013). This super adsorbent has been produced successfully, however, not used in pollutant adsorption studies to till date.

9.3.6 Adsorption of Dyes

Dyes are considered as one of the toxic pollutant, released from various industries. During the process of dyeing, about 10–20% of dyes is not utilized which releases with the effluent and reaches the water bodies. These discharges increase the biological oxygen demand and chemical oxygen demand of the water bodies and make them unsuitable for use. The dyes are complex molecules and therefore, not efficiently degraded by bacteria (Singh et al. 2013). The partial degradation of dyes leads to the production of toxic and mutagenic compounds like aromatic amines (Lade et al. 2015). Fungi possess a variety of enzymes that helps them to grow in a variety of environmental conditions. Moreover, live or dead biomass of fungi can adsorb a variety of pollutants. Consider this fact, fungal culture bearing spent mushroom substrate is used as adsorbent for dyes by many researchers (Toptas et al. 2014; Yan et al. 2015).

9.3.6.1 Spent Mushroom Substrate of *Agaricus bisporous*

The spent mushroom substrate of *Agaricus bisporus* was used for the dye adsorption. Toptas et al. (2014) developed the procedure to use spent mushroom substrate of *Agaricus* for adsorption of dyes. The collected *Agaricus* spent mushroom substrate was washed with water and then dried in an oven at 60 °C overnight. This was followed by grinding of spent mushroom substrate in fine particles of 0.2 mm or lesser. The characterization of spent mushroom substrate revealed the presence of chitin in the substrate (Toptas et al. 2014). This adsorbent was used in decolorization studies of Acid Red 111 and Basic Red 18 and Levafix Braun E-RN dyes in batch process. The dyes solutions were prepared in flasks and pH of the dye solution was adjusted with dilute hydrochloric acid and sodium hydroxide using pH meter. The spent mushroom substrate was added to the dye solution and then left at room temperature. After the fixed time intervals, samples were withdrawn and filtered to separate adsorbent and analyzed for absorbance at 418 nm for Levafix Braun E-RN and 504 nm for Acid red 111 or Basic red 18. The conditions were optimized for pH, contact time and amount of adsorbent. pH has an important role in adsorption of dyes. The effect of pH on the Acid red 111 dye adsorption by spent mushroom substrate was tested for a pH range from 2 to 6 and for different contact times and maximum uptake of Acid red 111 was reported at pH 3. The equilibrium was reached after 6 h depending on pH of the solution. pH of the solution affects both surface charges of spent mushroom substrate and dyes; and solubility of dyes and their colour in solution. Further, pH influences the ionic interaction between adsorbent and adsorbate due to its effect on the charge. At lower pH, the amino groups of chitin in spent mushroom substrate possess negative charge due to which excess hydronium ions are present on the surface of spent mushroom substrate. These negatively charged ions of spent mushroom substrate can bind with the cations of dyes. Hence, the adsorption of dyes on the surface of spent mushroom substrate occurs due to ionic interaction. The dye binding ability of chitin is not affected by changing the pH in the range of 2–7 because chitin remains insoluble and unaffected by the presence of protonated amines. At pH 3, contact time of 2 h was required to achieve equilibrium. Depending on pH, maximum time required to achieve the equilibrium is 6 h. With increasing the amount of spent mushroom substrate from 0.05 to 1.0 g to fixed dye concentration, i.e. 100 mg/L, rate of adsorption increased and 0.2 g was found to be the optimum amount of spent mushroom substrate. Initially, dyes adsorption efficiency was reported to increase with an increase in the amount of adsorbent up to 0.2 g due to increase in the availability of adsorption sites. However, the efficiency of adsorption did not increase beyond this amount (Toptas et al. 2014).

In the case of adsorption of Levafix Braun E-RN (LB) dye using *Agaricus* spent mushroom substrate, the pH range 2–5 was assessed in dye adsorption studies. Results of the study showed that the adsorption capacity decreased with increasing pH. The optimum adsorption was found at pH 2 (Toptas et al. 2014).

In case of reactive dyes, a covalent bond is formed between reactive groups of the dye molecule and nucleophilic group within the fibers of spent mushroom substrate. The hydroxyl group of cellulosic spent mushroom substrate, the amino and hydroxyl groups of proteins, and amino groups of polyamides contribute in the dye adsorption process (Toptas et al. 2014).

It is reported in the literature that the equilibrium data fitted well with the Langmuir and Freundlich isotherms in case of acidic and basic dyes. In contrast, equilibrium data fitted well with the Langmuir isotherm model in case of reactive dyes (Toptas et al. 2014). Thermodynamic parameters depicted that adsorption of dyes on spent mushroom substrate is spontaneous and exothermic. Fourier-transform infrared spectroscopy analysis revealed the involvement of hydroxyl, amine and carboxyl groups in the dye adsorption process. Therefore, dye adsorption depends on different parameters such as dye concentration, substrate concentration, pH and temperature.

9.3.6.2 Modified Spent Mushroom Substrate As Adsorbent

Oxalic Acid Treated Spent Mushroom Substrate

The spent mushroom substrate can also be used in modified form in order to increase the adsorption capacity. To enhance its adsorption capacity, spent mushroom substrate can be treated with chemicals. In a study, conducted by Yan et al. (2015) spent mushroom substrate was collected after the harvesting of mushroom fruit bodies and washed thoroughly with running tap water which was followed by rinsing with distilled water several times to remove impurities. The washed spent mushroom substrate was dried in an oven at 85 °C for 6 h. The dried spent mushroom substrate was ground into fine particles and sieved to 60–80 mesh particle size. The dried spent mushroom substrate was treated with 0.6 mol/L oxalic acid solution at 60 °C for 2 h. Then, the oxalic acid was removed by filtration. The filtrate was discarded and the oxalic acid treated spent mushroom substrate was dried initially at 50 °C for 24 h and then by increasing temperature at 120 °C for 3 h. After drying, oxalic acid treated spent mushroom substrate was stored in airtight container. The oxalic acid treated sms was used as adsorbent in the methylene blue (80 mg/L) adsorption experiments with 30 to 300 mg doses at original solution pH. The decolorization of dye solution was assessed at different temperature ranges 303–333 K for 12 h with continuous stirring. Adsorption kinetic experiments were performed by using 100 mg of oxalic acid treated spent mushroom substrate. Then, the flasks were taken out at some intervals for sample withdrawal. The adsorbent was removed by filtration through a 400 mesh nylon screen. The dye concentration of supernatant was measured by UV-visible spectrophotometer. Characterization of untreated and oxalic acid treated substrate by Fourier-transform infrared spectroscopy analysis revealed the stretches and new peaks in the region of 2800–2900 and 1670–1760 cm^{-1} which correspond to C-H stretching vibrations of carbonyl group in the other constituents or in the carboxylic acid, respectively. This shows the modification of surface of spent mushroom substrate in terms of increased number of carboxyl group (Yan et al. 2015). Oxalic acid treatment helps in increasing the number of carboxyl group on spent mushroom substrate which further increases the adsorption capacity.

In the adsorption experiment, conducted by Yan et al. (2015) methylene blue adsorption capacity of oxalic acid treated spent mushroom substrate was analyzed in the pH range of 2–10. The methylene blue adsorption capacity was reported to increase in pH range 2–4. Further, increase in pH did not improve the adsorption capacity. Methylene blue is basic dye and possesses positive charge in aqueous solution while in the same condition; spent mushroom substrate is surrounded by hydronium ions. Hence, methylene blue competes with the hydronium ions for binding sites on spent mushroom substrate and electrostatic repulsion occurs, which prevents the adsorption of methylene blue dye. Carboxylic groups are not deprotonated and ionize at pH below 4 which results in decreased adsorption. Oxalic acid treated spent mushroom substrate possesses negatively charged carboxylic groups that have ability to deprotonate at higher pH. Therefore, at higher pH 6, carboxylic groups are easily deprotonated and carried out methylene blue adsorption process due to electrostatic attraction between negative charged carboxylic group and positive charged dye. The oxalic acid treated spent mushroom substrate can also interact with methylene blue dye due to hydrogen bonds formation (Yan et al. 2015).

The effect of contact time and initial concentration revealed the maximum adsorption within the first 60 min., equilibrium was achieved in 120 min at dye concentration of 100 mg/L and thereafter, no adsorption or little adsorption occurred. Similar types of results were found at other concentrations. Again, this reveals the presence of a huge number of adsorption sites on oxalic acid treated spent mushroom substrate. When time is increased, the available site for adsorption decreased. With the increase in initial methylene blue concentration ranging from 40 to 100 mg/L, the driving force for the mass transfer between adsorbent spent mushroom substrate and dye solution increased which resulted in the increased adsorption capacity. It was also reported that equilibrium adsorption capacity decreases from 128.2 to 19.7 mg/g with increasing the amount of oxalic acid treated spent mushroom substrate from 25 to 200 mg. To study the effect of temperature on adsorption, equilibrium adsorption capacity was reported to increase from 89.3 to 97.2%. The lower temperature was found to favour the adsorption process. Boyd's film-diffusion method elucidated the mechanism of methylene blue adsorption by external mass transfer. The thermodynamic parameters indicated that the methylene blue adsorption process by oxalic acid treated spent mushroom substrate is exothermic, feasible and spontaneous. This study sheds the light on the fact that oxalic acid treated adsorbent can be used successfully for the adsorption of dyes and therefore, can be used for the treatment of effluent possess methylene blue dye (Yan et al. 2015).

Recently, spent mushroom substrate co-pyrolyzed with *Saccharina japonica* i.e. kelp seaweed biomass and used for adsorption studies of crystal violet dye by Sewu et al. (2017). The potential of this co-pyrolyzed biochar was compared with biochars having different compositions: (i) biochar from spent mushroom substrate alone (ii) biochar prepared by adding 10% kelp extract to spent mushroom substrate (iii) biochar from kelp extract added spent mushroom substrate. The results of this study showed that biochar from kelp extract containing spent mushroom substrate had the highest dye adsorption capacity with highest fixed carbon content

(70.60%) and biochar yield (31.6%). Spent mushroom substrate co-pyrolyzed with 10% kelp extract was also reported to be a good adsorbent with 2.2 times higher adsorption capacity i.e. 610.1 mg/g than spent mushroom substrate used alone i.e. 282.9 mg/g. Spent mushroom substrate co-pyrolyzed with 10% kelp extract had high ash content, abundant functional groups as revealed by Fourier-transformed infrared spectroscopy and coarse surface morphology. Langmuir model of adsorption is well fixed to the adsorption data (Sewu et al. 2017). This study shows that the adsorption potential of spent mushroom substrate can be increased by using kelp seaweed extract.

9.3.7 Adsorption of Pollutants

Industrial and agro-industrial activities lead to the release of effluent in the water bodies. This effluent is loaded with a variety of chemicals, dyes or pollutants which poses adverse effect on the environment and living beings. The natural remediation process is slow and depends on the presence of microbes in soil. The supplementation of soil and water with spent mushroom substrate can be useful in the remediation of pollutants.

9.3.7.1 Polycyclic Aromatic Hydrocarbon Degradation by Spent Mushroom Substrate of *Agaricus*

Polycyclic aromatic hydrocarbon is a contaminant, discharged by many industries, in the environment. Many polycyclic aromatic hydrocarbons are toxic, mutagenic and carcinogenic. These are lipid soluble and readily absorbed by gastrointestinal tract of mammals and remains in body fat (Abdel-Shafy and Mansourb 2016). Hence, it needs to be removed from the environment. Recently, García-Delgado et al. (2015) reported the use of spent mushroom substrate of *Agaricus bisporous* in polycyclic aromatic hydrocarbons remediation from soil. To analyze the effect of *Agaricus* spent mushroom substrate in terms of type or density of microbial population on polycyclic aromatic hydrocarbons removal, it was amended in autoclaved soil and un-autoclaved soil. First set was prepared in the autoclaved soil in order to assess the effect of indigenous microbial population on the spent mushroom substrate supplemented soil. This data provided the comparison of impact of indigenous soil microflora on the bioavailability of polycyclic aromatic hydrocarbons; and the remediation potential of spent mushroom substrate and indigenous microbes. Results indicated that naturally occurring indigenous microbial population is ineffective in removing polycyclic aromatic hydrocarbons. Therefore, soil was amended in two ways by using spent mushroom substrate. Firstly, spent mushroom substrate was used directly without treatment. Secondly, spent mushroom substrate was applied after sterilization and bioaugmented with *A. bisporus* in order to find out the use of spent mushroom substrate as a microbial carrier. Polycyclic aromatic hydrocarbon removal efficiency of spent mushroom substrate was 17%. No significant difference was reported to be present in terms of number of rings degradation. The bioaugmented *Agaricus bisporus* to sterilized spent mushroom substrate showed the most efficient degradation rate i.e. 29% as compared to spent mushroom compost alone i.e. 21%. Results showed that spent mushroom substrate bioaugmented with fresh *Agaricus bisporous* has great potential in removing the polycyclic aromatic hydrocarbons and it can be used as carrier molecule (García-Delgado et al. 2015).

This experiment showed that spent mushroom substrate has the highest potential in removing polycyclic aromatic hydrocarbons and therefore, can be used as a potent adsorption tool.

9.3.7.2 Pesticide/Fungicide Adsorption by Spent Mushroom Substrate

Pesticides are toxic chemicals, however, used to control the pest in the agricultural field. When pesticides used in an uncontrolled and unrestricted way to control the pest, they accumulate in the environment. They produce adverse effects in the living beings like toxicological effects, neurological disorder, cancer and hormonal disorder, fetal development. Hence, the use of pesticides must be controlled and strategies are required to remove them from the environment.

Recently, Álvarez-Martín et al. (2016a) performed the experiment on the adsorption of polar and non-polar pesticides/fungicides by spent mushroom substrate. In this study, cymoxanil and pirimicab were used as polar pesticides and tebuconazole and triadimenol were used as non-polar pesticides. The spent mushroom substrate was applied to the soil in different amounts that varies between 2 and 75%. The spent mushroom substrate amended soil showed 90% adsorption of non-polar pesticides. However, adsorption was only 56.3% for polar pesticides. Adsorption efficiency for non-polar pesticides was reported to increase with increasing the amount of spent mushroom substrate in soil. In contrast, such type of increment was not observed in the case of polar pesticides. The possible reason of this was indicated by increase in organic carbon content of the soil by spent mushroom substrate supplementation. Therefore, spent mushroom substrate can be used as a tool to adsorb non-polar pesticides from the soil and help in removing them.

The spent mushroom substrate can be used to immobilize pesticides when it is applied to the soil. The spent mushroom substrate is rich in organic matter and therefore, it can adsorb pesticides and reduces their bioavailability. In a study, conducted by Herrero-Hernández et al. (2011) for tebuconazole distribution in soil was assessed in the soil depth upto 50 cm after 124, 209 and 355 days of application of spent mushroom substrate. The study revealed the higher level of fungicide in the deep layer of amended soil compared to non-amended soil. This was possible due to the effect of organic matter of spent mushroom substrate on the soil. The spent mushroom substrate was reported to bind with the pesticide to immobilize it and further, prevents its spreading in the soil. Application of spent mushroom substrate and fungi together in the field requires validation of data by comparing the field data and laboratory data in order to prevent water and soil contamination (Herrero-Hernández et al. 2011). This also prevents the leaching of pesticides in soil and ground water. Thus, the spent mushroom substrate is an important tool not only to adsorb the pesticides, but also to degrade them by producing a variety of enzymes.

Further, the efficiency of spent mushroom substrate in the adsorption of linuron, diazinon and myclobutanil was also compared with sewage sludge and grape marc by Rodríguez-Cruz et al. (2012). The spent mushroom substrate was found to be more effective for myclobutanil pesticide adsorption while grape marc was reported to be effective for linuron and diazinon (Rodríguez-Cruz et al. 2012). Therefore, spent mushroom substrate can be used for adsorbing pesticides from the soil, however, it depends on a variety of factors which affects the adsorption of one pesticide not the other. These factors need to be investigated in detail and considered in order to apply spent mushroom substrate in the field.

The efficiency of spent mushroom substrate as an adsorbent of fungicides was evaluated by Sánchez-Martín and Rodríguez-Cruz (2012). In this study, different types of spent mushroom substrate were used with eight different fungicides. In fungicide adsorption studies by spent mushroom substrate, non-linear sorption isotherms were observed. Pre-adsorbed and post-adsorbed spent mushroom substrate was analyzed by Fourier-transform infrared spectroscopy and changes in peaks and bands revealed the active groups involved in the adsorption process. The spent mushroom substrate also showed very low potential to desorb the fungicides (Sánchez-Martín and Rodríguez-Cruz 2012). In a laboratory experiment, the efficiency of *Agaricus* spent mushroom substrate was assessed for carbendazim and moncozeb pesticides. The spent mushroom substrate was sterilized and used as carrier after loading with *Trichoderma* sp. and *Aspergillus* sp. (set 1). Another set (set 2) was loaded with *Trichoderma* sp., *Aspergillus* sp. and a bacterial isolate. The highest degradation of mancozeb was achieved with set 2 while the highest degradation of carbendazim was achieved with set 1 in 15 days of incubation at 30 ± 2 °C. The possible reason for this is the production of lignocellulolytic enzymes produced by fungi to degrade carbendazim. In spent mushroom substrate-amended soil, adsorption of fungicides results in decrease bioavailability of fungicides (Álvarez-Martín et al. 2016b).

Herrero-Hernández et al. (2015) reported the effect of spent mushroom substrate supplementation on the removal of azoxystrobin fungicide in laboratory conditions and natural field conditions with and without spent mushroom substrate supplementation. The spent mushroom substrate supplementation helps in more adsorption of fungicide from the soil compared to non-supplemented soil. Bioavailability of fungicide and its immobilization depends on the supplementation of soil with spent mushroom substrate. The fungicide showed a stimulatory effect on the dehydrogenase activity of soil. The spent mushroom substrate supplementation or non-supplementation directs the adsorption of azoxystrobin fungicide. There are significant differences in the behavior of fungicide in two conditions i.e. laboratory conditions and field condition. In laboratory conditions, the dissipation of fungicide much slower than that in field condition. Therefore, it is suggested to perform the experiment in field condition to derive any conclusion regarding the application of spent mushroom substrate.

The fungicide adsorption depends on rate of spent mushroom substrate amendment, use of composted and/or fresh spent mushroom substrate, incubation time. The effect of the addition of fresh and composted spent mushroom substrate to the soil was analyzed for penconazole and metalaxyl pesticides. The spent mushroom substrate amendment also leads to the increase in immobilization of metalaxyl (water soluble pesticide) and retention of penconazole (highly hydrophobic). Therefore, spent mushroom substrate supplementation immobilized metalaxyl and considered as good tool for removing metalaxyl from the soil (Marín-Benito et al. 2009). The spent mushroom substrate is a useful tool to increase the organic content and immobilize the pesticides. The spent mushroom substrate amended soil was found to adsorb more pesticide than the non-amended soil. Further, in the next experiment, the effect of composted or fresh spent mushroom substrate was assessed for iprovalicarb, penconazole, metalaxyl and pyrimethanil fungicides. The degradation rate of all fungicides decreased in the composted spent mushroom substrate amended soil. However, it decreased only for iprovalicarb and penconazole in fresh spent mushroom substrate amended soil. The highest mineralization of fungicides was obtained in non-amended soil for metaxyl and penconazole fungicide. However, the fresh spent mushroom substrate amended soil showed the formation of non-extractable residues with metalaxyl fungicide. This study shows the differences in the rate of degradation of fungicide with the fresh and composted spent mushroom substrate supplementation and the characteristics of spent mushroom substrate affecting the degradation process. Fresh and composted spent mushroom substrate has different abilities to adsorb fungicides and therefore, a detailed investigation is required for their application (Marín-Benito et al. 2012).

9.3.7.3 Adsorption of Antibiotics by Spent Mushroom Substrate

Sulphonamides are very popular antibiotics use to treat various diseases of human beings and animals. The treated patients or animals secret these antibiotic with excreta. These antibiotics reach the water bodies with run-off water; and agricultural field due to the application of animal manure. In China, spent mushroom substrate was used for the treatment of sulfa antibiotics containing water. Recently, experiment was performed in laboratory conditions by Zhou et al. (2016). For this purpose, spent mushroom substrate was collected and soaked in distilled water for 24 h, then washed, filtered and dried in an oven at 35 °C for 4 h. The dried material were sieved to the desired mesh size i.e. 100–300 μm and stored in airtight container. Experiments were conducted by varying contact time, initial concentration range 0.5–10 mg/L and pH 1–11. The result of this study indicated that the data best fit to pseudo second order kinetic model. Intra-particle diffusion study showed that film diffusion occurred during the adsorption of sulfadrugs on to spent mushroom substrate. Therefore, spent mushroom substrate is a good adsorbent to adsorb the traces of sulfa drugs from waste water (Zhou et al. 2016).

9.3.7.4 Modified Spent Mushroom Substrate for Pollutants Adsorption

Aluminum Hydroxide Coated Biochar for Fluoride Adsorption

Chen et al. (2016) suggested the use of aluminum hydroxide coated spent mushroom substrate biochar for the adsorption of fluoride. Spent mushroom substrate was modified to produce carbonized spent mushroom substrate biochar, which was further coated by aluminum hydroxide. The preparation of aluminum hydroxide-coated biochar was done by using 4 g spent mushroom substrate biochar and 40 ml aluminum sulfate solution. Both were added to the beaker and stirred vigorously at 60 °C. The pH was then adjusted to 5 by using sodium hydroxide and hydrochloric acid solution. This solution was filtered by vacuum filtration and put in the hot air oven at 110 °C for 3 h to coat the spent mushroom substrate biochar with aluminum hydroxide. The coated biochar was washed several times with distilled water in order to remove sodium and sulfate salts and then dried in hot air oven at 100 °C for 5 h. The coated spent mushroom substrate biochar was ground into powder. To keep uniform size particles, biochar was filtered through 6-mesh and then, placed in an airtight container. The coated and uncoated biochar were characterized for adsorption properties. The specific surface area of coated and coated spent mushroom substrate biochar was determined by BET method using the automatic surface area analyzer. A scanning surface image of the coated and uncoated spent mushroom substrate biochar was obtained by SEM technique. To analyze the elemental composition of coated and uncoated spent mushroom substrate biochar, energy-dispersive spectrometer was used. An X-ray powder diffractometer was used to analyze the structures and phases of uncoated and coated spent mushroom substrate biochar surface.

This adsorbent was used in the adsorption studies and impact of adsorbent dosage, initial fluoride concentration, contact time, pH, and coexisting fluoride ion adsorption. The adsorbent dosage between 0.4 and 8 g/L, initial fluoride concentration between 5–100 mg/L, contact time of 1–960 min was evaluated in 50 mL centrifuge tubes in a batch experiment. These tubes were kept at shaker which was set at the speed of 300 rpm for 180 min at room temperature i.e. 25 ± 2 °C. The solution was separated by filtration. Fluoride ion concentration was measured by an electrode based method using fluoride ion selective electrode (Chen et al. 2016). In this way, aluminum hydroxide coated spent mushroom substrate biochar was reported to be more effective in removing the fluoride as compared to uncoated spent mushroom substrate biochar. Langmuir isotherm is the best fit isotherm model to show fluoride adsorption. The maximum fluoride adsorption capacity by aluminium hydroxide coated spent mushroom substrate biochar was 36.5 mg/g and due to its application, fluoride concentration was reduced to 1 mg/L from its initial concentration i.e. 10 mg/L (Chen et al. 2016).

The coated spent mushroom substrate biochar was reported to be having fluoride ion adsorption capacity higher than that of other biomass-based adsorbents. Besides this, coated spent mushroom substrate biochar can be used over a wide pH range. It provides great operational advantages which are helpful in transferring this technology to the field. The spent mushroom substrate is generated as waste and has the capacity to remove fluoride; this technique is economic to remove fluoride from the water and hence is a very feasible method to implement.

9.4 Factors Affecting the Process of Adsorption

A number of factors influence the adsorption of metals from the effluents such as pH, temperature, concentration of adsorbent and adsorbate, and bioavailability of pollutants. The bioavailability of metal depends on various factors like buffering capacity, mineral content of the substrate, organic content of the substrate and cation exchange capacity. Besides, the use of living and dead biomass require different requirement for the removal of heavy metals and pollutants. Living biomass requires the optimum conditions for growth like nutrient requirement, pH and temperature, which is a dispensable factor for dead biomass (Gadd 2009).

Keeping all the factors in mind, an efficient method can be developed for the adsorption of heavy metals and pollutants to reduce the risk of exposure of living beings to heavy metals and pollutants (Ayangbenro and Babalola 2017). The factors affecting the adsorption process are discussed here.

9.4.1 pH

The pH is an important factor as it affects the selectivity of spent mushroom substrate. Therefore, it is necessary to maintain desired pH in order to induce the binding of spent mushroom substrate to a variety of pollutants and metals. The selectivity of spent mushroom substrate depends on the functional groups, which may vary according to pH. The binding properties of metal in the solution are also dependent on pH (Dursun 2006) as it also affects the solubility of metal ions in the solution. In order to demonstrate the effect of pH on adsorption capacity, several experiments were conducted with different metals and spent mushroom substrate (Tay et al. 2012; Siasar and Sargazi 2015; Chen et al. 2016).

In a study, the effect of pH was demonstrated on the uptake of copper ions by using different pH ranges 2–8 and found that copper ions adsorption increases with increase in pH values up to 6. The increased pH up to 6 corresponds to the increase number of negatively charged active sites which further facilitates the interaction with positively charged metal ions. At pH 2, the surface of biomass is protonated which exerts repulsive force on metal ions. With an increase in the pH up to 6, pollutants and metals bind to spent mushroom substrate due to electrostatic interaction and saturate the active sites of spent mushroom substrate which exert a repulsive force, resulting in decreased rate of adsorption after attaining a limit. In contrast, at higher pH values, the anionic hydroxides are formed. Siasar and Sargazi (2015) reported the formation of anionic hydroxide at pH 6. In contrast to this, Tay et al.

(2012) reported the formation of insoluble hydroxide at pH 8. Generally, at highly basic condition i.e. pH about 8, anionic hydroxide complexes are formed which competes for active sites and results in the decrease adsorption due to competition between anionic hydroxide and metals for the active binding sites (Vimala and Das 2009; Siasar and Sargazi 2015; Ayangbenro and Babalola 2017).

Similar type of observation was observed for nickel adsorption by spent mushroom substrate in aqueous solution. At low pH, the surface of spent mushroom substrate is negatively charged due to which it attracts protons and surface of spent mushroom substrate becomes protonated. When initial pH rises, the nickel adsorption increases due to deprotonation of binding sites. After saturation of binding sites of spent mushroom substrate with nickel (II), adsorption decreases. The optimum pH value for nickel adsorption is 4.5 which is also the initial pH of the aqueous solution of nickel and therefore, there is no need of adjusting pH (Tay et al. 2011). Similar type of effect of pH on adsorption was observed for lead and cadmium by spent mushroom substrate of *Pleurotus platypus*, *A. bisporus* and *C. indica,* respectively (Vimala and Das 2009) and lead uptake by *P. osteatus* (Liew et al. 2010). Hence, adsorption of cationic metals reduced at very low pH i.e. between 2 and 4 and increases with increase in pH up to 6. Again with increase in pH, adsorption decreases due to insoluble metal hydroxide formation.

In contrast to above, it is also reported that the anionic metal species like platinum chloride chromium oxide, gold cyanide adsorption increases with decrease in pH. These studies proved that the solubility and bioavailability of heavy metals can be affected by the pH values of the solution. Occasionally, adsorption process is not dependent on pH like adsorption of silver ions, mercury ions and gold chloride due to the formation of covalent complexes with nitrogen and sulphur containing ligands (Gadd 2009).

9.4.2 Bioavailability of Pollutants in Natural Condition

In natural condition, bioavailability of pollutant is considered as an important factor in planning the adsorption strategy. For e.g., soil characteristics play an important role in the adsorption of pollutants from the soil by using spent mushroom substrate. Soil properties are affected by the presence of organic matter because organic matter has a strong impact on the cation exchange capacity, buffer capacity, and on the retention and bioavailability of heavy metals. Soil with low organic matter usually found to have a high content of heavy metals which is bioavailable to plants and microbes. In contrast to this, organic content of the soil binds with the heavy metals and make them less mobile and less bioavailable to microbes and plants (Ayangbenro and Babalola 2017). Therefore, idea of using spent mushroom substrate is related to increase the organic content of the soil, which further immobilize metals in the soil due their adsorption and make them unavailable to plants. Therefore, spent mushroom substrate based amendments help in reducing the toxicity of heavy metals by reducing their bioavailability to the plants.

9.4.3 Temperature

Temperature also plays an important role in adsorption of heavy metals and pollutants. The raise of temperature increases the fluidity of liquid due to decrease in viscosity and hence, increases the adsorption. Another reason of high adsorption due to increase in temperature is related to increase rate of diffusion of adsorbate particles into adsorbent. Temperature also affects the stability of metal ions present in the solution (Ayangbenro and Babalola 2017). Therefore, increase in temperature increases the metal adsorption capacity.

9.4.4 Contact Time

Another important factor in the study of metal removal and pollutants removal by spent mushroom substrate is contact time. It is the time to which spent mushroom substrate is exposed to the metal or pollutant. The adsorption is a process in which attaining equilibrium is an important criterion. Adsorption of heavy metals, dyes and pollutants occurs initially at faster speed, however on increasing the contact time the process gradually decreases. After applying spent mushroom substrate to the solution, adsorption of heavy metals or pollutants gradually decreases with increase in the contact time. Initially, a large number of binding sites are available on the spent mushroom substrate to which metal or pollutant binds. However, on increasing the contact time, spent mushroom substrate covered with adsorbate and reduced vacant sites. The remaining vacant sites cannot be occupied further, due to repulsive forces between the molecules of adsorbate and pollutant or metal covered adsorbent (Siasar and Sargazi 2015).

9.4.5 Characteristics of Biosorbent

The most important characteristic of biosorbent includes its porosity. The biosorbent must be porous in order to allow the uptake of metals and pollutants. Secondly, it must possess active functional groups bearing negative charge like alkyl, hydroxyl, or amino compound, aliphatic alcohol, carboxyl and carbonyl groups. The spent mushroom substrate is rich in calcium because calcium salts are used in the preparation of mushroom substrate. These calcium ions can be replaced by the metal ions by ion exchange process during adsorption. This replacement of calcium ions with metal ions can be observed by changing peaks in the Fourier-transform infrared spectroscopy analysis (Tay et al. 2011).

The binding of cations on the negatively-charged surface of spent mushroom substrate may increase adsorption of anions. Occasionally, the binding of cations to spent mushroom substrate may enhance the adsorption of another cation due the pH based buffering effects. This can be understood by the example of adsorption of zinc on the calcium-rich spent mushroom substrate. In the preparation of mushroom substrate, calcium carbonate is used which saturate the spent mushroom substrate with the calcium ions. It is reported that this calcium containing spent mushroom substrate have better efficiency for zinc adsorption (Fourest et al. 1994) because calcium ions are replaced by zinc during adsorption process. The adsorption process also depends on the characteristic and charge of spent mushroom substrate and interference of metals ions. For e.g. some negative charge ions on spent mushroom substrate can increase the adsorption of metals. In contrast to this, presence of carbonate, chlorides and phosphate interferes in the adsorption process due to the formation of insoluble precipitates with metals. For e.g., chloride ions may form complex with cadmium like cadmium chloride, which may influence the adsorption process (Trevors et al. 1986).

9.4.6 Status of Fungal Biomass on Spent Mushroom Substrate

As mentioned earlier, the spent mushroom substrate is an immobilized source of mushroom mycelium. During mushroom cultivation, mushroom mycelium is immobilized on agricultural or agro-industrial wastes. During the mushroom cultivation, ambient conditions are provided to cultivate mushrooms. Therefore, these substrates possess living biomass. This biomass remains viable in spent mushroom substrate even after the harvesting of fruiting bodies. However, mycelium loses its viability when stored for a longer time. After long-term storage, mushroom mycelium can be used as source dead fungi. Besides long-term preservation of spent mushroom substrate, the viability of mycelium is also affected by its modification in any form. Initially, when it is applied immediately after collection, there is need to maintain the conditions in order to maintain its viability. After drying, chemical treatment, or using old/preserved spent mushroom substrate, better adsorption can be achieved without the need of maintaining the conditions like pH, temperature during adsorption process. Live mycelium bearing spent mushroom substrate, usually, adsorbs metal and pollutants on the basis of metabolism-dependent process. However, dead mycelium bearing spent mushroom substrate, treated spent mushroom substrate adsorbs the metals by the metabolism-independent process. This type of adsorption is the result of interaction between pollutant or metal ions and surface of spent mushroom substrate. The mushroom mycelium is composed of chitin and other complex macromolecules. These surface molecules possess negative charge due to the presence of carboxyl, sulfate, phosphate, carbonyl, amino groups. The presence of these groups remains unaffected by living or dead status of biomass. Therefore, the spent mushroom substrate can bind with positive charge metals and involved in metal chelation. In this way, spent mushroom substrate adsorbs metals which are present in the solution (Javanbakht et al. 2014).

9.4.7 Particle Size of Biosorbent

The particle size of biosorbent is an important property to consider for adsorption process. The fine particles have more surface area as compared to coarse particles. Therefore, fine particles can adsorb more compare to coarse particles. The adsorption is not a rate controlling process. It depends on intra-particle mass transfer, which controls the rate of adsorption and therefore, considered as a constraint for the adsorption process (Javanbakht et al. 2014).

9.4.8 Influence of Initial Metal Concentration

The initial concentration of pollutants, dyes, or metals poses a great influence on the adsorption process. Initially, adsorption increases with increase in the concentration of pollutant or metals due to their availability in high amount. There is interference of mass transfer resistance in the adsorption process. However, higher initial concentration of pollutant exerts high driving force to overwhelm the mass transfer resistance between pollutant/metal ions and adsorbents (Gadd 2009). This type of phenomenon for copper ions adsorption was reported by Tay et al. (2012).

9.5 Advantages of Spent Mushroom Substrate As Biosorbent

The spent mushroom substrate is waste from mushroom industry and therefore, it is beneficial to use for adsorption of metals and pollutants. Moreover, it is economic technique to implement in the field. A few studies conducted in the field shed the light on the suitability of spent mushroom substrate for adsorption of pollutants (Herrero-Hernández et al. 2011).

The spent mushroom substrate can be reused, recycled for the adsorption of pollutants (Javanbakht et al. 2014). The adsorption capacity of spent mushroom substrate may be increased by using different chemical treatments and by modifying it in activated carbon form (Tay et al. 2015; Md-Desa et al. 2016). There is also possibility of metal recovery after adsorption of metals on spent mushroom substrate. A detailed study on the metal recovery options will make the use and disposal of spent mushroom substrate, a safer option. Proper utilization of spent mushroom substrate will also reduce the generation of waste from mushroom industry. The spent mushroom substrate can be composted and stored for a longer time with maintaining its sorption capacity. It will not release any toxin which adversely affects the growth of soil microbes and living beings.

9.6 Limitations of Spent Mushroom Substrate As Biosorbent

As mentioned earlier, spent mushroom substrate is generated as waste from mushroom production units. Therefore, it is economic option, if used in natural form, to adsorb the pollutants from the environment. The cost is slightly higher in the cases where a special treatment is given to spent mushroom substrate to modify its properties. The major limitation with spent mushroom substrate is its disposal after adsorption. There is scarcity of reports on the fate of spent mushroom substrate after adsorption. As the spent mushroom substrate is loaded with high amount of pollutants and heavy metals, it need to be treated and disposed in a proper way in order to prevent the spread of its toxicity in the environment. The current options of disposing spent mushroom substrate like incineration and landfill are not feasible option (Javanbakht et al. 2014). Heavy metals loaded spent mushroom substrate may be used for the recovery of metals. The detailed methodology is required to be developed for the extraction of metals and reuse of spent mushroom substrate (Siasar and Sargazi 2015). Another limitation of using spent mushroom substrate for adsorption lies in the differences in the adsorption capacity of different species of mushroom. As mentioned in the aforesaid paragraph, a single species of mushroom do not possess the capacity to adsorb all types of pollutants from the environment. Moreover, there is scarcity of reports on the field scale studies. A laboratory based experiments do not provide complete information about the adsorption of pollutants from the environment because standard conditions cannot be maintained in the environment and interference of indigenous population cannot be avoided. Therefore, a detailed investigation is required for the adsorption of pollutant by spent mushroom substrate in field conditions. There is need of many efforts to improve biosorption process like optimization of process at pilot scale to implement technology.

9.7 Conclusion

In this chapter, the possibility of using mushroom and spent mushroom substrate as green adsorbent have been discussed along with their pros and cons. A detailed review of the adsorption of pollutants using spent mushroom substrate and mushroom revealed their suitability in the adsorption of pollutants. Mushroom and spent mushroom substrate can be modified for enhancing their adsorption capacities. This technology provides a good option for adsorption of pollutants. However, the main problem of using mushroom or spent mushroom substrate is the generation of toxic sludge after adsorption. It is necessary to address and solve the problem of toxic sludge generation and utilization by doing research in this area. The utilization of spent mushroom substrate has high potential to be developed into a sustainable technology. It is an environmental friendly approach for adsorbing pollutants from industrial effluents and soil. Moreover, the utilization of spent mushroom substrate will not only reduce the waste of mushroom farm, but also remove pollutants from the effluent and soil. Therefore, efforts need to be done to implement the technology in the field.

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Chapter 10
Green Adsorbents for Removal of Antibiotics, Pesticides and Endocrine Disruptors

Akeem Adeyemi Oladipo, Ayodeji Olugbenga Ifebajo, and Roozbeh Vaziri

Contents

Abstract The increasing number of pollutants in the environment poses a threat to the safety and health of aquatic species and humans. Particularly, their adverse effects, such as hindering metabolic processes and occupying hormone receptors when consumed by aquatic species and humans is of concern. Here we present an overview on endocrine disruptors, pharmaceuticals, pesticides and hormones, with emphasis on their potential risk of exposure in water, occurrences and environmental fates. Special emphasis is directed to the adsorptive removal of these micropollutants. We review recent developments in raw and modified green adsorbents for adsorption of antibiotics, pesticides and endocrine disruptors from wastewaters.

The major points are the following: several green adsorbents such as plant-based biochar, eggshells and waste fruit peels exhibit comparable adsorptive performance to most commercial adsorbents. Alkaline and acid modification of biochar increases

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its porosity for adsorption of organic micropollutants and oxyanions. Acid modification results in the abundance of carboxyl groups, while alkaline modification increases the hydroxyl groups of biochar. Particularly, nitric acid-modified garlic-based biochar removal capacity for quinolone antibiotics and hydrophobic pesticides, of 128–289 mg/g, was 15 times higher than the unmodified biochar, of 8.5–19.3 mg/g, and comparable with commercial activated carbon, of 32–263 mg/g. Alkaline-modified chicken bone ash exhibits remarkable adsorption (93%) of polar pesticides (carbaryl and oxamyl) compared to 75% removal recorded for hydrophobic pesticides azinphos-Me and chlorfenvinphos.

10.1 Introduction

For decades, investigations into water quality often focus on traditional priority pollutants such as acutely toxic synthetic dyes, heavy metals and industrial chemicals. These traditional pollutants remain a significant threat to the ecosystem and human health. Recently, the presence of a group of unregulated compounds has frequently been detected in surface, ground and drinking water. These contaminants, being considered as '*emerging pollutants*' are typically detected in a concentration range from ng L^{-1} to μg L^{-1} (Pal et al. 2014; Tijani et al. 2016; Rodriguez-Narvaez et al. 2017). The ecotoxicological effects, behaviour and fate of emerging pollutants are currently not well understood, unlike traditional priority pollutants.

Many of the emerging pollutants can transform in the environment and in wastewater by photolysis, microbial degradation and hydrolysis. Sometimes the transformation products are more toxic than the parent compounds, for instance, the photolysis products formed from sucralose and acesulfame, exhibited higher acute toxicity as measured in the Microtox assay (Pal et al. 2014). Also, the emerging pollutants and their transformation products can react with disinfectants in drinking water to form genotoxic by-products (Araujo et al. 2011; Richardson and Kimura 2016). An example includes the formation of the genotoxic compound when iopamidol reacts with chlorine (Duirk et al. 2011).

Generally, the emerging pollutants have been classified into five groups: steroids and hormones, pharmaceuticals, personal care products, surfactants and perfluorinated compounds (Patiño et al. 2015). However, with advancements in the chemical industry, the classification continues to grow as new micropollutants are identified. The emerging pollutants can be released from diffuse sources (agricultural run-off) or point pollution sources such as wastewater treatment plants (Geissen et al. 2015). These emerging pollutants are commonly found in the household products such as lotions, hair products, sunscreens, detergents, pharmaceuticals and food packaging. Hence, they are majorly released into the environment via wastewater effluents. The transport of emerging pollutants is strongly dependent on the properties of the interacting compartments and the emerging pollutants properties such as polarity, volatility, persistence, adsorption properties (Geissen et al. 2015; Aydin and Talinli

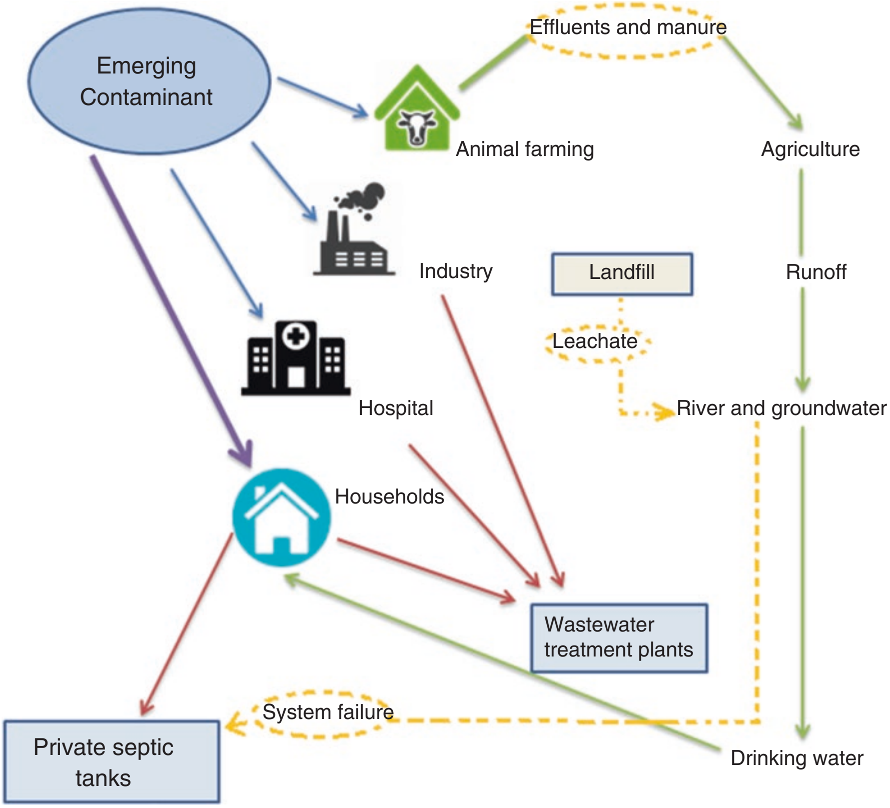

Fig. 10.1 Potential pathways and sources of emerging pollutants into the environment. After use, the emerging pollutants are released into the domestic wastewater and wastewater effluents. These are transported to surface run-off and agricultural run-off which then serve as a source of entry into the environment. (Adapted from Grassi et al. 2012)

2013; Singh et al. 2018). Specifically, the fate of emerging pollutants depends on where they are used and how the products are disposed of. The potential sources and possible pathways of the emerging pollutants are depicted in Fig. 10.1.

To address the emerging contaminant issues, several research laboratories and federal agencies have directed efforts to understand the fate and transport of these micropollutants. Recently, some reviews regarding the removal of some emerging pollutants have been published (Brillas and Sirés 2012; Grassi et al. 2012; Cizmas et al. 2015; Tapia-Orozcoa et al. 2016). Various researchers have adopted various advanced oxidation processes for the elimination of emerging pollutants (Pignatello et al. 2006; Boroski et al. 2009). However, some of these methods are complex, not suitable for small community, requires high investment and maintenance costs and formation of unknown oxidation intermediates etc. (Pouretedal and Sadegh 2014; Oladipo and Gazi 2017). Also, physicochemical methods such as coagulation, volatilization, sedimentation, and filtration and flocculation processes were reported to be unable to efficiently remove personal care products, endocrine disrupting compounds and pharmaceuticals (Grassi et al. 2012).

Conversely, adsorption has emerged as a feasible process for concentrating or elimination of the emerging pollutants. It is relatively superior due to its insensitivity to toxic substances, the simplicity of design and minimal operation cost (Oladipo et al. 2014, Gazi et al. 2018). Few publications have been devoted to reviewing the adsorption of emerging pollutants by various adsorbents (Brillas and Sirés 2012; Patiño et al. 2015; Rodriguez-Narvaez et al. 2017). The scope of this chapter is to explore the adsorption behaviour of unmodified and modified green adsorbents for adsorptive removal of emerging pollutants in waters. Adsorptive mechanism of the green adsorbents towards emerging micropollutants are discussed.

10.2 Removal of Emerging Pollutants by Adsorption

Adsorption processes have been widely applied to eliminate pollutants from liquid media (Oladipo and Gazi 2014; Oladipo et al. 2015; Sekulić et al. 2018). The technique is a surface phenomenon involving the transfer of pollutant (adsorbate) from one phase (e.g wastewater) into another phase (adsorbent). The process occurs when absorbable molecules come in contact with the solid surface; the intermolecular forces of attraction cause some of the adsorbates to be retained at the solid surface. The creation of an adsorbed phase with a different composition from that of the bulk phase constitutes the basis of separation by adsorption technique (Oladipo and Gazi 2017). Adsorption treatment is a simple and cost-effective approach to remove organic pollutants from the aqueous solutions, it is highly insensitive to toxic pollutants and does not produce harmful by-products (Oladipo and Gazi 2015).

If the interaction between the adsorbent and the adsorbate occurs because of chemical bond formation, the process is referred to as *chemisorption*. The adsorbates chemisorbed on the adsorbent surface are hardly removed due to stronger chemical forces. The chemisorption is accompanied by an increase in entropy of the adsorption system and the heat of adsorption of the first monolayer is much stronger than the heat of adsorption of the following layers. Contrary to chemisorption, physisorption occurs if the attraction forces between the adsorbed substances and the solid surface are due to physical bonding. Specifically, these physical interactions are van der Waals forces and, the processes are reversible since the attractions are weak and often occurs close or lower to the critical temperature of the adsorbed species. Under favourable conditions, both processes can occur alternatively or simultaneously (Grassi et al. 2012).

In recent years, many studies were conducted to remove emerging pollutants by adsorption process via commercial adsorbents such as activated carbons, synthetic resins, metal oxides, polymer and inorganic metal frameworks. Activated carbon is widely used for eliminating hydrophobic organic and small-sized contaminants due to its high adsorption capacity. However, its widespread use is often limited due to the high costs, and the adsorption of large-size molecules such as organic polyelectrolytes and pharmaceutical antibiotics on activated carbon is reported to be suppressed due to the existence of size exclusion effect (Li et al. 2017). Another major challenge in the utilization of activated carbon for emerging pollutants removal is the trace concentrations. The low concentrations of emerging pollutants result in low driving force for the adsorption process and thus make the separation of emerging pollutants challenging (Tagliavini et al. 2017).

The common adsorbents reported for the elimination of emerging pollutants are summarized in Table 10.1. Relatively, these adsorbents exhibited a varying degree of success in terms of removal performance, desorption kinetics and reusability. However, high cost, excessive use of chemicals and energy during the preparation of most of these adsorbents is increasingly restricting their widespread use. Therefore, there is great interest in the utilization of eco-friendly, effective and economical materials that offer opportunities to establish adsorption-based separation platforms with flexible control of selectivity.

Increasing focus has been directed toward the development of low-cost alternative adsorbents referred herein as green adsorbents. The green adsorbents may be classified on basis of their (1) availability and synthesis pathway, i.e., (i) green routes synthesized products (ii) natural materials (iii) agricultural/domestic/industrial by-products or wastes; (2) nature, i.e., (i) organic (ii) inorganic material. These green adsorbents are highly abundant and present advantages of cost-effectiveness, the simplicity of use, and biodegradability besides being effective alternative sorbents for eliminating emerging pollutants. Most green adsorbents possess multiple functional groups and effective adsorptive surfaces suitable to chemically and physically adsorbed pollutants (Fig. 10.2).

10.3 Green Adsorbents: Sources, Synthesis and Modification

The use of abundantly available economical adsorbents has been investigated as an alternative to current cost-intensive methods for the removal of threatening pollutants from aqueous solutions. Various approaches have been investigated for the development of cheaper and more effective technologies, both to reduce the quantity of polluted wastewater discharged and to improve the quality of the treated effluent. In recent years, the search for eco-friendly adsorbents with high performance, no hazardous by-products and low cost has been in focus. In this perspective, the use of natural, agricultural, industrial and domestic materials has gained wide attention in recent years due to their abundance availability, eco-friendly characteristics, high uptake capacity, less sludge generation, low-cost and possible regeneration (Crini 2006; Gazi et al. 2018; Oladipo et al. 2017a). These materials are herein referred to as green or eco-friendly adsorbents.

The green adsorbents can also be synthesized via green synthesis route. Conventional synthesis of adsorbents can involve expensive chemical and physical processes that utilize toxic materials with potential hazards (Shah et al. 2015). The toxicity may arise from the stabilizers, organic solvents and the reducing agents that

Table 10.1 Removal capacity of selected emerging pollutants by various adsorbents under varying experimental conditions

Adsorbate	Adsorbent	Experimental conditions	Removal capacity (mg/g)	Reference
Pharmaceutical				
Nalidixic acid	Multi-walled carbon nanotube	V = 50 mL, pH = 7 ± 0.5, T = 25 °C, t = 7 h adsorbent = 1 mg	111.7	Patiño et al. (2015)
	MWCNT-COOH		79.3	Patiño et al. (2015)
Norfloxacin	Carboxylated multiwall carbon nanotube	Adsorbent = 0.05 g, pH = 7, Co = 100 mg/L, T = 30 °C, V = 100 mL	88.5	Yang et al. (2012)
Norfloxacin	Fe-MCM-41	pH = 7, Co = 60 mg/L, T = 25 °C, V = 200 mL	102.9	Chen et al. (2015)
Cephalexin	MgO	V = 10 mL, adsorbent = 0.45 g/L, T = 20 °C, pH = 9, Co = 300 mg/L	500	Fakhri and Adami (2014)
Cefixime		V = 10 mL, adsorbent = 0.45 g/L, T = 20 °C, pH = 9, Co = 100 mg/L	526.3	
Pesticides				
Metazachlor	Tetradecanedioic acid hydrotalcites	pH = 7, time = 24 h, Co = 97 mg/L, V = 30 mL, adsorbent = 20 mg	60.1	Pérez et al. (2017)
Bentazon	Calcined hydrotalcite	pH = 5, Co = 100 mg/L, V = 30 mL, adsorbent = 20 mg, time = 24 h	123.1	
Alachlor			8.9	Kyriakopoulos et al. (2005)
Amitrole	Amberlite XAD-7	pH = 6.5, T = 30 °C, t = 4 h, C_o = 2 mg/L, V = 10 mL, adsorbent = 1 g	7.0	
Prometryn			3.2	
Endocrine disruptors				
Bisphenol A	Nylon 6,6 membrane	T = 30 °C, pH = 7, adsorbent = 0.1 g, Co = 100 mg/L, V = 50 mL	91.3	Jasni et al. (2017)
Bisphenol A	Single-walled carbon nanotubes	Co = 1 μM, t = 4 h; SWCNT dose = 30 mg/L, V = 40 mL, pH = 8.5	13.4	Joseph et al. (2011)
17α-Ethinyl estradiol			35.5	
Bisphenol S	Nano-zeolite secony mobil-5	pH = 4, Co = 5 mg/L, T = 25 °C, adsorbent = 1 g/L, V = 50 mL, t = 2 h	41.0	Goyal et al. (2017)

(continued)

Table 10.1 (continued)

Adsorbate	Adsorbent	Experimental conditions	Removal capacity (mg/g)	Reference
Stimulant & β-blocker drug				
Caffeine	Multi-walled carbon nanotube	T = 30 °C, pH 7.8 ± 0.2, V = 25 mL, t = 5 h	41.6	Sotelo et al. (2012)
	Carbon nanofibers		28.3	
Atenolol	Commercial activated carbon	pH = 6, t = 90 min, T = 25 °C, V = 100 mL, Co = 20 mg/L sorbent = 5 g/L	18.8	Haro et al. (2017)
Propranolol	Ionic liquid iron composite	Co = 50 μg/L; t = 40 min, pH = 9.0, adsorbent = 1.0 g/L and T = 25 °C	0.094	Ali et al. (2017)
p-Chloro-m-xylenol	MIL-101-$(OH)_3$	V = 25 mL, adsorbent = 5 mg, Co = 50 mg/L, pH = 7, t = 12 h, T = 25 °C	79.0	Song and Jhung (2017)
Triclosan	Glycol-electrospun fibrous membrane	pH = 6, Co = 10 mg/L, T = 25 °C, t = 6 h, adsorbent = 100 mg, V = 100 mL	130.0	Xu et al. (2015)
Methylparaben	Magnetic phenyl group nanoparticles	Adsorbent = 10 g/L, T = 25 °C, t = 24 h, pH = 3, Co = 10 mg/L	0.6015	Chen et al. (2017)

MIL-101-$(OH)_3$: Hydroxyl functionalized metal-organic framework
Fe-MCM-41: Fe modified Mobil Composition of Matter no. 41
MWCNT-COOH: Carboxyl modified multi-walled carbon nanotube

are used during the synthesis. Hence, to synthesize green adsorbents, there is widespread interest in using environment-friendly green processes, benign and bio-inspired synthesis route. Recent studies have demonstrated that green based synthesis of adsorbents using plants and microorganisms is an environment-friendly alternative, inexpensive and safe (Oladipo et al. 2017b). There are criteria based on source, wastes, process and performance to consider when selecting green adsorbents for green adsorption. Particularly, to achieve green adsorption, the adsorbents need to be cost-effective, easy to process, abundant and environmentally friendly to dispose of.

Despite the availability of a significant number of publications on the green or eco-friendly adsorbents, their industrial applications are still far from realization due to performance and separation constraints. The modification of green adsorbents to advance their efficiency is increasingly becoming attractive. Various parameters including the pore volume, specific surface area, surface functional groups and pore- size distribution influence the adsorption capacity of adsorbents; hence these parameters may be tailored to have the desired chemical and physical attributes to enhance the adsorbents (Gautam et al. 2014).

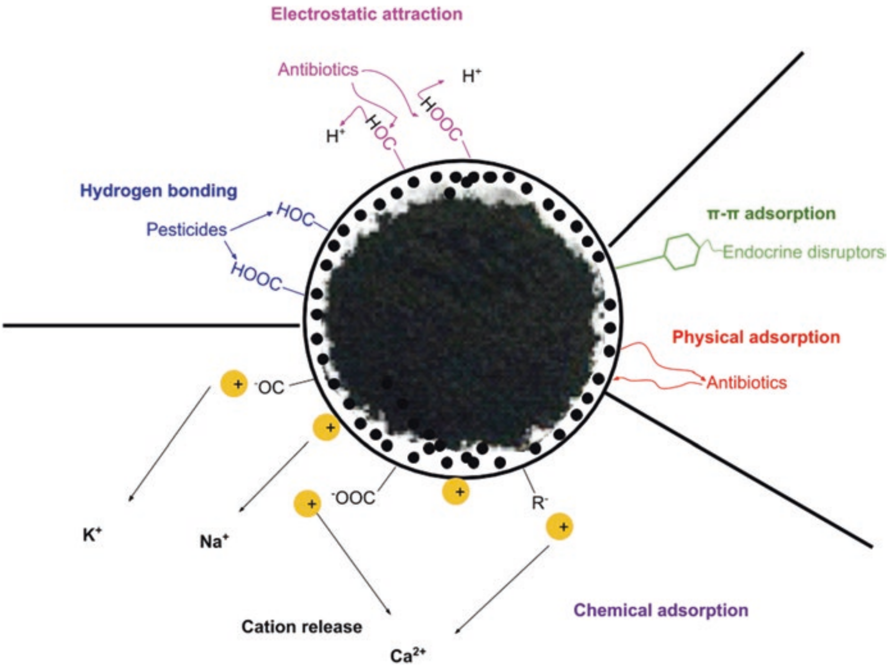

Fig. 10.2 Schematic illustration of adsorption of the organic micropollutant on green adsorbent (biochar). The biochar multiple functional sites are suitable to physically and chemically adsorbed antibiotics, endocrine disruptors and pesticides. Note the release of cations from the biochar surface facilitates the electrostatic interactions with micropollutants

There are numerous reports on the physical (heat, microwave treatments) and chemical modification of green adsorbents. These reports have proved that modification could enhance the removal capacity, separation, regeneration or selectivity of the adsorbents via physical treatment or introducing functional groups on the surface of green adsorbents (Zhao et al. 2017; Oladipo et al. 2017b). Table 10.2 compares the modification techniques of adsorbents with regard to technical aspects.

The modification procedures are achieved via a different mechanistic pathway and thus confer varying functionalities on the adsorbents. The physical modification of adsorbents via steam activation forces high-temperature steam through the pores of the adsorbents which increases the surface area and porosity of the adsorbents (Sizmur et al. 2017). However, Shim et al. (2015) reported that the Cu^{2+} sorption capacity of steam modified biochar was not significantly improved even though the steam activation increased the biochar surface area. Rather, an increase in aromaticity was observed and decreased functional groups. In our lab, we applied steam activation to biochar produced from chicken bones, interestingly, the surface functional groups increased alongside the surface area and sorption capacity. Hence, steam activation appears to be more effective when applied prior to a second modification step that creates functional groups.

Table 10.2 Technical advantages and disadvantages of modification techniques modified from (Gautam et al. 2014)

Modification	Treatment	Advantages	Disadvantages
Biological	Bioadsorption	Prolongs adsorbent bed life by rapid oxidation of organics by bacteria.	Thick biofilm may impede diffusion of adsorbate species
Physical	Heat, steam, microwave	Increases surface area and pore character of adsorbents	May decrease oxygen surface functional groups
Chemical	Basic	Enhances uptake of organics	May, in some cases, decrease the uptake of metal ions
	Acidic	Increases acidic functional groups on adsorbent surface and thus enhances chelation ability with metal species	May decrease BET surface area and pore volume

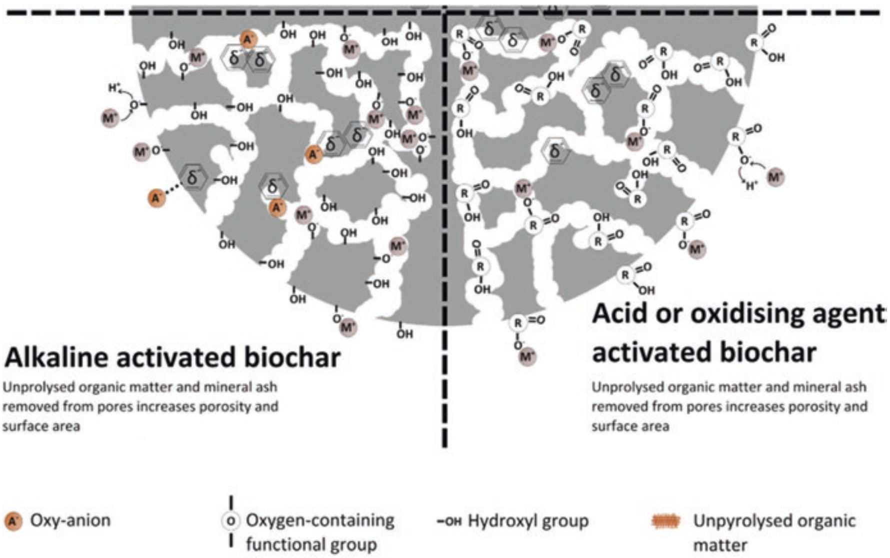

Fig. 10.3 Alkaline and acid modification of biochar increases its porosity for adsorption of metal cations and oxy-anions. Note that acid modification results to abundance of carboxyl groups while alkaline modification increases the hydroxyl groups of the biochar for adsorption of micropollutants. (Adapted from Sizmur et al. 2017)

The chemical modification techniques expose the adsorbents to either alkaline or acidic solutions which create oxygen-containing functional groups via oxidation of the surface (Fig. 10.3). The more oxygenated functional groups on the adsorbent surfaces increase its potential to chemically bind positively charged pollutants through specific adsorption (Sizmur et al. 2017). Hadjittofi et al. (2014) modified cactus fibre derived biochar with HNO_3 to increase the carboxylic groups on the surface of the biochar, the authors reported increased strong Cu^{2+} uptake as compared with the unmodified biochar.

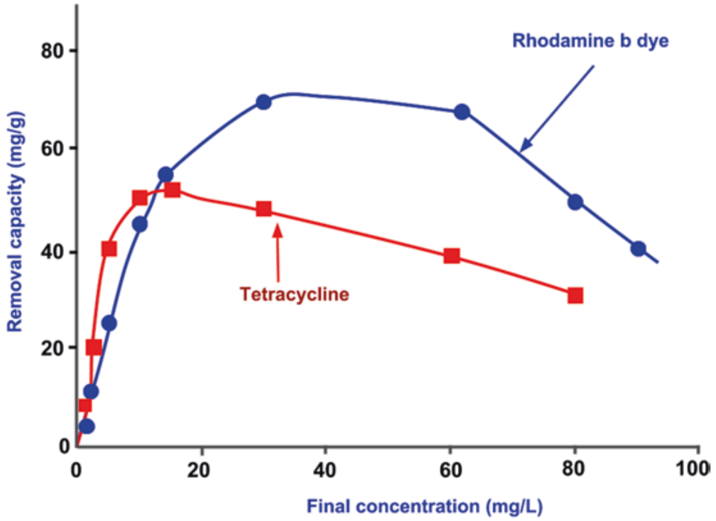

Fig. 10.4 Adsorption of rhodamine b dye and tetracycline antibiotics in a multi-component system (Initial concentration: 100 mg/L, pH: 10, dose: 0.5 g). Note that the concave-shaped curves observed indicate significant competition and interference between the rhodamine b dye and tetracycline with increases in initial concentration. (Adapted from Oladipo et al. 2017b)

10.4 Antibiotics Removal

In recent years, by-products from agriculture and other industries have been identified as viable the sources of green adsorbents due to their abundance and eco-friendliness. Specifically, some previous studies reported the ability of lignocellulosic materials and processed animal wastes to quantitatively accumulate antibiotics (Zhao et al. 2017; Oladipo et al. 2017b). Adsorption of the antibiotics by the green adsorbents is generally achieved via the interactions with the carboxyl and hydroxyl groups. Furthermore, the modification of the green adsorbents is reported to significantly increased the green adsorbent selectivity, separation and removal capacity even greater than that of activated carbons.

Oladipo et al. (2017b) prepared biochars from waste chicken bones for antibiotic (tetracycline) removal from synthetic wastewater. To enhance the application of the as-prepared biochar, the authors prepared magnetic biochar via bio- inspired synthesis route in the presence of magnetite. The magnetic biochar selectivity and sorption capacity for tetracycline in a multicomponent system of tetracycline and rhodamine b dye were significantly higher than the unmodified biochar (Fig. 10.4). Approximately 63.3 and 77.9 mg/g of tetracycline was adsorbed at pH 10 within 180 min contact time with raw biochar and magnetic biochar, respectively. The magnetic biochar was separated rapidly after spent by an external magnet, desorbed easily with base-spiked H_2O and reused without loss in stability or structural integrity after 8 use-reuse cycles, and thus significantly outperformed the unmodified

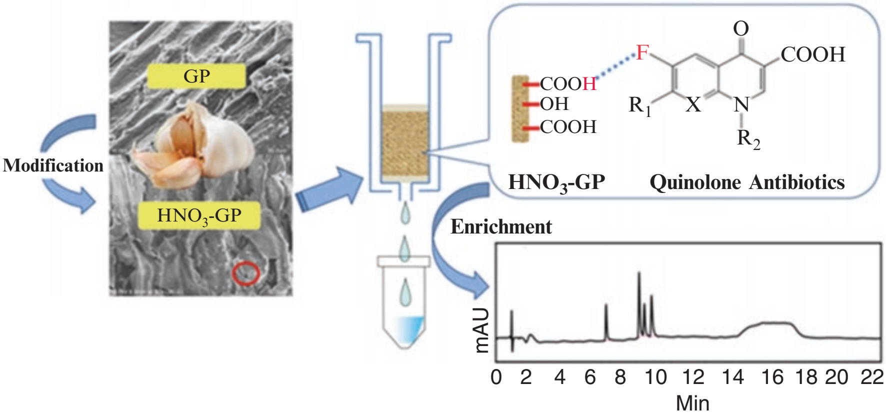

Fig. 10.5 Quinolone adsorptions of garlic peel and HNO_3 modified garlic peel were evaluated. The surface morphology of HNO_3 modified garlic peel exhibited corroded net structure and smaller pore irregularly distributed on the surface compared with raw garlic peel. Note that the modified garlic peel showed a significant improvement in adsorption capacity compared with raw garlic peel. (GP: garlic peel and HNO_3-GP: nitric acid modified garlic peel). (Adapted from Zhao et al. 2017)

biochar. The efficiency of magnetic biochar was investigated for competitive adsorption of rhodamine b and tetracycline antibiotic. By comparing the rhodamine b and tetracycline uptakes in the multi-component system with their corresponding single isotherm results, a decrease of 26.5% for tetracycline and 39.8% for rhodamine b was recorded in the multicomponent system.

The authors reported an operating cost of 1.12 US$/L for the treatment of 5.0 L of 100 mg/L tetracycline, where 97% removal efficiency was achieved. The cost of magnetic biochar is comparatively lower than most commercial resins such as Amberlite IRA-64 and Duolite ES- 468 (21–45 US$). Therefore, magnetic biochar is considered a viable economic alternative adsorbent for treatment of pharmaceutical wastewaters (Oladipo et al. 2017b). Quinolone antibiotics is a commonly used pharmaceutical that has obtained increasing attention because its resistance in the environment can induce undesirable effects on human health and aquatic ecosystems. Zhao et al. (2017) presented a simple modification method of garlic peels by nitric acid to improve its adsorption capacity, and garlic peel and HNO_3 modified garlic peel were evaluated as green adsorbents for removal of quinolone antibiotics, an emerging organic pollutant as shown in Fig. 10.5.

Results revealed that HNO_3 modification increased the total amount of oxygen acidic groups of the garlic peel, which led to the higher affinity for quinolone antibiotics. Under optimized conditions, For Langmuir isotherm model, the calculated maximum adsorption capacity q_m of HNO_3 modified garlic peel was 9.89 mg/g, which was 15 times of the q_m of garlic peel (0.65 mg/g). Furthermore, the authors applied HNO_3 modified garlic peel in solid-phase extraction technique, which was

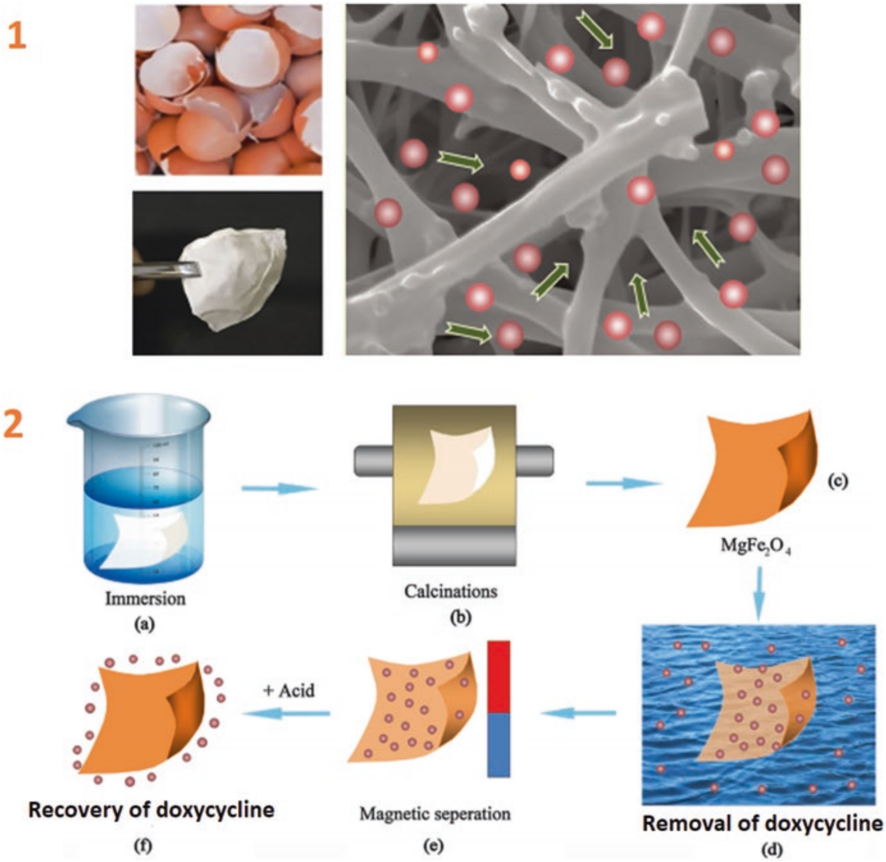

Fig. 10.6 Scheme of the eggshell based green adsorbent and doxycycline antibiotic decontamination and recovery. Part **1** shows the eggshell membrane with a porous structure which permit molecules or ions to diffuse through the frameworks smoothly. Part **2** (*a*); calcination of the infiltrated eggshell membrane at different temperatures to obtain $MgFe_2O_4$ (*b* and *c*); adsorption of doxycycline (*d*); magnetic separation of adsorbed $MgFe_2O_4$ (*e*), and recovery of doxycycline through acid treatment (*f*). (Adapted from Li et al. 2017)

demonstrated to be an environmentally friendly, effective and economical method for the determination of four quinolone antibiotics in water samples.

Li et al. (2017) reported an eggshell membrane-derived $MgFe_2O_4$ as an effective green adsorbent for the capture and removal of doxycycline antibiotic and its subsequent recycling for cyclic utilization. The maximal adsorption capacity of eggshell membrane-derived $MgFe_2O_4$ is about 308 mg/g for doxycycline, and the adsorbed green adsorbent was reused after magnetic separation from water and acid treatment. The authors reported that the eggshell based green adsorbent exhibited 3D framework structure composed of interconnected and penetrated fibres consisting of $MgFe_2O_4$ nanoparticles with plentiful surface oxygen-containing functional groups on their surface as shown in Fig. 10.6. Several recent publications reported that the

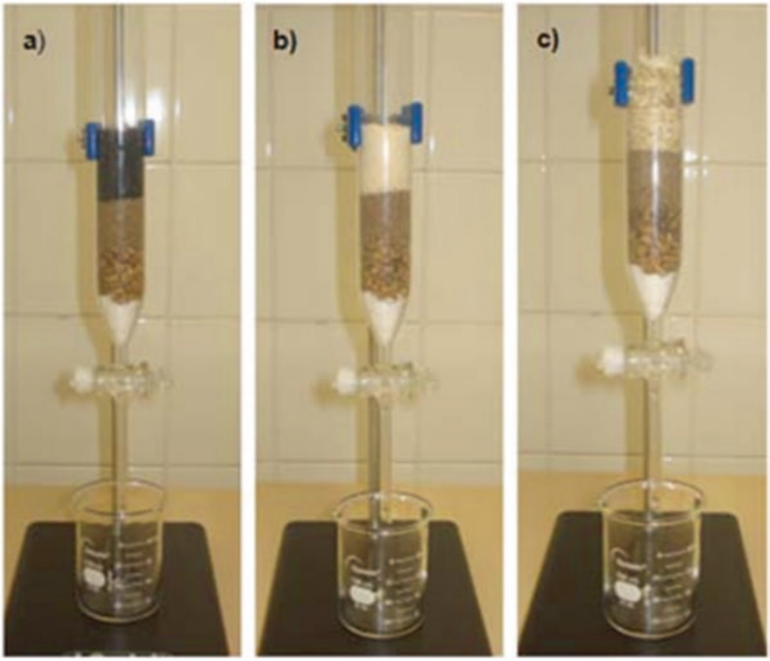

Fig. 10.7 Application of mixture of green adsorbents for removal paracetamol from municipal water. Columns containing real systems in water treatment plants: gravel, sand and activated carbon (**a**); gravel, sand and sugar cane bagasse (**b**); and gravel, sand and vegetable sponge (**c**). The results from studies showed that highest paracetamol removal was achieved in column b and relatively more attractive than other columns in terms of price. (Adapted from Ribeiro et al. 2011)

efficiency of most green adsorbents is relatively comparable and often higher than the synthetic commercial adsorbent for the removal of pharmaceuticals.

Ribeiro et al. (2011) evaluated the efficiency of sugar cane bagasse and vegetable sponge, two natural adsorbents commonly found in Brazil, for retaining paracetamol molecules dispersed in aqueous solutions via the fixed-bed system. After optimisation, the authors obtained relatively high paracetamol sorption capacity for sugar cane bagasse (120.5 μg/g) and vegetable sponge (37.5 μg/g). As shown in Fig. 10.7, the fixed-bed systems contained a mixture of green adsorbents and exhibited higher removal efficiency when compared with commercial activated carbon under similar experimental conditions. Furthermore, the authors applied the mixture of the green adsorbents in real matrices from a municipal plant water catchment enriched with paracetamol at 5 μM. The results from their studies showed that sugar cane bagasse was more attractive than activated carbon in terms of price and efficiency (60% against 45% adsorption, respectively). Thus, green adsorbents can be classified as viable materials to remove antibiotics (paracetamol) from water used for human consumption.

10.5 Pesticides Removal

Several recent publications reported the use of green adsorbents sourced from agricultural wastes, industrial and domestic by-products. Agricultural and industrial wastes such as sludge, watermelon peels, rice bran, carbon slurry, pine sawdust, fly ash, tea leaves can be used as adsorbents for pesticides removal. The research activities relating to green adsorbents, type of pesticides, experimental conditions, and adsorption capacities are reported are summarized in Table 10.3.

Memon et al. (2007) reported the removal of carbofuran and methyl parathion pesticide from water using thermally and chemically treated watermelon peels as a green adsorbent. The experimental results indicated that modified treated watermelon peels are effective adsorbents for the removal of methyl parathion pesticide from water and higher removal efficiency was recorded at acidic pH range. Taha et al. (2014) reported the adsorption of a mixture of 15 different pesticides (with individual pesticide concentrations of 400 mg/L) from water by untreated and phosphoric acid treated biochars and charcoal. The phosphoric acid treated rice straw biochar takes only 120 min to reduce the individual pesticide concentration in water (pH 7) to <0.005 µg/L except for oxamyl, which was reduced to <0.068 mg/L after 24 h. Also, the authors observed that the adsorption percentages of polar pesticides (carbaryl, acetamiprid and oxamyl) were significantly reduced when the water/rice straw biochar ratio was increased from 100 to 500, while those of highly hydrophobic pesticides (azinphos-Me, chlorfenvinphos and flusilazole) were slightly reduced as illustrated in Fig. 10.8.

In our lab, we investigated three different green adsorbents (pomegranate seed powder, calcined cigarette filter and magnetic olive pomace) for the removal chlorpyrifos, endosulfan and deltamethrin. The heat treatment markedly increased the surface area and surface functional groups of the calcined cigarette filter. The removal efficiency was noted to be high for lower concentration (5 mg/L) of chlorpyrifos and 198.8 mg/g uptake was recorded after 6 h treatment time in a pH neutral solution. Also, the endosulfan removal efficiency of the as-fabricated olive pomace (surface area; 658 m^2/g) is relatively comparable (341 mg/g) with that of commercial activated carbon (363.5 mg/g) of surface area; 789 m^2/g. Herein, we concluded that the presence of magnetite on the surface of the olive pomace contributed to the increased uptake of the target pesticide (Oladipo and Gazi 2017).

Bras et al. (1999) investigated the capability of pine bark through fixed bed column to adsorb organochlorine pesticides from aqueous solutions. An average of 97% removal efficiency was recorded from spiked organochlorine water solutions ranging from 1 to 10 μg/L for dieldrin, heptachlor, aldrin and endrin. Also, EL Bakouri et al. (2009a) examined the potential of ecological adsorbents to reduce pesticide contamination of groundwater resources. The authors reported that date and olives stones present high removal efficiency. The experimental results indicated that the solution temperature and pH of pesticide solutions significantly inhibit the adsorption process. The removal efficiency of endosulfan was observed to decrease in the following order: date stones, bamboo canes, olive stones, peanut

Table 10.3 Removal capacity of selected pesticides by various green adsorbents under varying experimental conditions

Adsorbates	Adsorbents	Experimental conditions	Removal capacity	Reference
Carbofuran	Chestnut shells	T = 30 °C, t = 30 min, pH = 6, Co = (0.45–4.5) × 10^{-4} Mol/dm^3	10.8 ± 0.3 × 10^{-6} Mol/g	Memon et al. (2007)
Methyl parathion		T = 30 °C, t = 30 min, pH = 6, Co = (0.38–3.80) × 10^{-4} Mol/dm^3	22.5 ± 0.5 × 10^{-6} Mol/g	
Lindane	Bagasse fly ash	Co = 0–10 μg/L, pH = 6, T = 30–50 °C, t = 60 min	(2.4–2.5) × 10^{-3} μg/g	Gupta et al. (2002)
Malathion		Co = 0–10 μg/L, pH = 6, T = 30–50 °C, t = 60 min	(2.0–2.1) × 10^{-3} μg/g	
Endrin	Date stones	Co = 0.5–20 mg/L, t = 3.5 h, T = 25–45 °C	5.98 mg/g	El Bakouri et al. (2009a, b)
Dieldrin			6.98 mg/g	
Aldrin			6.37 mg/g	
Isoproturon	Lignocellulosic substrate	Co = 0.2–50 μmol/L, t = 4 h, T = 20 °C, pH = 4.8	61.8 g/kg	Boudesocque et al. (2008)
Terbumeton			11.2 g/kg	
Desethyl terbumeton		Co = 0.2–300 μmol/L, t = 4 h, T = 20 °C, pH = 4.8	9.8 g/kg	
Dimetomorph			107.3 g/kg	
Atrazine	Bottom ash	Co = 0.5–7.5 mg/L, t = 210 min, T = 27 °C, pH = 5.8–6.0	0.146 mg/g	Alam et al. (2000)
2,4-Dichlorophenoxyacetic acid			0.13 mg/g	
Simazine	Soil	Co = 200 µg/L, V = 50 mL, T = 25 ± 2 °C, dose = 0.6 g, t = 4 h	3.92 mg/g	Rojas et al. (2015)
Chlorpyrifos			20.2 mg/g	
Chlorfenvinphos			12.4 mg/g	
Trifluralin			20.2 mg/g	
Atrazine	Eucalyptus bark biochar	V = 10 mL, t = 24 h, dose = 10 mg, Co = 10 µg/mL, T = 27 °C	511.3 mg/g	Mandal et al. (2017)
Imidacloprid	Rice straw biochar		1706 mg/g	

(continued)

Table 10.3 (continued)

Adsorbates	Adsorbents	Experimental conditions	Removal capacity	Reference
Thiamethoxam	Chestnut shells	V = 50 mL, dose = 1 g, t = 48 h, T = 25 °C, Co = 10–30 mg/L	14.31 mg/g	Cobas et al. (2016)
Acetamiprid			4.69 mg/g	
Imidacloprid			8.51 mg/g	
Paraquat	Spent coffee grounds	V = 50 mL, pH = 7, Co = 0.2 g/L, dose = 20 g/L, T = 27 °C	27.87 ± 1.57 mg/g,	Pavlović et al. (2014)
Deltamethrin	Pomegranate seed powder	V = 20 mL, dose = 1.5 g, t = 8 h, T = 25 °C, Co = 5–50 mg/L	134.9 mg/g	Authors
Chlorpyrifos	Calcined cigarette filter		198.8 mg/g	
Endosulfan	Magnetic olive pomace		341 mg/g	

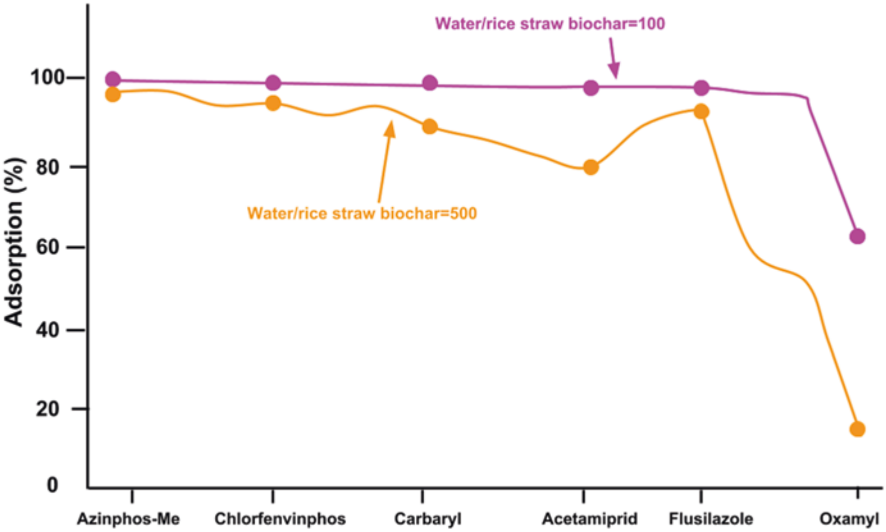

Fig. 10.8 Adsorption percentages of the pesticides mixture on phosphoric acid treated rice straw biochar at different water/biochar ratio. Note that as the water/rice straw biochar ratio increased, the competition of water molecules for the polar functional groups on the biochar increased leading to lower the competitive adsorption of the polar pesticides (carbaryl and oxamyl) compared to hydrophobic pesticides (Azinphos-Me and Chlorfenvinphos)

shells, avocado stones, *O. compactum.* Ahmad et al. (2010) compiled a range of green adsorbents for the removal of pesticides, however, a significant amount of these green adsorbents was tested via the batch system and there is limited literature on the actual cost of utilizing the green adsorbents in a practical sense. Hence, more work and studies are required to cover the knowledge gap regarding utilization of green adsorbents to eliminate pesticides in continuous column or fixed bed adsorption system.

10.6 Removal of Endocrine Disrupting Chemicals

The substances interfering with the hormone system of human beings and animals are considered as an issue of increasing interest in the public. The substances causing endocrine disruption can be grouped into two classes including natural sexual hormones (estrogens, progesterone and testosterone) and xenobiotic substances including synthetic hormones as the contraceptive 17α-ethinylestradiole (Clara et al. 2004; Sotelo et al. 2012). There is an urgent need to develop effective techniques for the rapid removal of endocrine-disrupting chemicals from aqueous solutions.

Clara et al. (2004) investigated the adsorption of bisphenol-A, 17β-estradiole and 17α-ethinylestradiole by activated and inactivated sludge from wastewater treatment

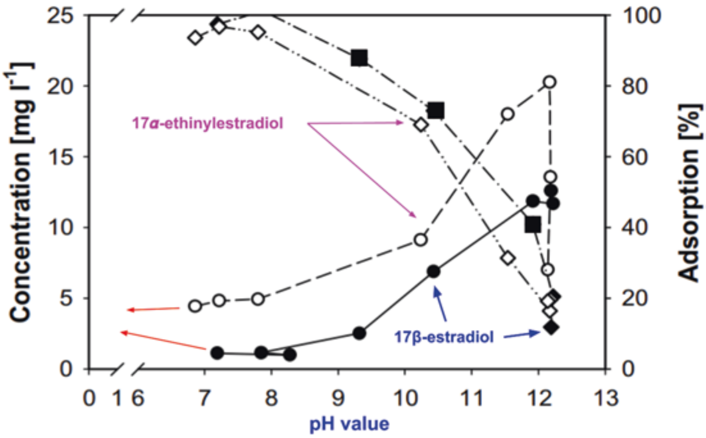

Fig. 10.9 The concentrations (mg/L) of the investigated endocrine-disrupting chemicals and relative adsorbed amount (%) to inactivated sludge as a function of solution pH. Note that at high pH values beyond 9, the adsorption efficiency of inactivated sludge decreased remarkably and concentration of 17α-ethinylestradiol in the liquid phase was higher than values observed for 17β-estradiol. (Adapted from Clara et al. 2004)

plants. The authors reported that all substances showed a high adsorption affinity to the adsorbent despite the utilization of very high initial concentrations, no saturation level was reached. The adsorption was also found to depend on pH as illustrated in Fig. 10.9. Importantly, desorption occurred at high pH values and the adsorptive capacity of the inactivated sludge decreased remarkably.

Jung et al. (2013) investigated the potential of commercialized powdered activated carbon and chemically activated biochar produced under oxygenated (O- biochar) and oxygen-free (N-biochar) conditions for green adsorption the adsorption of endocrine-disrupting chemicals: bisphenol A, atrazine, 17α-ethinylestradiol and pharmaceutically active compounds; sulfamethoxazole, carbamazepine, diclofenac ibuprofen. Oxygen-free biochar exhibited the higher adsorption capacity compared with the oxygenated biochar, suggesting that oxygen-free biochar derived from loblolly pine chip is a promising green adsorbent for environmental remediation of antibiotics and the commonly detected endocrine disruptors. As illustrated in Fig. 10.10, the solid-state NMR spectra of the oxygen-free biochar indicated that it has relatively higher aliphatic carbon fractions; paraffinic or alkyl and less condensed aromatic structure which agrees well with its higher H/C and O/C ratios than those of oxygenated biochar. Implying that the polar functional groups of the oxygen-free biochar contributed significantly to the adsorption of endocrine disruptors and antibiotics (Jung et al. 2013).

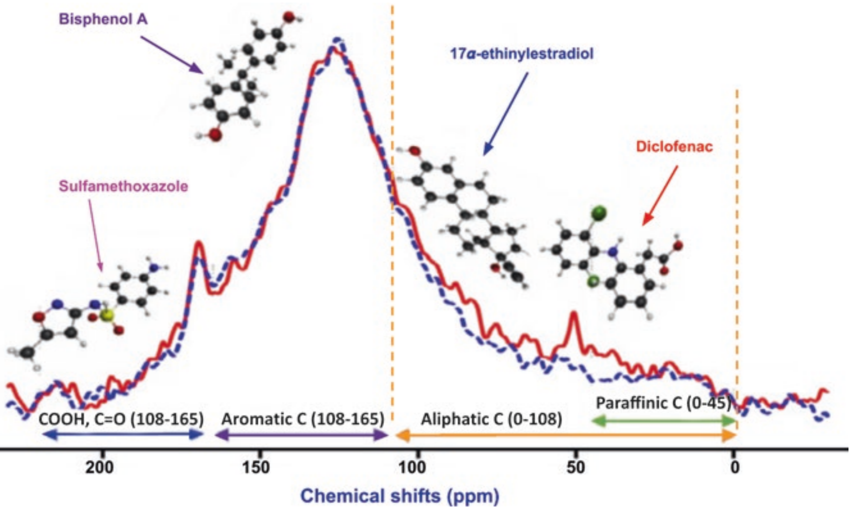

Fig. 10.10 Solid-state NMR results of the adsorptive behavior of oxygen-free biochar for the elimination of selected endocrine disrupting compounds and pharmaceuticals. Note that the oxygen-free biochar consisted of higher polarity moieties with more alkyl (0–45 ppm), methoxyl (45–63 ppm), O-alkyl (63–108 ppm), and carboxyl carbon (165–187 ppm) content than oxygenated biochar. The oxygen-free biochar has a less condensed aromatic structure suitable for bisphenol A and sulfamethoxazole adsorption and carbohydrate functional groups suitable for diclofenac antibiotics removal. (Modified from Jung et al. 2013)

10.7 Engineered Green Adsorbents for Removal of Emerging Pollutants

Lately, there is an increasing interest in monitoring emerging pollutants, unfortunately, little agreement exists on the list of substances to be monitored (Rodriguez-Narvaez et al. 2017). Hence, it becomes difficult to design effective treatment technologies for the elimination of emerging pollutants. To address this issue, highly effective, robust and stable eco-friendly adsorbents need to be developed that would suitable for removal of multiple micropollutants. Therefore, the conventional adsorbents need to be engineered to improve their performance and stability.

Sekulić et al. (2018) investigate the ability of the phosphoric acid functionalized *Prunus armeniaca* stones biochar prepared by thermochemical activation to remove heavy metals, naproxen and chlorophenols from aqueous wastes. The engineered biochar was well characterized (Fig. 10.11), and the adsorption mechanism was found to be controlled by particle, film and pore diffusion throughout the entire adsorption period. For a comparative purpose, the engineered biochar significantly

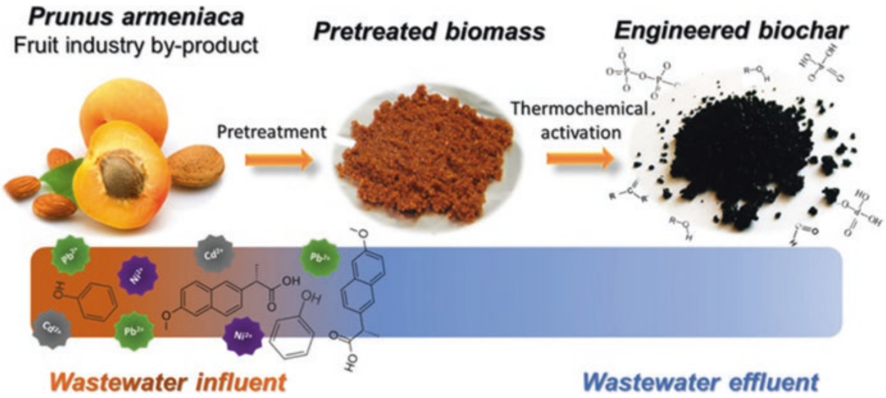

Fig. 10.11 Engineered biochar for hazardous priority and emerging pollutants removal. The production cost and properties suggest that it can be a promising green adsorbent. The biochar functionalization was performed by thermochemical conversion at 500 °C with 50 vol% phosphoric acids. Note that the external surface of the engineered biochar is enhanced with oxygen containing functional groups and suitable for elimination of naproxen from wastewater. (Adapted from Sekulić et al. 2018)

outperformed the conventional biochar under same experimental conditions. The cation-exchange capacity of the engineered biochar increased drastically to 0.571 mmol/g. Also, the surface of the engineered biochar is reported to be rich in chemically reactive phosphoric and oxygen-containing functional groups, which creates a better adsorption structure for varieties of pollutants.

10.8 Perspectives

The use of abundantly available green adsorbents would drastically reduce treatment cost of domestic and industrial wastewater. The green adsorbents have been recognized as viable and promising alternative material. Also, the chemical modification of green adsorbents is another area of concern. If the chemically modified adsorbents or composite adsorbents are not stable, then it is not safe to be utilized. However, less research has been directed to study the stability of composites adsorbents. Therefore, the stability of composite modifications over time should be monitored in future studies as some of the embedded materials in the green adsorbent matrix can leach away if not fully fixed. Leaching tests are needed to address this issue. Specific scenario worthy of investigation is the stability of metal-green adsorbent composites in various pH environments.

Also, to ascertain the readiness of green adsorbents for industrial use, researchers should direct attention to the use of green adsorbents for removal of emerging pollutants in tap water matrix. Investigation of the effect of those major components of tap water matrix on adsorption of emerging pollutants using green adsorbents requires urgent attention. Finally, since the costs of a treatment process is a significant factor in choosing a process, therefore, researchers should direct their attention to the development of small-scale column treatment system and cost-benefit analyses should be included in the publications. The cost-benefit analyses will be useful to determine the actual performance of selected green adsorbents from an industrial perspective.

10.9 Conclusion

In this chapter, the elimination of various micropollutants from wastewater streams by green adsorbents with their shortcomings and efficiency of adsorption are discussed with green chemistry perspectives. Over the last decade, antibiotics, pesticides and endocrine disruptors have been frequently detected in various water streams. Recent research indicated that these micropollutants can induce adverse effects and may cause potential damage to human health. Hence, their removal from water streams is extremely important to environmental safety. While numerous reports regarding micropollutants removal by advanced and conventional water treatment processes are available, the wider utilization of these processes is still limited due to cost and complex technicalities.

Adsorption process has been widely applied to remove lethal compounds from wastewater streams, due to its ease of operation, availability of adsorbents, low power consumption and relatively superior performance. Here, the range of green adsorbents for the removal of various micropollutants is reviewed. The green adsorbents exhibited comparable performance to most commercial adsorbents and could be fully utilized as an alternative material for the elimination of emerging pollutants.

Despite the significant publications on the utilization of green adsorbents, the real applications of green adsorbents from an industrial perspective are still far scanty. Most of the reported studies are performed in the batch process; hence, efforts should be directed toward the use of modified green adsorbents via the continuous flow systems for adsorption of micropollutants in tap water matrix. Finally, the authors wish to direct the attention of the readers to the circular economy model— by configuring the green adsorbents to recover valuable emerging pollutants from wastewater and purify the recovered materials for industrial use.

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Chapter 11
Pillared Interlayered Clays for Pollution Remediation

Prashant Pandey and Vipin Kumar Saini

Contents

Abstract This chapter reviews recent applications of clay-based porous nanomaterials, particularly pillared interlayered clays, to mitigate environmental pollution. Pollutants such as heavy metals and some gases degrade the quality of water and air. This leads acute to chronic effects on human beings. For their mitigation several adsorption or catalysis-based techniques are a viable option for pollution control. Selection of appropriate porous materials with wide applicability, low-cost, natural occurring, and structural regularity is vital. In this context, pillared interlayered clays structures have interesting properties like high surface area, pore volume and extended pore size from micropore to mesopore, higher thermal stability, strong surface acidity and catalytic active substrates/metal oxide pillars. These unique characteristics make pillared clays as candidates for catalytic decomposition by oxidation and adsorption of pollutants from gaseous and aqueous phases.

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11.1 Introduction

Porous materials plays critical role in a number of pollutants removal techniques, both from aqueous or gaseous phase and for catalytic reactions as well. Generally, the porous materials are characterized based on pore size i.e., pore diameter, microporous materials which is less than 2 nm, mesoporous, with pore diameter between 2–50 nm, and macroporous materials, with pore diameter more than 50 nm. The porous materials are integral part of adsorption where the change in concentration of a given substance is observed at the interface in comparison with the neighbouring phases (Dąbrowski 2001; Ghosh 2009; McShane and Lvov 2009). This fundamental process possesses enrichment of guest species at the interface of a certain adsorbent (Hicks et al. 2008; Wu and Zhao 2011). Being universal phenomena, the adsorption has always being one of the most potent processes among several of techniques for the removal of pollutant either from wastewater or air streams (Khan and Ghoshal 2000; Shukla et al. 2002; Ahmaruzzaman and Gupta 2012; Liu et al. 2016). Nevertheless, for these applications scientists have practiced several techniques, such as photocatalysis, catalytic degradation, ion exchange, filtration and membrane separation in amputation of pollutant either from aqueous or air streams (Abumaizar et al. 1998; Gil et al. 2014). But most of these techniques serve with their own limitation and shortcomings. Some of them are energy intensive and others are resource consuming. Whereas, porous materials based technologies like catalysis and adsorption bring into being to be economical as well as efficient. Photocatalysis, catalytic degradation, ion exchange, filtration, and membrane separation techniques shows low efficiency of pollutant removal at trace level which is always being a challenge. To overcome these challenge adsorption based process attracted researchers, because of its convenience, simplicity in design, high affinity towards pollutant and easy operation, low cost up to a certain limit. The wide applicability of adsorption technology in field of environmental pollution control is now well recognized.

The application of adsorption phenomena is used since ancient time. The first time experiment conducted by Scheele in 1773 and Fontana in 1777 for the quantitative observation of gases uptake by charcoal and clays is one of the evidence (Dąbrowski 2001). But their modern applicability is so far, connected with Lowitz's pioneer experimental work where he used the charcoal as an adsorbent for the decolourisation of tartaric acid solutions, showing the uptake of organic impurities. Later on, de Saussure, 1814, found that any porous substance such as sea-foam, cork, charcoal, asbestos can be used to take or adsorb up the gases. Further, he also demonstrated about the exothermic characteristics of adsorption process (Dąbrowski 2001). However, beside of all above mentioned researches the term 'Adsorption' was proposed by Bois–Reymond and Kayser the first one who introduced this term in literature. Since then, lots of research has been demonstrated, explained and updated on this phenomenon at their applicability, mechanism, adsorbate-adsorbent interaction and improvement. In wide application of adsorption technique, this is always applied potentially in field of environmental pollution control.

11.2 Types of Porous Materials

An adsorbent, which is a critical part of adsorption process are found in a large variety. These varieties depends upon their external and internal surface, chemical structure, pores size; pore volume, which ultimately facilitated to adsorb the pollutants (Kruk et al. 2000; Marsh and Reinoso 2006; Khin et al. 2012). On their availability and synthesis, the adsorbents are also classified as natural and synthetic. Natural adsorbents cover charcoal, clay, clay minerals, zeolites and ores (Mohan and Pittman 2007; Wang and Peng 2010; Ali et al. 2012). Whereas, adsorbents prepared from agricultural products and waste, household waste, industrial waste and from other organic or inorganic materials are considered under synthetic adsorbents (Namasivayam and Senthilkumar 1998; Yang et al. 1999; Jain et al. 2004; Ahmaruzzaman and Gayatri 2010; Loganathan et al. 2013). At their early stage of application, Zelinsky in 1915 who firstly suggested the application of activated carbon as porous adsorbents due to their porosity, chemical inertness and high surface area (Dąbrowski 2001). A pioneer work by Barrer and Breck, in 1956 who invented the method for zeolites synthesis, and later in 1960s, synthetic microporous zeolites comes in a role of adsorbent with well-controlled framework structures along interconnected cavities (Masters and Maschmeyer 2011). The zeolites were used in several fields (Corma 1997) but also lead in some disadvantages. One of them is their small pore size such as sodium form of zeolite A has a pore opening of approximately 4 Å which were not suitable for adsorption of large molecules (Song and Rees 2000; Pires et al. 2001). Hence, development and advancement on nanoporous materials gained huge practical importance and it becomes a continuing object of research. As a result, ordered porous materials like MCM-41, SBA-15 with high surface areas, regular pore sizes, large pore volumes, and interconnected frameworks. They possess active pore surface for easy alteration or functionalization (Kresge et al. 1992). Which also serves as a capable adsorbent (Zhao et al. 1998; Xu et al. 2002). Due to pore size these materials are called ordered mesoporous materials particularly known as OMMs, was first time reported as Mobil Crystalline Material, number 41 also called as MCM-41 in 1992 (Kresge et al. 1992). Inspite of their high applicability (Wu and Zhao 2011) these materials are always considered under high cost adsorbents. Thus, researchers always keen on those adsorbents, which possess some of following features such as, (1) high adsorption capacity; (2) large pore volume; (3) low catalytic activity; (4) hydrophobic surface (5) thermal and hydro- thermal stability; (6) an easy regeneration capability, and (7) naturally available (Dubinin 1989; Li et al. 1996; Nicholson 2004; Hiyoshi et al. 2005).

11.2.1 Evolution of Microporous Materials with Larger Pore Size

Alongside with concepts of new, advanced and robust adsorbents, the researchers also worked over low-cost and naturally available materials for adsorption (Bhatnagar and Sillanpää 2010). Inspiration originated from the concept of Barrer and MacLeod for transforming lamellar solids into a porous structure by inserting laterally spaced molecular props between the layers of a smectite clay mineral (Sanabria et al. 2009). Applying this approach to layered clay give rise to a new type of natural and low-cost of adsorbents. In 1950s, Barrer first employed the organic cations and metallic chelates between the layers of clays (Behrens 1993). Later, in 1970, Brindley & Semples and Vaughan & Lussier while working on smectite-type of clay minerals introduced the term ‘pillared’ and ‘pillaring’ (Vaccari 1998). In 1973, due to escalating price of oil and fuel crises (Issawi 1978; Gelb et al. 2002; Hirsch 2008) this concept received much attention. Pillaring concept looked over for the transformation of layered crystalline inorganic compounds to materials having microporosity and mesoporosity (Corma 1997; Linssen et al. 2002; Zhou et al. 2010). Crystalline layered compounds having atoms in layers are cross linked by covalent bonds and those atoms are in adjacent layers are interacted by vander waal force. The single layer is referred as sheet or layer. The guest specie means pillaring agent is used to insert in inter-layered region which are the adjacent layers of layered compound along the retention of layered structure, this is so called intercalation and the modified clay structures originated from pillaring, are called as pillared interlayered clays or pillared clay (Figueras 1988; Vaccari 1999; Gil et al. 2000; Ding et al. 2001; Bergaya and Lagaly 2013). Between 1977 and 1981 pillaring of aluminium in clays was reported by several authors. Initially, researches used organic molecules for pillaring in clays, but they lack in thermal stability and their shape get deformed on heating. This problem was solved on intercalation of clays with inorganic polyoxocations, which results in a new solid nanomaterial with higher thermal stability (Gil et al. 2000) (Fig. 11.1). Along pillaring agent, parent clays also plays a key role in extension of pore size.

For pillaring, the smectite clay group is always preferred over the illite of kaolinite, posses the plastic character and are abundantly available. Bentonite clay falls under this group which is an aluminium phyllosilicate, contains mostly of montmorillonite clay mineral. Bentonite is rich in trioctahedral smectite, in ratio of 2: 1, where, layer of alumina octahedral sheet is sandwiched between two layers of tetrahedral silica shown in Fig. 11.1 that favours isomorphous substitution. Hence, this establishes bentonite clay as a good parent material for synthesis of pillared interlayered clays. The clay like montmorillonite can be found in a number of soils and exist abundantly. (Adams 1987; Figueras 1988; Morfis et al. 1998; Murray 1999; Jagtap and Ramaswamy 2006).

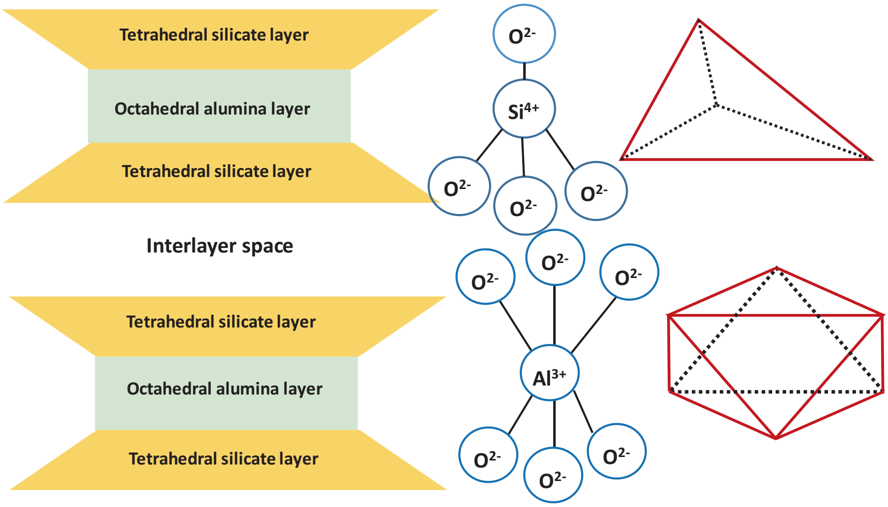

Fig. 11.1 Structure of 2:1 montmorillonite clay mineral characterized by two-dimentional sheets of corner sharing SiO_4 tetrahedra and/or AlO_4 octahedra. Tetrahedral silica sheets connected with oxygen at tree corners and octahedral alumina sheets surrounded by six oxygen atoms

11.2.2 *Pillaring Agents*

Several pillaring agent have been reported in literature such as polynuclear complex inorganic ligands e.g., hydroxo and chloro ligands, large metal complex ions with organic ligands and polyhydroxy cations (e.g., $AlCl_3.6H_2O$, $ZrOCl_2.8H_2O$ and hydroxyl zirconium) metal ions (polycation), metal complex or neutral particles (such as silica-sol-particle). The synthesis of pillared clay as a catalyst in oil cracking was focused in use of inorganic hydrated polyoxocations as pillaring agents (Kloprogge et al. 2005). This pillaring agent results in irreversible metallic oxide pillars on calcinations that increase its thermal and hydrothermal stability (Canizares et al. 1999; Jiang et al. 2002; Huang et al. 2010) (Fig. 11.2). Aluminium polycation ($[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$) is most widely referred pillaring agent in literature among Zr, Cr, Fe, Be, Mg, Ti, Nb, Ce, Ta, Ga, Mo, Ni, Cu, B, Si, and Bi (Manohar et al. 2005; Bergaya et al. 2006). Table 11.1 shows different pillared clay having different types of inorganic polyoxo cations that serves with some specific characters and their applicability.

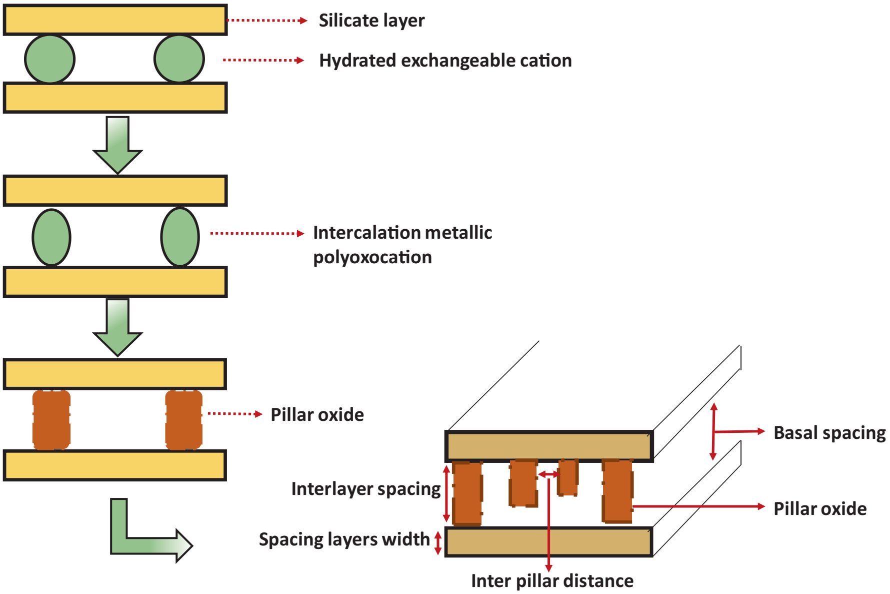

Fig. 11.2 Intercalation of pillaring agent in interlayer of montmorillonite clay. In which pillaring agents such as polynuclear complex inorganic ligands, metal ions, metal complex or neutral particles are intercalated between the layers and are results in irreversible metallic oxide pillars on calcinations that increase its thermal and hydrothermal stability

11.3 Application of Pillared Interlayered Clays

Initially, pillared clays were only considered for their applicability as heterogeneous catalyst (Gil et al. 2000; Das et al. 2006; Herney-Ramirez et al. 2010). But later on their other applications also have been explored such as thermal insulators, pigments, electrodes, membranes and applications in field of environmental process for removal of pollutants (Itaya and Bard 1985; Coche-Guérente et al. 1998; Murray 2000; Bergaya et al. 2006; Wang et al. 2006; Rouquerol et al. 2013). Figure 11.3 shows pillared clays as an extended form of clay and its applicability as adsorbent material for the removal of heavy metals from waste water, hazardous VOCs, components of biogas such as methane (CH_4), carbon dioxide (CO_2), ethane, hydrogen sulphide (H_2S) and organic waste water (Pereira et al. 1998; Xu et al. 2002; Zuo and Zhou 2006; Ramesh et al. 2007; Bhattacharyya and Gupta 2008a, b; Zuo et al. 2012; Đukić et al. 2015).

The following literature review focus on how the pillared clays have been used as a potential adsorbent candidate for environmental pollution control. It also narrates an overview of the factors affecting the rate of adsorbent efficiency.

Table 11.1 Different pillared clay (PILC) having types of inorganic polyoxocation serve with some specific characters and their applicability

	Polycations	Pillared clays	Specific characters achieved	Applications	References
1	Aluminium	Aluminium pillared clay	Their polymerization is well known	Adsorption of heavy metals, gases or vapours	Kikuchi and Matsuda (1988); Dąbrowski (2001); Jiang et al. (2004)
2	Zirconium	Zirconium-pillared clay	Their polymerization is well known	Adsorption of heavy metals, gases or vapours	Bhattacharyya and Gupta 2008a, b; Yan et al. 2008
3	Lanthanum-aluminium	Lanthanum-aluminium pillared clay	Basal spacings ~ 26 Å and surface areas of 300–500 m^2/g	Removal of phosphate from waste water	Tian et al. (2009)
4	Cerium-aluminium	Cerium-aluminium pillared clay	Basal spacings ~ 25 Å and surface areas of about430m^2/g	Adsorption of dyes (orange II), oxidation of phenol	Mnasri-Ghnimi and Frini-Srasra (2016); ye et al. (2016)
5	2-(2 trichlorosilylethyl) pyridine (TCSEP)	Silicon pillared clay	Gave a number of interlayer spacing (up to 10 Å)	Filler material	Simons (1979)
6	Tantalum	Tantalum pillared clays	Basal spacing of 26 Å and was stable to 600 °C	Cracking of vegetable oil	Kloprogge et al. (2005)
7	Titanium	Titanium pillared clay	Regular structure and was stable at 600 °C	Photocatalyst	Bovey et al. (1996)
8	Chromium-aluminium	Chromium-aluminium pillared clay	Chromium-aluminium pillared clays were more thermal than chromium pillared clays	CO oxidation, reduction of nitrogen oxide	Tomul and Balci (2009)
9	Cerium	Cerium pillared clay	Shows good performance at broad range of temperature	Reduction of nitrogen oxide	Lin et al. (2007)
10	Gallium-aluminium	Gallium-aluminium pillared clay	These samples are more crystalline	Cracking of heavy oils, adsorption if heavy metals	Domınguez et al. (1998)

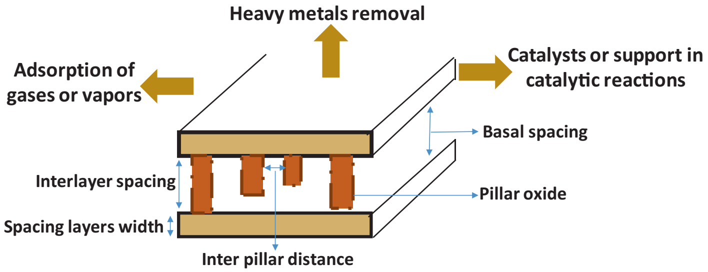

Fig. 11.3 Application of pillared interlayered clays. They can be used as thermal insulators, pigments, electrodes, membranes and as adsorbents and catalysts in field of environment

11.3.1 Removal of Heavy Metals from Waste Water

Natural and anthropogenic activities are two sources for heavy metals in water and beyond the permissible limit, their presence is always known to perilous for living species (Bhattacharyya and Gupta 2006a, b). Table 11.2 summarized some of heavy metals, their industrial emission and their harmful effects on human. Environmental Protection Agency (EPA) has determined range in concentration of metals beyond which organisms may be distorted, even die, and produce corrosion on different solids. Due to the large discharge amount of heavy metals from industrial activities such as Cd, Cr, Cu, Ni, As, Pb, and Zn (Volesky 1990; Sud et al. 2008; Barakat 2011; Fu and Wang 2011), their removal is always being the challenge (Volzone 2004). Some of heavy metals even at small concentration show acute and chronic effects on living beings (Bryan 1971; Duruibe et al. 2007).

Hence, different types of pillared clay materials have been experienced to adsorb these heavy metals from waste water. In this section we had discussed about few heavy metals that are frequently discharged from industries and application of some pillared clays for their adsorption. In this regard Al- pillared clays and Al- pillared clays serve as most attractive adsorbent. The application of pillared clays has been also investigated for the removal of cobalt (Co II) from aqueous solution. Manohar et al. (2006) prepared Al- pillared clays using bentonite as a parent material and investigated them on adsorption of Co (II) from waste water. The adsorption removal efficiency of parent clay and Al- pillared clays was found 87.0% and 99.8% respectively, at pH 6.0 (Manohar et al. 2006). Guerra and Airoldi (2008) used the smectite clay as a parent material, collected from Serra de Maicuru, Pará State, Brazil. They prepared the intercalated clay by intercalating Al and Zr polyoxocations followed by calcinations process. They employed these pillared clays for the removal of Cobalt ion from solutions of pH 5.0 at 298 ± 1 K (Guerra and Airoldi 2008). Bhattacharyya and Gupta (2008a, b) for the removal of Co (II) from aqueous solution used kaolinite and montmorillonite clay as parent material (Bhattacharyya and Gupta 2008a, b). Huang et al. (2016) successfully intercalated the 3-aminopropyl triethoxysilane (APTES) into the gallery of Ca-montmorillonite for Co (II) removal from aqueous solution. They also studied the synergistic effects of ion exchange and

Table 11.2 Heavy metals, their industrial emission and their harmful effects on human

	Heavy metals	Industrial sources	Effects	Pillared clays	References
1	Arsenic	Wood processing industry	Skin manifestations, visceral cancers, vascular disease	Al, Ti, Fe-pillared clays	Lenoble et al. (2002); Srivastava and Majumder (2008)
2	Chromium	Electroplating and metal surface treatment processes, wood processing industry, petroleum refining	Headache, diarrhea, nausea, vomiting, carcinogenic	Zr-pillared clay, montmorillonite-supported magnetite nanoparticle	Nriagu and Nieboer (1988); Bhattacharyya and Gupta (2006a, b); yuan et al. (2009)
3	Copper	Wood processing industry	Liver damage, Wilson disease, insomnia	Al, Fe- pillared clays	Phillips (1976); Nriagu (1990); Vengris et al. (2001); Caudo et al. (2007)
4	Cadmium	Electroplating and metal surface treatment processes	Kidney damage, renal disorder, human carcinogen	Al, Fe- pillared clays	Davis (1984); Yan et al. (2008); Wu et al. (2009)
5	Nickel	Printed circuit board (PCB) manufacturing, petroleum refining	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	Al- pillared clays	Patterson (1985); Manohar et al. (2006); Das et al. (2008)
6	Zinc	Electroplating and metal surface treatment processes	Depression, lethargy, neurological signs and increased thirst	Al, Zr, Ti- pillared clays	Vengris et al. (2001); Srivastava and Majumder (2008); Guerra et al. (2009)
7	Lead	Printed circuit board (PCB) manufacturing	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	Alminiumsulpahte modified kaolinite	Volesky and Holan (1995); Järup (2003); Jiang et al. (2009)
8	Mercury	Coal combustion, smelting, incineration, cremation	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	Al pillared clays, Ce-MnO x/Ti-pillared clays, silica-titania pillared clays	Dean et al. (1972); Lindqvist et al. (1991); Takahama et al. (1992); Manohar et al. (2006); Eloussaief et al. (2013); he et al. (2014)

coordination interactions on adsorption and hence, a significant improvement of Co (II) adsorption by the modified clay was achieved (Huang et al. 2016).

Lenoble et al. (2002) synthesised pillared clay using titanium (IV), iron (III), and aluminum(III) as an pillaring agent to adsorbe arsenic from industrial effluents. In their study maximum adsorption of arsenic was favoured by acidic medium and obtained pH between 4 to 9 as an optimal condition. At higher pH, greater than 10, adsorption decreases as a result of damage in pillared clay. Ramesh et al. (2007) employed polymeric Al and Fe species in interlayer of montmorillonte clay to remove organic and inorganic As (III) and As (V) from aqueous solution. In their work pH plays a vital role in adsorption of arsenic. The maximum adsorption of Al/Fe modified montmorillonite results was obtained in the pH range of 3.0–6.0 for As (V), 7.0–9.0 for As (III). Su et al. (2011) selected the bentonite clay and expand their inlayer by using octadecyl benzyl dimethylammonium and employed to adsorbe for both the states of arsenic from waste water. They evaluated the maximum adsorption capacity 1.48 mg/g and 0.82 mg/g for As (V) and As (III) respectively. Further they also explained that for the first 30 min adsorption seems to be very fast and equilibrium was achieved within 240 min. and 360 min for As (III) and As (V), respectively.

Chromium is another heavy metal found in two oxidation states Cr (III) and Cr (VI) in waste water (Sarin and Pant 2006; Kumar et al. 2011). Khan and Khan (1995) assessed the removal of Cr (III), Cr (VI) from waste water using bentonite clay. Yuan et al. (2009) prepared montmorillonite-supported magnetite nanoparticles for adsorption of Cr (VI) from waste water. In their synthesis montmorillonite-supported magnetite nanoparticles lies on the surface or inside the interparticle pores of clays, with better dispersing and less coaggregation than the ones without montmorillonite support. They also explained that the Cr (VI) adsorption was mainly executed by a physico-chemical process that includes an electrostatic attraction followed by a redox process where Cr (VI) reduced into trivalent chromium. Their adsorption was highly pH-dependent and follows Pseudo-second-order kinetic model (Yuan et al. 2009). Bhattacharyya and Gupta (2006a, b) developed the pillared kaolinite clay with polyoxozirconium and tetra butyl ammonium as pillaring agent for the adsorption of Cr (VI). The Cr (VI) adsorption was strongly pH dependent and uptake increased with pH from 1.0 to pH 7.0, then afterwards their adsorption decreased (Bhattacharyya and Gupta 2008a, b; Yan et al. 2008). Ghorbel-Abid et al. (2009) used the natural clay from northwest of Tunis, Tunisia, North Africa and Na- purified clay for the Cr (III removal. They explained that the adsorption of Cr (III) by the purified clay at pH 4 was rapid. The quantity removed from the solution reached a maximum value within 15 min after mixing and 1 h for the natural clay. The adsorption capacity of natural clay was about 117.5 mg/g and 61.4 mg/g with the Na-purified clay (Ghorbel-Abid et al. 2009). The same year, Akar et al. (2009) investigated the removal of Cr (VI) using Turkish montmorillonite clay and also evaluated the effect of activation and modification. They concluded that the removal of Cr (VI) using modified clay by hexadecyltrimethylammonium bromide was greater than the clay modified by acid and heat treatment (Akar et al. 2009). Zhang et al. (2012) modified the clay using the combination of pillared bentonite *i.e.*, OH-Al-bent along zero valent iron (ZVI) to enhance the adsorption capacity for Cr (VI). They explained their mechanism of removal where the mass transfer of Cr (VI) from aqueous to iron surface due to adsorption and further the reduction accelerated by ZVI (Li et al. 2012; Zhang et al. 2012).

Karamanis and Assimakopoulos (2007) synthesised the modified montmorillonite clay by introducing the Al metal in interlayer to expand the gallery of clay. The adsorption efficiency of this modified clay was investigated on the removal of copper. pH 4–6 was optimum for high adsorption of copper. They also explained that the Al and clay ratio have a significant effect on the adsorption of copper over modified clay, their adsorption increases with increasing Al and clay ratio. Bhattacharyya and Gupta (2006a, b) worked with both clays- kaolinite, and montmorillonite as a parent material and modified both the clay with introducing zirconium and tetrabutylammonium (TBA) in interlayers. They used theses nanomaterials for the copper adsorption from aqueous solution. Eren and Afsin (2008) selected bentonite clay and activated the clay by acid activation treatment (acid activated bentonite) for the sorption of copper. They found the parent bentonite has more adsorption affinity 42.41 mg/g towards copper than acid activated bentonite which possess 32.17 mg/g (Eren and Afsin 2008). Later Bhattacharyya and Gupta (2008a, b) again used these kaolinite and montmorillonite clay along there acid activated forms for copper sorption. In study they explained about the detailed interaction of metal ions to the clay. They reviled that the interactions were fast and equilibrium were achieved within 360 min.

Zhang and Hou (2008) intercalated montmorillonite clay for lead adsorption from waste water. Their results explained that the adsorption is dependent on the pH and the adsorption of Pb (II) increases with the increasing pH. Chaari et al. (2008) used Tunisian smectite-rich clay; activate it by acid activation treatment followed by calcination at different temperature. They used all these acid activated clay for the sorption of lead from aqueous solution. Wang et al. (2009) studied their adsorption on Na-bentonite, and found it was strongly pH dependent. They explained that at low pH, the adsorption was dominated by outer-sphere surface complexation and ion exchange with Na^+/H^+ on Na-bentonite surfaces, whereas inner-sphere surface complexation was the main adsorption mechanismat high pH for lead ions. Galindo et al. (2013) studied the adsorption of lead using sodic bentonite clay type Fluidgel modified that was further thermally activated at 750 °C for 24 h.

11.3.2 Adsorptive Removal of Gases

Several VOCs, and harmful gases such as methane, ethane, hydrogen sulphide, sulphur dioxide, etc. are released from industrial activities and from indoor environment (Donham et al. 1982; Khan and Ghoshal 2000; Hessel et al. 2007; Seinfeld and Pandis 2016). They directly or indirectly show their negative impact on humans and environment (Hackney et al. 1975; Kampa and Castanas 2008). Therefore, their separation and removal is always being at priority. Since many decades pillared clays are used as an alternative candidate to mitigate these nuisances (Long and Yang 2001; Churchman et al. 2006; Volzone 2007). Many evidences have been reported in literature that strongly indicates pillared clays can be potentially used in abatement of these pullulated gases. In this section, we had presented some of pillared clays that could be potentially practiced for their adsorption. Pires et al. (2001), studied the adsorption of some VOCs (1, 1, 1-trichloroethane, trichloroethylene, methanol and propanone) over the pillared clay. They prepared the aluminium and zirconium oxide pillared clays using the smectite and laponite as a parent clay for their investigation. The isotherm for VOCs adsorption was of type 1. Pereira et al. (2001) synthesised zirconium oxide pillared clays using raw clay from different sources. These pillared clays were applied for adsorption of methane and ethane. Further Pereira and group used these adsorbents to adsorb hydrocarbon components of natural gas, at the temperature range between 215 and 293 K up to the atmospheric pressure. Venaruzzo et al. (2002) modified the two natural bentonite clay collected from Patagonia, Argentina by acid treatments. They applied the clay material to adsorb carbon monoxide, carbon dioxide and sulphur dioxide gases. Their result shows the retention values of SO_2 were 0.636–1.232 mmol/g by clay minerals were higher than CO_2 that was 0.218–0.516 mmol/g and CO, 0.075–0.119 mmol/g. Pinto et al. (2005) developed a composite adsorbent material by supporting a pillared clay material in polyurethane foam. They evaluate the performance of material by adsorbing nitrogen and toluene. Zuo and Zhou (2006) prepared Al-pillared clays supported rare earths (RE/Al- pillared clays). They used this material for the oxidation of benzene at low concentration (130–160 ppm). López et al. (2008) synthesized three modified clay material. Al- pillared clays was one the material and used this adsorbent for the removal of benzene and toluene. Pires et al. (2008) used the pillared clay as a potential adsorbent to improve the biogas quality by adsorbing carbon dioxide, methane, ethane and nitrogen. They prepared the pillared clays from two different natural montmorillonite clays, by using Al_2O_3 and ZrO_2 as a pillaring agents. Ding et al. (2015) developed novel composite AlCr-pillared clays (Al/Cr-PILC), by ion exchange. They used the synthesized pillared clays for the adsorption of benzene and found their adsorption capacity much higher than starting clay.

11.3.3 Catalyst or Catalyst Support in Catalytic Reactions

Pillared clays with larger pore size and thermally stable are has been used as a catalyst or support for catalytic reactions. In this section of review, we had discussed about the application of pillared clay as a catalyst or an effective support for catalytically active components such as oxides, metals and organometallic complexes. Pillared clays possess bimodal pore size distribution greater than the zeolites, which provides space for catalytic reactions. In 1930s at emerging time of modified clays, acid treated clays were frequently used in oil cracking reactions. In 1960s, their positions were taken over by advent of zeolites and aluminosilicates. Later on pillared clays having thermal stability used were used as cracking catalyst. In several of organic reactions acid treated and iron exchanged clays were efficiently used as catalysts. Mishra and Parida (1997) prepared pillared clay nanomaterial using Fe (III), Cr (III), Mn (III) and used them as a catalyst for nitration of chlorobenzene. In result they discussed about their affinity, where calined, at 300 °C, acid activated clays have higher affinity than non-acid activated clays (Mishra and Parida 1997). Gil et al. (2001) synthesized Al-pillared clay using hectorite, montmorillonite and saponite clays. This pillared clay is further considered as a support for platinum catalyst. They applied these catalysts for catalytic combustion of acetone and methyl-ethyl-ketone (MEK). In year 2002, the same authors prepared manganese oxide catalysts supported on the unpillared and Al and Zr pillared clays using montmorillonite and Saponite clay minerals. They used theses catalysts for the complete combustion of acetone (Gandıa et al. 2002). Carriazo et al. (2005a, b) successfully pillared with mixed polyhydroxocationic solutions of Al–Fe or Al–Ce–Fe, with the iron in small quantities, to generate a modified Fenton process on the surface of the pillared clays. They used these catalysts for the wet peroxide oxidation of organic pollutants from industrial wastewaters. The catalyst found effective in phenol oxidation reaction (Carriazo et al. 2005a, b). Shimizu et al. (2008) prepared different cations exchanged montmorillonite (K-10) clays and assess their catalytic action for acetylation of alcohol. Thomas et al. (2011) explained the clays having Ce^{3+}, Al^{3+}, Fe^{3+} in interlayer are found effective catalysts for acetalization of carbonyl compounds with methanol. Further, the clays treated with mineral acid can be used as a catalyst for isomerisation of α-pinene, glycerol dehydration and for reduction of nitric oxide (Thomas et al. 2011). Vijayakumar and Rao (2012) prepared montmorillonite, K-10, as support for $ZrOCl_2$. $8H_2O$.These catalysts had been evaluated for the synthesis of 3, 4-dihydropyrimidin-2(1H)-ones/thiones. Banković et al. (2012) prepared heterogenous catalysts (Al,Fe-pillared clays). They used the catalysts in catalytic wet peroxide oxidation of tartrazine azo-dye in water. In their study application of H_2O_2 and Fe-containing pillared clays considerably improve the removal of dye. Higher iron content lead to more efficient catalytic removal of the dye. In Table 11.3 we had summarized some important pillared clays as catalyst or support for catalytic reactions and their participation in reactions. Timofeeva et al. (2014) synthesized Al, Ga, and Zr, Al-pillared clays as Al-montmorillonite, Ga- montmorillonite, and Zr, Al- montmorillonite by intercalating Al, Ga, and Zr- polyoxocations into three layered aluminosilicates with various pore diameter and Si/Al molar ratio and Zr content), and type of Al salt (nitrate or chloride). They used these nano pillared clays to inspect their catalytic efficiency in synthesis of 1-methoxy-2-propanol from methanol and propylene oxide. They explained that the catalytic properties of Zr, Al-pillared clays depended on the textural properties as pore diameter, chemical composition as Si/Al molar ratio and Zr content, and type of Al salt such as nitrate or chloride used as the Al source. Metal cations with different types in the polyoxocations affected rate of reaction and isomer selectivity. Al- montmorillonite was found to exhibit a higher catalytic efficiency than Ga- montmorillonite and Zr- montmorillonite.

Table 11.3 Pillared clays as a catalyst or support for catalytic reactions and their participation in reaction

S. No.	Pillared clays as catalysts	Reactions	References
1	Acid treated clays	Oil cracking reactions	Christidis et al. (1997); Kloprogge et al. (2005)
2	Pt/Al-pillared clays	Combustion of methyl-ethyl-ketone	Gil et al. (2001); Barrera-Vargas et al. (2005); Zuo et al. (2010)
3	Fe-Al pillared clays, Al-pillared clays bentonite	Hydroxylation of phenol	Letaïef et al. (2003); Timofeeva et al. (2010)
4	Al-Zr pillared clays, Pd/Zr-pillared clays	Oxidation of benzene, alkylation of benzene	Figueras et al. (1989); Shufeng et al. (2011)
5	Ce-Zr- pillared clays	Synthesis of 1,3-dioxolane	Mnasri-Ghnimi and Frini-Srasra (2014)
6	Al–cu pillared clay catalysts	Catalytic wet oxidation of reactive dyes	Kim and lee (2004)
7	Pillared saponite impregnated with several iron salts	Degradation and mineralization of Orange II solutions	Ramirez et al. (2007)
8	Ti-pillared clays	Selective catalytic reduction (SCR) of NO by NH_3 in presence of oxygen have been evaluated	Boudali et al. (2003)
9	V/Ti- pillared clays	Selective catalytic oxidation of hydrogen sulfide (H_2S)	Bineesh et al. (2011)
10	Al,Fe-pillared clays (PILCs)	Catalytic wet peroxide oxidation of tartrazine azo-dye in water, decolorization	Banković et al. (2012)
11	Al, Cr-pillared clays	CO oxidation	Tomul and Balci (2009)
12	Fe- pillared clays, Cr- pillared clays, Cr-(Fe- pillared clays) and Fe-(Cr- pillared clays	Acylation of alcohols	Akçay (2004)
13	Chromium pillared clay (Cr-pillared clays)	Support for dispersion of silicotungstic acid	Kar and Mishra (2013)
14	Co, Mo and CoMo catalysts supported on a montmorillonite clay and Al-pillared	Dehydrogenation of ethylbenzene	Moronta et al. (2006)
15	Al/M-pillared clays (M = Fe, cu, Mn)	Degradation of organic Pollutants in aqueous streams	Galeano et al. (2014)
16	Cu, ag and Fe contain titanium-pillared bentonite	Catalytic activity for removal of bisphenol A from aqueous solution	Tomul et al. (2016)

11.4 Conclusion

Montmorillonite pillared clays drawn attention of researchers as a potential adsorbent candidate in environmental pollution control. Recent work on pillared clays shows steady increase in adsorption selectivity and efficiency in these materials. Intercalation of polyoxocations in interlamellar region of clay serves in increased adsorption efficiency towards heavy metals, gases or vapours. They have been also employed potentially as a catalyst or provide supports in catalytic reactions. However, there are some important issues that still need to be addressed, relating to application of these materials in environmental applications:

(a) Cost in pillaring agents that modify the clay, however increase the capital cost of process, hence the pillaring should be at consideration with low cost.
(b) Researchers addressed a lot work in literature for removal of heavy metals, organic compounds from wastewater, but evidences are lacking for pharmaceutical drugs removal from wastewater.
(c) Applicability of pillared clays shows their importance among several techniques for VOCs adsorption but data are still lacking for indoor VOCs removal.
(d) Most of the pillared clay pollutant follows second order kinetics but the interaction between adsorbent and adsorbate yet to be explained in details about their mechanisms.

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Chapter 12
Green Sorbents for Radioactive Pollutants Removal from Natural Water

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Contents

Abstract Natural and anthropogenic radionuclides are a major pollution of natural waters in some locations. Effective, appropriate and eco-friendly technologies are required to mitigate this problem. Natural materials can be used, which may help in rehabilitation and reduction in migration of radionuclides execution green technological concept. This chapter reviews the development of green sorbents and their

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use for the removal of radioactive wastes. Main types of green sorbents are discussed, such as activated carbons based on vegetable materials, chemically modified waste from the food industry, sorbents based on natural and technical cellulose, hydrolytic lignin, as well as living and dead phytoplankton. It is shown that activated carbons are effective sorbents for a wide spectrum of radionuclides including isotopes of cesium, strontium, lanthanides, uranium, thorium, plutonium and radon; the typical method of activated carbon production is also discussed. This chapter also presents the main sorption characteristics of various sorbents based on chemically modified natural and technical cellulose with respect to yttrium, strontium, uranium, cesium and some other radionuclides. mixed nickel-potassium ferrocyanide based on cellulose from rice husk shows distribution coefficient of cesium as high as $3.9 \cdot 10^5$ L/kg. Overall, green materials usually possess relatively low sorption properties; however, selectivity of these materials can be significantly improved via chemical modification by inorganic compounds such as phosphates, hexacyanoferrates, alkali and other. Moreover, in contrast to inorganic sorbents, natural organic materials allow obtaining sorbents with various textures such as granules, fibres and textile.

12.1 Introduction

Assorted anthropogenic activities are major sources of radionuclides in the environment. Establishments like nuclear fuel cycle enterprises, nuclear reactor facilities, and nuclear weapon tests explosions result in pollution of radionuclides especially in soil and adjoining water bodies (Gupta et al. 2016). Once contaminated, the radionuclide can migrate far away distance from the release source and expanding the contaminated zone radioactively (Gupta and Walther 2014). Further, radionuclide can enter into the animal food chain as a result of consumption of contaminated food grown in the area irrigated with water having radionuclide(s) (Walther and Gupta 2015). Effective, appropriate and eco-friendly technologies are required to mitigate the problem of radionuclide contamination in natural water. Natural materials can be used which may help in rehabilitation and reduction in migration of radionuclides execution green technological concept. Among green sorbents for radioactive pollutants removal various materials are present like activated carbons, cellulose, lignin, humic acids and phytoplankton. This chapter encompasses the up-to-date information on the development of green sorbents and their use for removal of radioactive wastes. It gives the main sorption characteristics of a number of sorbents based on chemically modified natural and technical cellulose with respect to yttrium, strontium, uranium, cesium and some other radionuclides.

12.2 Radioactive Contamination of Natural Waters

Radioactive contamination of the environment is an important part of contamination affecting the quality of the environment and public health. In general, natural and artificial (anthropogenic) radionuclides are two types of radionuclides in the environment; however, some radionuclides such as tritium (^{3}H) and radiocarbon (^{14}C) have both natural and anthropogenic sources of release to the environment. According to the recommendations of the International Commission on Radiological Protection (ICRP 2007), approaches to control of radioactivity in the environment should be the same for both natural and artificial radionuclides.

Natural radioactivity in the environment is presented as long-lived primordial radionuclides (^{40}K, ^{87}Rb, ^{238}U, ^{235}U, ^{232}Th and some others) (Gupta et al. 2014, 2016), and cosmogenous radionuclides (^{3}H, ^{14}C, ^{7}Be). However, uranium, thorium and their daughter nuclides (mainly, ^{226}Ra, ^{228}Ra, ^{210}Po and ^{210}Pb) contribute more than half of annual internal dose of humans (Gupta et al. 2014). Typical natural waters containing elevated activities of these nuclides are ground waters, especially near uranium/thorium deposits (Lauria and Godoy 2002; Kozłowska et al. 2007; Onishchenko et al. 2010) and mining sites (Chałupnik et al. 2017; Lourenço et al. 2017).

Among the main anthropogenic radionuclides occurring in the environments, there are fission products ($^{129,\,131}$I, ^{90}Sr – ^{90}Y, $^{134,\,137}$Cs, ^{106}Ru, ^{99}Tc), transuranium elements (long-lived isotopes of Np, Pu, Am and in a less degree heavier elements) and activation products (^{3}H, ^{14}C, ^{60}Co, ^{55}Fe, ^{56}Mn, etc.). Nuclear tests in 1950s–1960s resulted in release of $2{\bullet}10^{20}$ Bq to the environment (Choppin 2006); global fallout still remains to be the dominant source of anthropogenic radionuclides in the environment (Povinec et al. 2004). This type of radioactive contamination is very intensive at the former test sites (Vintró et al. 2009). Another one important source of anthropogenic radionuclide in the environment is daily work of plants for plutonium production and irradiated nuclear fuel reprocessing such as La Hague in France, Sellafield in the Great Britain, Savannah River Site in the USA (Beals and Hayes 1995) and Mayak PA in Russia (Shutov et al. 2002; Shishkina et al. 2016) and some others. Finally, the third main source is nuclear accidents at nuclear power plants and enterprises of nuclear fuel cycle. Two most significant accidents are Chernobyl disaster in 1986 resulted in a world-wide contamination of rivers (Vukovic et al. 2006), seas (Polikarpov et al. 1991) and groundwater (Roux et al. 2014) as well as Fukishima Dai-ichi accident in 2011 (Ueda et al. 2013; Fuma et al. 2017). Release of radionuclides after Chernobyl disaster was estimated to be $7{\bullet}10^{17}$ Bq; approximately 90% of this activity was presented as the short-lived ^{131}I, whereas ^{137}Cs activity was near to $7{\bullet}10^{16}$ Bq (Myasoedov 1997). Release at Fukushima Dai-ichi was near to 10% of Chernobyl release.

Besides radioactive decay, radionuclides may be eliminated from natural water bodies due to natural processes, such as (co)precipitation, sorption, and evaporation (for radon in surface waters). For example, Simpson et al. (1982) reported that fallout strontium-90 has been largely removed from the lake water in California, probably as a result of co-precipitation with calcium carbonate. Also, it is well-known that cesium is intensively sorbed by natural clayey mineral such as zeolites (Chesnokov et al. 1999, 2000); whereas plutonium interacts with oxide minerals (Romanchuk et al. 2016). It is reported that ^{60}Co is sorbed by bottom sediments (Murray and Mayer 1986) presenting predominantly in hydrophilic fraction of sediments (Caron and Mankarios 2004). The rest part of radionuclides may be intercepted by plants (Hirono and Nonaka 2016) and animals (Kennamer et al. 2017) and thus be involved into migration through food chains. Finally, the radionuclides occurring in water and living creatures may be consumed by humans causing the exposure of internal irradiation doses. Thus, elimination of radionuclides from drinking water and prevention of their migration through food chains is a very important task from the point of view of radiation safety and public health.

12.3 Role of Green Technologies in Rehabilitation of Radioactively Contaminated Landscapes

Solving the problem of radiation safety to the population and the environment may be possible as a result of use of effective and eco-friendly methods for rehabilitation of radioactively contaminated natural environment and water bodies (Shao et al. 2014; Olszewski et al. 2016). Green technologies based on natural materials became a significant part of these methods. Green sorbents can be obtained from organic components of natural ecosystems; therefore, these sorbents meet all ecological requirements. They possess a number of properties being important for decontamination of aqueous media, such as hydrophilic surface, suitable pores structure, functional groups on the surface, mechanical and chemical stability.

Natural organic raw materials and phytogenic farm wastes are the most attractive materials for green sorbents production (Bhatnagar and Sillanpää 2017). Sorption materials based on vegetable substance and wood waste such as sawdust, wood chippings, etc. may possess successful mechanical, chemical and radiation stability, very low cost and the possibility of further volume decrease by pyrolysis. Wood and such wood components as cellulose, lignin and their derivatives are also relatively low cost sorbents (Hokkanen et al. 2016). Production of these sorbents requires low capital investment and it can be organized at any region that would allow for decrease of transport charges.

Activated carbons, waste of food industry, natural and technical cellulose, lignin, phytoplankton and humic acids are used as green sorbents for various radionuclides separation from various aqueous media. Basic properties and examples of use of these green sorbents are described below.

12.4 Green Sorbents in Radioactive Pollutants Removal

12.4.1 Activated Carbons Based on Vegetable Materials

Activated carbons are the most widely used sorption materials among all green sorbents. These porous carbonic sorbents may be obtained using various raw materials such as turf, coal (Liu et al. 2014; Zhong et al. 2016), wood (Vanderheyden et al. 2016), wood waste (Caccin et al. 2013), etc. Classical methods of activated carbons production include primary heat of the raw material without air access resulting in elimination of volatile compounds and formation of macroporous structure of the material. Classification of pore is as following: micropores have the size up to 2 nm, mesopores are 2–20 nm and macropores have the size more than 20 nm. After this, the carbon is activated through oxidation by oxygen, carbon dioxide or water vapor at the temperature of 800–900 °C (Voronina et al. 2010):

$$C + O_2 \rightarrow CO_2$$

$$2C + O_2 \rightarrow 2CO$$

$$C + H_2O \rightarrow CO + H_2$$

$$C + CO_2 \rightarrow 2CO$$

The activation process results in formation of micropores. Thus, as a result of this two-stage treatment, porous substances with sponge-like structure are obtained. The nature of raw material and the synthesis method strongly affect pore size of the activated carbon. Furthermore, activation of a carbon results in formation of oxide compounds closely associated with the carbon surface. After contact with water, these compounds are transformed into carboxylic or hydroxyl functional groups conditioning cation and anion exchange properties of activated carbons.

Activated carbons possess relatively low ion exchange capacity and almost do not sorb ionic forms of radionuclides. However, they can be used for separation of radionuclides being associated with organic matter and colloidal particles. Activated carbons are used for elimination of ^{131}I, ^{90}Sr, ^{90}Y, ^{137}Cs, and ^{106}Ru from natural waters. Easy peptization and low chemical stability are the main disadvantages of activated carbons. Cation exchange activated carbons based on coal, wood and turf after treatment by concentrated sulfuric, phosphoric and some other acids possess elevated chemical stability in alkaline solutions (Voronina et al. 2010, 2015a). Acidic treatment allows for formation of additional ion exchange functional groups on the surface of the activated carbon. For example, sulfuric acid treatment results in appear of sulfate ion exchange groups. Thus, change of ion exchange properties, chemical and mechanical stability of the carbon occurs as a result of sulfuric acid treatment.

Use of prospective raw materials and new methods of chemical activation for production of activated carbons allows for increase of porosity, selectivity and exchange capacity of these products. Moloukhia et al. (2016) described the method of synthesis and physicochemical properties of activated carbons based on coconut shells. The method allows for introduction of new ion exchange functional groups, increase of surface area and pores volume of the activated carbon. Coconut shells are preliminary treated by 20% H_3PO_4 in order to improve texture of the surface and increase its porosity. After this, carbonizing is performed by heating this paste at the temperature of 500 °C for 3 h with the heating rate of 10 °C per minute (Moloukhia et al. 2016). Chemical modification of the activated carbon based on coconut shells are performed via sequential oxidizing by 4M H_2O_2 and 6M HNO_3 solutions. The activated carbon shows a high affinity for hydrolyzable ions Eu^{3+} and Ce^{3+}, but a significantly lower affinity for Sr^{2+} and Cs^+. In addition, the results have shown a low selectivity of the activated carbon in presence of Na^+ ions.

Ershov et al. (1993a) suggested a method for synthesis of a sorption material from wood sawdust *via* soft oxidation of carbonized sawdust. The first stage of synthesis includes sawdust carbonizing in a rotating pipe furnace at the temperature of 300–350 °C for 2 h. The second stage includes oxidation by air at the temperature of 200–250 °C for 2 h. After this treatment, a new ion exchange material, oxidized wood carbon was obtained. Its total ion exchange capacity determined by KOH solution is ~5.0 mg-eqv/g; content of strong acid carboxylic groups, weak acid groups and phenolic groups is 2.0, 2.7 and 0.3 mg-eqv/g respectively (Bykov 2011). Ershov et al. (1993b, c) and Bykov (2011) studied physicochemical properties of sorption-active materials based on modified phytomaterials using modern methods of analysis; the authors determined content of ion exchange groups and studied the kinetics of sorption of cesium, strontium, uranium, americium, thorium, plutonium and technetium from various aqueous solutions.

It is shown that oxidized wood carbon possess good sorption properties; distribution coefficients and total exchange capacities of oxidized wood carbon for cesium, thorium, americium and plutonium are higher than these values obtained for untreated sawdust and birch activated carbon. Bykov (2011) reported the following distribution coefficients obtained for oxidized wood carbon (L/kg): $Cs^+ - 5.4 \cdot 10^3$, $UO_2^{2+} - 3.5 \cdot 10^2$, $Am^{3+} - 5.8 \cdot 10^3$, $Pu^{4+} - 1.8 \cdot 10^3$, $Th^{4+} - 2.1 \cdot 10^3$. The oxidized wood carbon was tested on both simulated solutions and real groundwater samples from influence zone of Chernobyl nuclear power plant. As it is reported, K_d values of radionuclides ^{90}Sr, ^{137}Cs, ^{243}Am and ^{239}Pu obtained on the aqueous extract from a soil sample from radioactive waste storage near Buryakovka settlement are 7, $5.2 \cdot 10^3$, $1.1 \cdot 10^3$ and $1.2 \cdot 10^4$ L/kg respectively. The data obtained on simulated solutions coincided with those obtained on the real samples of radioactively contaminated natural water.

The last but not the least one important example of activated carbons use for radionuclide separation is connected with radon elimination form radon-rich underground waters (Turtiainen et al. 2000; Alabdula'aly and Maghrawy 2011; Karunakara et al. 2015; Guo et al. 2017). Due to an extended surface area, activated carbons can successfully separate isotopes of radon due to absorption mechanism. This is mainly

Table 12.1 The degrees of radon sorption by certain types of activated carbon. It can be noted that Carbotech (Germany) activated carbon showed the best selectivity for radon

Type of activated carbon	The degree of radon sorption, %
Birch activated carbon, BAU (Russia)	78
Activated carbon from coconut shells, NWC (Malaysia)	77
Activated carbon from coconut shells, Carbotech (Germany)	91
Activated carbon from coconut shells, Carbotech impregnated by silver ions (Germany)	92

for the most long-lived isotope ^{222}Rn with the half-life of 3.83 days. Relatively low exchange capacity of activated carbons is not a problem in this case because of a very low concentration of radon in water. For example, even 10,000 Bq/L of ^{222}Rn corresponds to its concentration of as low as $8 \bullet 10^{-15}$ mol/L. The sorption method is very effective; it provides 95–100% elimination of radon. As compared with physical methods of radon elimination from drinking water such as air bubbling, boiling, etc., the main advantages of absorption by activated carbons are additional elimination of radon short-lived daughter radionuclides (^{214}Pb, ^{214}Bi) and prevention of radon transfer to air (Semenishchev et al. 2017). As an example, in our experiment, we have studied ^{222}Rn sorption from water by four types of activated carbons. In this experiment, 5 L of natural water from a spring near Ekaterinburg city (Russia) containing nearly 100 Bq/L of ^{222}Rn was passed through an 18-mm column containing 20 g of an activated carbon at the flowrate of 100 mL/min. The results are given in Table 12.1. The Carbotech (Germany) activated carbon showed the best results; however, in this case other types of activated carbon were also enough to decrease the radon level down to values less than the maximal permissible level (60 Bq/L).

12.4.2 Chemically Modified Waste of Food Industry

Annually, renewable, large-tonnage and cheap wastes of food industry can be used as sorbents for radionuclides separation from various aqueous solutions. Velichko and his research group obtained a number of phytosorbents based on malt sprouts (PS-710, PS-744, PS-745 and PS-761) and on sawdust (PS-768). The method of synthesis included high-temperature treatment of raw materials by a solution containing carbamide, dimethyl formamide and phosphoric acid. Use of the phytosorbents based on sawdust, malt sprouts and barley husk for heavy metals and radionuclides separation from various types of natural water is described in a number of publications (Velichko et al. 2002; Medvedev et al. 2003; Likhacheva 2005). The authors have found radionuclides distribution coefficients from water of Irtyash Lake and industrial water bodies of the Mayak PA. It was shown that the chemical composition of water significantly affect sorption properties of the sorbents. As reported, values of distribution coefficients of ^{137}Cs, ^{90}Sr and uranium under various

Table 12.2 Distribution coefficients (K_d) and rate constants (β_{c1} and β_{c2} for the first and the second sections of kinetic curves) for various radionuclides from seawater by TLIS based on wood cellulose

Sorbent	Radionuclide	K_d, L/kg	β_{c1}, min^{-1}	β_{c2}, min^{-1}	Reference
IPF-C[a]	^{137}Cs	$3.2 \cdot 10^5$	29.8	–	Betenekov et al. (1987)
BS-C[a]	^{133}Ba	$2 \cdot 10^4$	10^{-2}	10^{-4}	Vinogradov et al. (1985)
TH-C[a]	^{91}Y	$2 \cdot 10^4$	0.14	$4 \cdot 10^{-2}$	Kaftailov et al. (1985)
ZnS-C[a]	^{60}Co	$2 \cdot 10^4$	0.1	–	Betenekov et al. (1986)
CdS-C[a]	^{106}Ru	$4 \cdot 10^4$	0.1	10^{-2}	Betenekov et al. (1977)
CuS-C[a]	^{212}Pb	$2 \cdot 10^3$	0.1	10^{-2}	Betenekov et al. (1984a)
TH-C[a]	^{233}U	$1.2 \cdot 10^4$	10^{-2}	10^{-4}	Betenekov et al. (1984b)

In these sorbents, technical cellulose is used as an eco-friendly support, whereas different inorganic compounds provide selectivity for certain radionuclides

[a] Designation of the TLIS based on cellulose (C): *IPF* iron-potassium ferrocyanide, *BS* barium sulfate, *TH* titanium hydroxide, *ZnS*, *CdS* and *CuS* zinc, cadmium and copper sulfides respectively

conditions are $n \cdot 10^2$–10^3 and $n \cdot 10^3$ L/kg respectively. The PS-728 sorbent (modified sawdust) showed the best sorption properties for strontium and uranium; whereas, the PS-761 (based on malt sprouts) was the most effective for cesium sorption.

12.4.3 Sorbents Based on Natural and Technical Cellulose

Sawdust, having huge functional surface, which can sorb ionic and colloidal forms of radionuclides as well as radioisotopes being sorbed on fine suspensions (Voronina et al. 2010). The main advantage of sawdust use for radioactive water treatment is the possibility of its further pyrolysis resulting in a multifold decrease of volume of radioactive waste. The weight of sawdust after pyrolysis decreases by 40 times or more. Radioactive isotopes are strongly fixed on the surface of the ash that makes further radioactive deposition easier. However, some radionuclides may evaporate during the pyrolysis process resulting in air radioactive contamination. Prevention of this secondary contamination requires the use of special complex equipment. Ion exchange capacity of the cellulose is usually low; therefore, use of cellulose is reasonable in case of diluted solutions with low concentrations of the main components. It is possible to improve ion exchange properties of the cellulose due to either chemical oxidation or introduction of various functional groups (Wang et al. 2017). Sorbents based on cellulose may appear as fibrous granulated materials as well as textile (acetyl cellulose). Use of textile allows for more rapid sorption kinetics as compared with fibrous granulated materials.

Thin-layer inorganic sorbents (TLIS) were synthesiszed by chemical deposition of thin films of sparingly soluble compounds onto the surface of natural cellulose (sawdust) (Betenekov et al. 1976). TLIS retain improved sorption and kinetic properties with respect to radionuclides due to increase of internal diffusion rate. Sorption properties of selected TLIS are given in Table 12.2.

Table 12.3 Distribution coefficients of various radionuclides sorption from tap water by technical cellulose and surface-modified sorbents based on cellulose

	Distribution coefficient K_d, L kg^{-1}		
Sorbent	^{90}Sr	^{90}Y	^{137}Cs
Cellulose from oat husk (untreated)	No sorption	$(7.5 \pm 0.5) \cdot 10^3$	$(8 \pm 1) \cdot 10^2$
Cellulose from oat husk (treated by ozone)	–	–	$(3.1 \pm 0.5) \cdot 10^4$
Cellulose from oat husk (treated by H_3PO_4)	–	–	$(3.5 \pm 0.5) \cdot 10^3$
Cellulose from buckwheat husk (untreated)	No sorption	$(1.0 \pm 0.4) \cdot 10^4$	$(2.2 \pm 0.1) \cdot 10^3$
Cellulose from rice husk (untreated)	No sorption	$(2.1 \pm 0.1) \cdot 10^4$	$(5 \pm 1) \cdot 10^2$
Cellulose from oat straw (untreated)	No sorption	$(9.2 \pm 0.6) \cdot 10^3$	$(2.20 \pm 0.09) \cdot 10^3$
Nickel-potassium ferrocyanide based on cellulose from buckwheat straw	–	–	$(1.9 \pm 0.3) \cdot 10^4$
Nickel-potassium ferrocyanide based on cellulose from rice husk	–	–	$(3.9 \pm 0.5) \cdot 10^5$
Nickel-potassium ferrocyanide based on cellulose from oat straw	–	–	$(1.0 \pm 0.5) \cdot 10^4$
Nickel-potassium ferrocyanide based on cellulose from oat husk	–	–	$(5.2 \pm 0.8) \cdot 10^3$
Phosphated cellulose from buckwheat straw	$(1.7 \pm 0.9) \cdot 10^2$	–	–
Phosphated cellulose from rice husk	20 ± 78	–	–
Phosphated cellulose from oat straw	86 ± 90	–	–
Phosphated cellulose from oat husk	86 ± 80	–	–
Commercially phosphated oat husk	$(2.7 \pm 1.1) \cdot 10^2$	–	–

Adapted from Voronina et al. (2013)

Bykov and Ershov (1996) obtained a sorbent with a high phosphor content (16.5% wt.) and high affinity to uranium as a result of wood phosphorylation. The maximal value of K_d for uranium ($1.9 \cdot 10^4$ L/kg) was reached at pH 2–3; for Tc(VII), the maximal K_d value at pH 9 is reported to be 75.9 L/kg. The phosphorylated wood is not selective for cesium and strontium radionuclides; therefore, sorption of these radionuclides is possible only in absence of Na^+, H^+ and Ca^{2+} ions.

Besides wood cellulose and products of its modification, technical cellulose being obtained from waste of food industry can be used as a sorbent. Minakova (2008) described a method for synthesis of technical cellulose from waste of corn production. Sorption properties and exchange capacity of this cellulose may be improved by chemical modification. The method for synthesis of surface-modified sorbents based on various sorption-active supports (hydrated titanium and zirconium dioxides, aluminosilicates and, technical cellulose, etc.) was developed by Voronina et al. (2012, 2015b, 2017; Voronina and Nogovitsyna 2015). Voronina et al. (2013) studied sorption properties of untreated and chemically modified samples of the technical cellulose with respect to ^{137}Cs, ^{90}Sr and ^{90}Y radionuclides on spiked tap water at static and kinetic conditions. Table 12.3 presents distribution coefficients of various radionuclides sorption from tap water by untreated and chemically modified technical cellulose obtained waste of corn production.

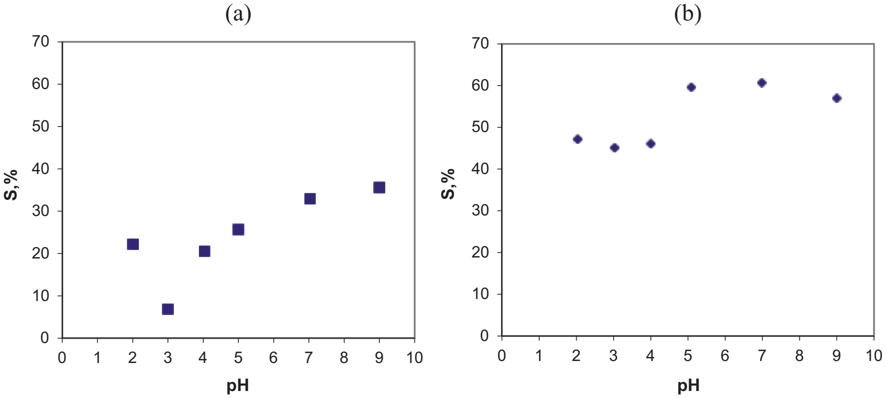

Fig. 12.1 pH dependences of cesium sorption by cellulose from oat husk (**a**) and cellulose from rice husk (**b**). It can be seen that unmodified cellulose shows a relatively low selectivity for cesium and works mostly at neutral and slight alkaline media

The data from Table 12.2 show that sorption properties of the technical cellulose depend on the type of vegetable raw material: the cellulose obtained from straw shows higher distribution coefficients as compared with the cellulose obtained from husk. However, selectivity of untreated cellulose for cesium does not exceed 10^2–10^3 L/kg. Thermal treatment of the technical cellulose in presence of ozone or H_3PO_4 results in increase of K_d values by the order of a magnitude due to incorporation of additional function groups into the sorbent. Furthermore, the results showed that the technical cellulose cannot sorb ^{90}Sr; however, it can sorb its daughter radionuclide ^{90}Y with distribution coefficients as high as 10^3–10^4 L/kg.

Carboxylic groups without hydrogen bonds among them are the main sorption-active functional groups of cellulose materials. The value sorption capacity of the cellulose (0.011–0.1 mg-eqv/g) is conditioned by the quantity of the carboxylic groups in the polymer matrix; this quantity is affected by the quality of decontamination from organic and inorganic impurities as well as by the method of thermal treatment (Nikiforova et al. 2009).

Furthermore, the technical cellulose has a developed fibrous surface that gives a good possibility for sorption of radionuclides presenting as colloidal particles. This is a quite important possibility because Voronina et al. (2015b) reported that the part of colloidal fraction of ^{137}Cs in spiked samples of tap water varied from 10% in spring to 50% in autumn. This difference is conditioned by various chemical composition of tap water at various seasons.

Carboxylic groups are weak acid cation exchange functional groups; therefore, they can dissociate at neutral and alkaline pH ranges. Figure 12.1 shows the pH dependences of cesium sorption by the technical cellulose obtained from waste of corn production. It is obvious that degree of cesium sorption by the samples of the technical cellulose is maximal at the pH range of 5–9.

The results showed that carboxylic groups provide very low selectivity for radionuclides. Sorption of radionuclides by the technical cellulose occurs mainly due to retention of their colloidal forms that is confirmed by the experiments on yttrium and cesium sorption. Yttrium shows more affinity to colloids formation than cesium; therefore, cellulose sorbs yttrium better than cesium. By contrast, the technical cellulose does not sorb strontium presenting in a solution only as ionic forms.

Chemical modification of the cellulose with obtaining nickel-potassium ferrocyanide allows for introduction of new sorption sites resulting in a significant increase of cellulose selectivity for cesium. Mixed nickel-potassium ferrocyanide based on cellulose from rice husk showed the best sorption properties; for this sorbent, cesium distribution coefficient was found to be as high as $3.9 \cdot 10^5$ L/kg (Voronina et al. 2013).

The relationships described above, agree well with the data obtained by Minakova (2008). The technical cellulose from rice husk possess a low degree of crystallinity (25%), extended absorbency (150 g/m^2) and a high water retention (280%); due to these properties, this cellulose is easily saturated by modifying solutions and therefore, its modification occurs more effectively. As compared with other types of cellulose, the cellulose from rice husk contains more amorphous clusters that are probably conditioned by special vegetation process and morphological structure of rice. High content of amorphous clusters affects easy penetration and retention of aqueous solutions.

Thus, the cellulose from waste of food industry modified by nickel-potassium ferrocyanide possesses excellent sorption and kinetic properties; it can be successfully used for rehabilitation of natural water bodies and decontamination of natural waters and technogenic solutions containing ^{137}Cs.

12.4.4 Hydrolytic Lignin

Hydrolytic lignin is a solid by-product of hydrolysis of wood and some other vegetable materials. It consists of various chemical organic compounds. Hydrolytic lignin contains approximately 10–11% of methoxylic, 5–6% of carboxylic and 3% of phenolic functional groups in terms of the absolutely dry product (Chudakov 1983).

Nikiforov and Yurchenko (2010) showed that distribution coefficient of ^{90}Sr by hydrolytic lignin at distilled water is ~ 12 ± 1 L/kg; whereas, for lignin treated by concentrated sodium carbonate, ammonium hydroxide and sodium hydroxide solutions, K_d values increased up to 417 ± 21, 353 ± 19 and 4532 ± 124 L/kg respectively. In addition, these authors studied the effect of Na^+ and Ca^{2+} concentrations on ^{90}Sr sorption. It was shown that distribution coefficient of ^{90}Sr in 0.01 M NaCl and $CaCl_2$ solutions decreased by factors of 3 and 40 respectively as compared with normal K_d values obtained in distilled water.

Sorption of Ra, Th and U by hydrolytic lignin from solutions with a composite chemical structure was studied by Rachkova et al. (2006). Based on the achieved results, the method of rehabilitation of radioactively contaminated soils using hydrolytic lignin was suggested (Rachkova and Shuktomova 2008).

As other green sorbents, hydrolytic lignin can be chemically modified in order to increase its selectivity for radionuclides. For example, the sorbent based on phosphorylated lignin with high phosphorus content (16.6% wt.) was obtained for actinides sorption. For this sorbent, uranium and thorium distribution coefficients are $9.7 \bullet 10^3$ and $3.0 \bullet 10^3$ L/kg respectively (Bykov and Ershov 2009, 2010).

12.4.5 *Living and Dead Phytoplankton*

In natural water bodies, phytoplankton participates in radionuclides sorption and natural decontamination of water due to radionuclides transfer from water to bottom sediments; thus, phytoplankton may be considered as a prospective biosorbent. The effectiveness of biological mechanism of radionuclides interception and transfer from the surface to lower layers was mentioned by Warner and Harrison (1993). Vertical distribution of plutonium in seawater is conditioned by on the one hand weight and density of plutonium-containing particles and on the other hand interception of plutonium by phytoplankton living at a certain depth (Romanchuk et al. 2016). Maximal plutonium concentrations were found at the depth of 100–177 m.

Both accumulation factor and distribution coefficient may be used for quantitative characterization of a biosorbent. The phytoplankton shows higher accumulation factors in fresh water as compared with seawater due to rather lower concentration of mineral salts. For example, accumulation factor of ^{90}Sr by algae from seawater is 20, whereas for fresh water this value is $5 \cdot 10^5$; accumulation factors of iron by fish is 10^5 and 10^3 in river and ocean water respectively (Voronina et al. 2010). Phytoplankton accumulates activation radionuclides (^{65}Zn, ^{60}Co, ^{55}Fe, ^{56}Mn) better than fission products.

Polyakov et al. (2016) studied the difference of sorption behavior of living and dead freshwater plankton. Sorption of Sr, Ba, Mn, Fe, rare earth elements, Th and U is studied in this work. It is shown that for almost all elements (excluding Mg) sorption by living plankton is more intensive and with higher values of distribution coefficients than by dead plankton; the reverse dependence is observed for magnesium. For these radionuclides, distribution coefficients vary from 10^3 to 10^5 L/kg. It is also shown than living plankton has a higher sorption capacity as compared with dead plankton.

12.4.6 *Humic Acids and Their Derivatives*

Humic acids are natural organic compounds with unstable structure and composition. They contain many types of ion exchange functional groups such as –COOH, –OH, $-OCH_3$, etc. that can exchange hydrogen by alkaline and alkaline earth cations. In soils, humic acids usually present as calcium, magnesium, ammonium and sodium humates rather than free acids. These organic compounds affect radionuclides behavior in underground waters (Geckeis et al. 2011). Humic compounds can affect the fate of radionuclides in the environment as well as possibility of their separation from waters and soils. The presence of humic acids in groundwater may cause either increase of decrease of radionuclide mobility due to formation of complex compounds (Koopal et al. 2001). The type of this influence depends on chemical properties of a radionuclide.

Covering the surface of mineral particles, humic acids may block their sorption sites. In this case, ^{137}Cs may increase its mobility because it is strongly sorbed by clayey minerals, whereas stability constants of cesium humates are very low (Lofts et al. 2002; Voronina et al. 2010). Helal et al. (2007) reported that Cs^+ forms weak complex compounds with humic acids and does not bind with fulvic acids. No similar dependence is observed for strontium. By contrast to cesium, mobility of plutonium significantly decreases in presence of humic acids because plutonium interaction with humates is more preferable than sorption on clayey minerals.

Use of humic acids as sorbents is very complicated because of their high solubility in aqueous solutions at $pH > 3.5$ (Guthrie et al. 2003; Baker and Khalili 2003). It is experimentally shown that humic acids are nonselective sorbents. Precipitates of humic acids can sorb thorium (IV) and uranium (VI) ions with distribution coefficients $K_d \sim 10^3–10^4$ L/kg; for strontium, aluminum and iron (II) ions distribution coefficients are found to be ~10^3 L/kg (Polyakov 2007; Volkov 2015). Distribution coefficients of chromium (III), manganese (II) and alkaline earth metals significantly decrease down to $10^{0-}10^2$ L/kg with the increase of concentration of humic acid in the solution; this can be explained by formation of complex compounds of these cations with free humic acid (Volkov 2015).

Presence of humic acids in soil solutions results in an increase of Pu and Am leaching from soils by a factor of 4–8, depending on the type of a soil (Goryachenkova et al. 2009). Pu and Am distribution in various groups of humic and fulvic acids with different molecular weight and size were studied. Understanding the regularities of the actinides distribution in fractions of humic acid makes it possible to affect actinides mobility: decrease of actinides mobility may be achieved by controlling the dispersed state of humic acids in aquifers.

Humic matter possesses reducing properties; therefore, they are able to reduce some actinides from the highest oxidation states to the tetravalent or pentavalent state. For example, Np(VI) and Pu(VI) may be reduced to Np(V) or Np(IV) and Pu(V) or Pu(IV) respectively (Sapozhnikov et al. 2006; Shcherbina et al. 2007). Plutonium forms various complex compounds with humic and fulvic acids. These reactions can be described as either interaction with a functional group or interaction with the whole macromolecule. Humic acids can form organomineral aggregates with the size of 60–500 nm; behavior of these particles is an average between behavior of soluble complex compounds and colloidal particles. As it is shown by Romanchuk et al. (2016), plutonium complexes with organic compounds may exist as dissolved forms or colloidal particles. Thus, actinides binding into soluble humate complex compounds should affect actinides behavior in the environment.

Furthermore, humate complex compounds are available for interception by plants; thus, plutonium can be involved into migration in food chains.

Humic acids can affect the sorption properties of natural and synthetic inorganic sorbents with respect to radionuclides. This affect is intensively reported by examples of Pb(II) sorption by goethite (Orsetti et al. 2006), Co(II), Sr(II) and Se(IV) sorption by goethite (Masset et al. 2000), Np sorption by goethite and hematite (Khasanova et al. 2007), U(VI) and Np(V) sorption by kaolinite (Niitsu et al. 1997; Křepelova et al. 2006), Th (IV) sorption by bentonite (Xu et al. 2006). Polyakov et al. (2015) studied sorption of Cs (I), Mg (II), Ca (II), Al (III), Co, Ce (III), Th (IV) and U (VI) by iron (III) hexcyanoferrate (II). Malakhov and Voronina (2016) reported the effect of presence of humic acids on sorption of Cs (I) and Sr (II) by clinoptilolite, glauconite and nickel-potassium ferrocyanide based on these minerals.

Perminova et al. (1996) showed the possibility of synthesis of humic acids derivatives with required properties via chemical modification of natural humic acids. These derivatives can be used for radionuclides elimination from contaminated underground waters. Pumping the soluble humic acids derivatives into a water bearing stratum through a system of wells allows for creation of a geochemical barrier without soil extraction; this should reduce the cost of activities for decontamination of radioactive underground water (Kalmykov et al. 2005; Shcherbina 2009).

12.5 Conclusion and Future Prospective

The problem of radionuclides elimination from large volumes of natural media (soils, natural waters with various salt contents including drinking water) cannot be solved using synthetic inorganic sorbents because of their high cost and low affinity to the environment. In spite of all advantages of synthetic inorganic sorbents (high K_d values, selectivity and exchange capacity), these sorbents find a limited applications. Synthetic sorbents may become a potential secondary source of the environmental pollution by chemical compounds due to destruction of the sorbents after a long-term contact with various aqueous solutions. Using these sorbents is possible only after the study of their chemical stability at the conditions similar to natural; the study of their toxicity and carcinogenicity should be also performed.

Sorption methods based on use of natural or chemically modified natural materials may become an eco-friendly way for decontamination of natural ecosystems from radionuclides and decrease of radionuclides migration in the environment. For example, natural inorganic sorbents (zeolites, etc.) have been already widely used for decontamination of radioactively contaminated natural waters and soils. Green sorbents attract some practical interest and have certain perspectives. Among the green sorbents, there are old and reputed types widely used for water decontamination, such as activated carbons. In addition, some new materials were developed and studied for last decades. New methods of chemical modification of vegetable raw materials allow for improvement of physicochemical and sorption properties of these materials. These green sorbents show successful chemical stability, and selectivity comparable with that of natural inorganic sorbents. In contrast to inorganic sorbents, the natural organic materials allow obtaining sorbents with various textures such as granules, fibres and textile. Due to these various textures, green sorbents may be successfully used in both static and kinetic regimes of sorption. A complex approach combining use of natural organic and inorganic sorbents will allow improving the quality of the environment due to decrease of radioactive contamination.

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