

Chapter 2

Removal of Emerging Contaminants from Water and Wastewater by Adsorption Process

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Abstract Emerging contaminants are chemicals recently discovered in natural streams as a result of human and industrial activities. Most of them have no regulatory standard and can potentially cause deleterious effects in aquatic life at environmentally relevant concentrations. The conventional wastewater treatment plants (WWTPs) are not always effective for the removal of these huge classes of pollutants and so further water treatments are necessary. This chapter has the aim to study the adsorption process in the removal of emerging compounds. Firstly, a brief description of adsorption mechanism is given and then the study of conventional and non-conventional adsorbents for the removal of emerging compounds is reviewed with the comparison between them.

Keywords Conventional adsorbents · Low-cost adsorbents · Pharmaceuticals · Personal care products · Endocrine disruptors

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2.1 Introduction

Since the end of the last century a large amount of products, such as medicines, disinfectants, contrast media, laundry detergents, surfactants, pesticides, dyes, paints, preservatives, food additives, and personal care products, have been released by chemical and pharmaceutical industries threatening the environment and human health. Currently there is a growing awareness of the impact of these contaminants on groundwater, rivers, and lakes. Therefore the removal of emerging contaminants of concern is now as ever important in the production of safe drinking water and the environmentally responsible release of wastewater [1, 2].

Although very little investment has been made in the past on water treatment facilities, typically water supply and treatment often received more priority than wastewater collection and treatment. However, due to the trends in urban development along with rapid population increase, wastewater treatment deserves greater emphasis. Several research studies showed that, treated wastewater, if appropriately managed, is viewed as a major component of the water resources supply to meet the needs of a growing economy. The greatest challenge in implementing this strategy is the adoption of low cost wastewater treatment technologies that will maximize the efficiency of utilizing limited water resources and ensuring compliance with all health and safety standards regarding reuse of treated wastewater effluents.

Treatment options which are typically considered for the removal of emerging contaminants from drinking water as well as wastewater include adsorption, Advanced Oxidation Processes (AOPs), Nanofiltration (NF), and Reverse Osmosis (RO) membranes [3, 4]. However, the shortcomings of most of these methods are high investment and maintenance costs, secondary pollution (generation of toxic sludge, etc.) and complicated procedure involved in the treatment. On the other hand physicochemical treatments such as coagulation/flocculation processes were generally found to be unable to remove Endocrine Disrupting Compounds (EDCs) and Pharmaceuticals and Personal Care Products (PPCPs). Although AOPs can be effective for the removal of emerging compounds, these processes can lead to the formation of oxidation intermediates that are mostly unknown at this point.

Conversely adsorption processes do not add undesirable by-products and have been found to be superior to other techniques for wastewater treatment in terms of simplicity of design and operation, and insensitivity of toxic substances [5]. Among several materials used as adsorbents, Activated Carbons (ACs) have been used for the removal of different types of emerging compounds in general but their use is sometimes restricted due to high cost. Furthermore when AC has been exhausted, it can be regenerated for further use but regeneration process results in a loss of carbon and the regenerated product may have a slightly lower adsorption capacity in comparison with the virgin-activated carbon. This has resulted in attempts by various workers to prepare low cost alternative adsorbents which may replace activated carbons in pollution control through adsorption process and to overcome their economic disadvantages [6].

Recently natural materials that are available in large quantities from agricultural operations have been evaluated as low cost adsorbents and environmental friendly [7]. Moreover the utilization of these waste materials as such directly or after some minor treatment as adsorbents is becoming vital concern because they represent unused resources and cause serious disposal problems [8–11]. A growing number of studies have been carried out in recent years to evaluate the behavior of emerging adsorbents such as agricultural products and by-product for emerging contaminants removal.

On the other hand industrial wastes, such as, fly ash, blast furnace slag and sludge, black liquor lignin, red mud, and waste slurry are currently being investigated as potential adsorbents for the removal of the emerging contaminants from wastewater.

This chapter presents the state of art of wastewater treatment by adsorption focusing in special way on removal of emerging contaminants. A brief introduction of the process is first given and then the use of commercial (activated carbons, clay and minerals) and unconventional adsorbents (agricultural and industrial waste) is discussed, taking into account several criteria such as adsorption capacities (q_e), equilibrium time (t_e) and emerging contaminant removal efficiency, which make them more or less suitable to be considered green.

2.2 Adsorption Process

2.2.1 Mechanisms and Definitions

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface. The substance being adsorbed is the *adsorbate* and the adsorbing material is termed the *adsorbent*. The properties of adsorbates and adsorbents are quite specific and depend upon their constituents. The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from wastewater [7].

If the interaction between the solid surface and the adsorbed molecules has a physical nature, the process is called *physisorption*. In this case, the attraction interactions are van der Waals forces and, as they are weak the process results are reversible. Furthermore, it occurs lower or close to the critical temperature of the adsorbed substance. On the other hand, if the attraction forces between adsorbed molecules and the solid surface are due to chemical bonding, the adsorption process is called *chemisorption*. Contrary to *physisorption*, *chemisorption* occurs only as a monolayer and, furthermore, substances chemisorbed on solid surface are hardly removed because of stronger forces at stake. Under favorable conditions, both processes can occur simultaneously or alternatively. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic.

2.2.2 Adsorption Isotherms

In a solid–liquid system adsorption results in the removal of solutes from solution and their accumulation at solid surface. The solute remaining in the solution reaches a dynamic equilibrium with that adsorbed on the solid phase. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm according to the general Eq. (2.1):

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2.1)$$

where q_t (mg/g) is the amount of adsorbate per mass unit of adsorbent at time t , C_0 and C_t (mg/L) are the initial and at time t concentration of adsorbate, respectively, V is the volume of the solution (L), and m is the mass of adsorbent (g).

Taking into account that adsorption process can be more complex, several adsorption isotherms were proposed. Among these the most used models to describe the process in water and wastewater applications were developed by (i) Langmuir, (ii) Brunauer, Emmet, and Teller (BET), and (iii) Freundlich.

The Langmuir adsorption model is valid for single-layer adsorption, whereas the BET model represents isotherms reflecting apparent multilayer adsorption. So, when the limit of adsorption is a monolayer, the BET isotherms reduce to the Langmuir equation. Both equations are limited by the assumption of uniform energies of adsorption on the surface.

The Langmuir isotherm is described by the Eq. (2.2):

$$\frac{q_e}{q_m} = \frac{bC_e}{1 + bC_e} \quad (2.2)$$

where q_e (mg/g) is the amount of adsorbate per mass unit of adsorbent at equilibrium, C_e is the liquid-phase concentration of the adsorbate at equilibrium (mg/L), q_m is the maximum adsorption capacity (mg/g) and b is the Langmuir constant related to the energy of adsorption (L/mg).

With the additional assumption that layers beyond the first have equal energies of adsorption, the BET equation takes the following simplified form:

$$q_e/q_m = (BC_e)/((C_e S - C)[1 + (B - 1)(C_e/(C_e S))]) \quad (2.3)$$

in which C_S is the saturation concentration of the solute, B is a constant which takes into account the energy of interaction with the surface, and all other symbols have the same significance as in Eq. (2.2).

The data related to adsorption from the liquid phase are fitted better by Freundlich isotherm equation [12]. It is a special case for heterogeneous surface energies. Freundlich isotherm is described by the Eq. (2.4):

$$q_e = K_F C_e^{1/n} \quad (2.4)$$

where K_F (mg/g) (L/mg)^{1/n} is the Freundlich capacity factor and $1/n$ is the Freundlich intensity parameter. The constants in the Freundlich isotherm can be determined by plotting $\log q_e$ versus $\log C_e$.

2.2.3 Factors Affecting Adsorption

The factors affecting the adsorption process are: (i) surface area, (ii) nature and initial concentration of adsorbate, (iii) solution pH, (iv) temperature, (v) interfering substances, and (vi) nature and dose of adsorbent.

Since adsorption is a surface phenomenon, the extent of adsorption is proportional to the specific surface area which is defined as that portion of the total surface area that is available for adsorption [13, 14]. Thus more finely divided and more porous is the solid greater is the amount of adsorption accomplished per unit weight of a solid adsorbent [15]. The major contribution to surface area is located in the pores of molecular dimensions. For example, the surface area of several activated carbon used for wastewater treatment is about 1,000 m²/g, with a mean particle diameter of about 1.6 mm and density of 1.4 g/cm³. Assuming spherical particles, only about 0.0003% of the total surface is the external surface of the carbon particle [16].

The physicochemical nature of the adsorbent drastically affects both rate and capacity of adsorption. The solubility of the solute greatly influences the adsorption equilibrium. In general, an inverse relationship can be expected between the extent of adsorption of a solute and its solubility in the solvent where the adsorption takes place. Molecular size is also relevant as it relates to the rate of uptake of organic solutes through the porous of the adsorbent material if the rate is controlled by intraparticle transport. In this case the reaction will generally proceed more rapidly with decrease of adsorbate molecule [15, 17–19].

The pH of the solution affects the extent of adsorption because the distribution of surface charge of the adsorbent can change (because of the composition of raw materials and the technique of activation) thus varying the extent of adsorption according to the adsorbate functional groups [15, 20–22]. For example Hamdaoui [23] showed that adsorption of methylene blue on sawdust and crushed brick increased by increasing pH (until a value of 9). For pH lower than 5 both adsorbents were positively charged: in this case, the adsorption decreased because methylene blue is a cationic dye.

Another important parameter is the temperature. Adsorption reactions are normally exothermic; thus the extent of adsorption generally increases with decreasing temperature [15, 24–26].

Finally, the adsorption can be affected by the concentration of organic and inorganic compounds. The adsorption process is strongly influenced by a mixture of many compounds which are typically present in water and wastewater. The compounds can mutually enhance adsorption, may act relatively independently, or

may interfere with one other. In most cases, as also shown hereinafter, natural organic matter (NOM) negatively affects the adsorption of emerging compounds in surface waters and wastewaters [22, 27, 28].

2.3 Removal of Emerging Compounds by Adsorption

Emerging contaminants are defined as compounds that are still unregulated or in process of regularization and that can be a threat to environmental ecosystems and human health [29, 30]. The words “emerging compounds” encompass a huge quantity of pollutants, including PPCPs, synthetically and naturally occurring hormones, industrial and household chemicals, nanomaterials, and some disinfection by-products (DBPs), as well as their transformation products [30]. Sources and pathways of emerging compounds into the environment depend on how (and where) they are used and how the products containing them are disposed. Figure 2.1 shows the possible contamination pathways of emerging contaminants.

The most of emerging compounds are sent to conventional Wastewater Treatment Plants (WWTPs) that allow only partial removal of micropollutants by stripping, sorption, and biological degradation.

Stripping is negligible compared with the other ones because most of emerging compounds are characterized by low volatility property. It has been demonstrated that stripping efficiency is not relevant even for musk fragrances which are slightly volatile with an Henry constant (H) value about of 0.005 [31, 32].

Sorption on primary and secondary sludge is more important than stripping process. It occurs like *absorption* on the lipid fraction of the sludge, especially on the primary sludge, and *adsorption* onto sludge through electrostatic interactions between positively charged compounds and negatively charged microorganisms surface [32]. So acid and lipophilic compounds (e.g. hormones, anti-inflammatories, fluoroquinolones) are efficiently removed in WWTPs unlike basic (clofibrac acid, bezafibrate), neutral (diazepam, phenazone, and carbamazepine), and polar compounds (beta-lactam antibiotics) [33, 34].

In addition to chemical properties of specific compounds, WWTPs operating conditions are also important to study the adsorption onto sludge of emerging compounds. For example, ciprofloxacin, a polar compound, sorbed very well onto suspended solids [34], while diclofenac, which is an acid drug, is characterized from a strong variability in the removal percentage (15–80%) because of different WWTPs conditions [33, 35].

Another mechanism removal is biological degradation which is described by reaction rate constant k_{biol} . According to this parameter, compounds can be classified in [31, 32]:

- Highly biodegradable $k_{\text{biol}} > 10 \text{ L/g}_{\text{SS}} \text{ d}$;
- Moderately biodegradable $0.1 < k_{\text{biol}} < 10 \text{ L/g}_{\text{SS}} \text{ d}$;
- Hardly biodegradable $k_{\text{biol}} < 0.1 \text{ L/g}_{\text{SS}} \text{ d}$.

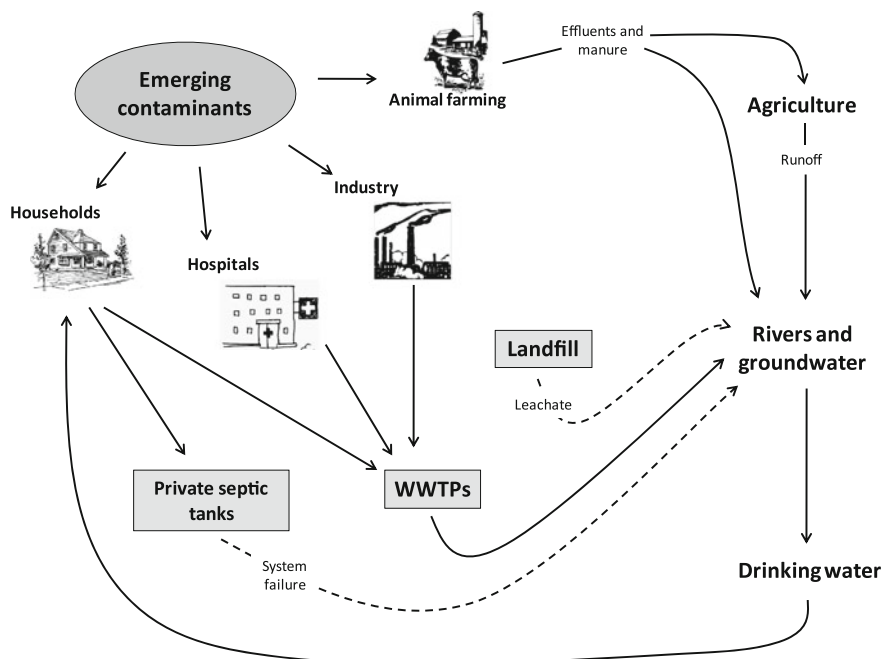


Fig. 2.1 Potential sources and pathways of emerging compounds into the environment

Also in this case biological operating conditions are of relevant importance. Indeed, biological decomposition increases with the age of sludge [31, 34] and hydraulic retention time [36]. Some compounds are removed with low sludge age (2–5 days), other ones are hardly degradable also with sludge age greater than 20 days [34]. So, in many cases, WWTPs do not have right operating conditions to remove well-defined emerging compounds. This implies the upgrading of the plant or the use of a tertiary treatment to avoid the input of pollutants into the environment.

In the last years many studies were carried out to remove emerging pollutants by adsorption process. The most used adsorbents were commercial ones (such as natural clays, minerals, and activated carbons).

2.3.1 Commercial Adsorbents

2.3.1.1 Activated Carbon

Activated carbon prepared from different source materials (e.g. coal, coconut shells, lignite, wood, etc.) is the most popular and widely used adsorbent in wastewater treatment throughout the world. Its application in the form of

carbonized wood (charcoal) has been described first in the Sanskrit medical lore and then in the Egyptian papyrus. Sanskrit writings, dating about 2,000 BC, tell how to purify impure water by boiling it in copper vessels, exposure to sunlight, and filtering through charcoal [6].

Activated carbon is produced by a process consisting of pyrolysis of raw material followed by activation with oxidizing gases. The product obtained is known as activated carbon and generally has a very porous structure with a large surface area ranging from 600 to 2,000 m²/g.

Most studies concerning the removal of micropollutants in aqueous solution by adsorption are carried out by using activated carbon. However, with the aim of implementing the technology at full scale application, studies of water and wastewater are most significant. For this reason in this section only works concerning emerging contaminants found in drinking water and in wastewater will be discussed.

Redding et al. [37] evaluated the efficiency of rapid small-scale column for the treatment of a lake water spiked with 29 EDCs and PPCPs with concentration values of 100–200 ng/L. Authors studied the behavior of two kinds of carbons: a conventional activated carbon and two modified lignite carbons prepared utilizing a high-temperature steam and methane/steam. The conventional one showed a shorter bed life than modified lignite carbons. Indeed lignite variants removed EDCs/PPCPs 3–4 times longer than did commercial carbon. Furthermore the most adsorbed compounds were steroids (androstenedione, estradiol, estriol, estrone, ethynylestradiol, progesterone, and testosterone) which are characterized by quite similar molecular volume, which averaged 80 mL/mol.

The removal of 17 β -estradiol from a raw drinking water was studied from Yoon et al. [22] using 5 mg/L of PAC (coal-based). The removal percentage was >90% regardless contact times and at a very low pollutant concentration (27 ng/L). This compound was also studied in the work of Yoon et al. [17]. In this study two raw drinking waters were spiked with three contaminants: 17 β -estradiol, 17 α -ethynylestradiol, and bisphenol A. They were removed by adsorption on several different PAC coal-based except a wood-based one. After 1 h contact time and 45 mg/L of PAC the removal was 99% for all compounds. Increasing contact time (4 and 24 h) PAC doses were reduced (15 and 9 mg/L respectively). It is evident that contact time and adsorbent dose are important parameters in the adsorption process [28, 38]: a right combination of each allows to reach the right operating conditions in a full-scale plant.

Another important parameter is water-octanol partition coefficient (log K_{ow}). In particular, depending on log K_{ow} , hydrophobic pollutants (log K_{ow} > 4) have higher adsorption capacity [39–41], also if this is not always true [42, 43]. For example, Westerhoff et al. [42] evaluated the removal of 62 different EDCs/PPCPs (10–250 ng/L) in three drinking water sources. Results showed a relation between percentage EDCs/PPCPs removal and log K_{ow} , but not for all compounds (e.g. caffeine, pentoxifylline). This may be related to the difficulties to accurately estimate the log K_{ow} for some heterocyclic or aromatic nitrogen-containing compounds. Some results obtained by Westerhoff et al. [42] are reported in Fig. 2.2.

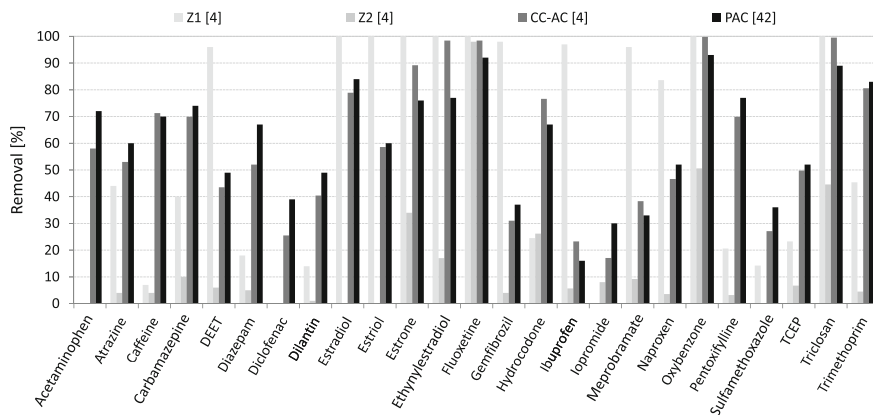


Fig. 2.2 Removal percentages correspond to 1 mg/l dose of activated carbon CC-AC, 100 mg/l dose of Z1 and Z2 and three weeks contact time, 5 mg/l dose of PAC and 4 h contact time. Amended from Ref. [4] with kind permission of © Elsevier (2009)

As previously said, another parameter which can negatively affect adsorption process is NOM, which competes with the specific compounds for adsorption sites. It is obvious that the presence of organic matter can block pores of activated carbon and, for this reason, the removal percentage decreases if compared with results of tests carried out on model water [18, 22, 28, 44].

The problem of organic materials in water gets worse for wastewater treatment and greater carbon doses or a combination of different treatments are needed to reach a good removal percentage and to control the problem of fast deterioration of adsorbents. For instance, Hartig et al. [45] investigated the removal by PAC adsorption of two micropollutants (N-n-butylbenzenesulphonamide and sulphamethoxazole) from tertiary wastewater effluents prior to and after filtration with a tight ultrafiltration membrane. The results showed that membrane filtration prior to PAC adsorption may lead to improved elimination rates for adsorbable and low molecular weight micropollutants. Another example was reported by Baumgarten et al. [46] who examined the removal of floxacins and their precursors present in wastewater by a combination of membrane biological reactor (MBR) with PAC adsorption. PAC addition into wastewater of MBR pilot plant significantly improved removal rates (floxacin >95% and fluoroquinolonic acid as high as 77% removals at 50 mg/L initial PAC dose). Furthermore, PAC adsorption process was used to treat the permeate of MBR plant. In this case two kinds of PACs were used. The best adsorbent allowed to reach removal percentages >70% with a PAC dose of 50 mg/L. Increasing PAC dose up to 500 mg/L, a nearly complete elimination of fluoroquinolonic acids and floxacins was achieved.

The removal of micropollutants from wastewater was also carried out by the addition of commercial PAC directly to the activated sludge system with and without the adsorbent recycling to biological process [47]. Results showed that the

removal efficiency increased from 30 to 50% with PAC (10 mg/L) recycling into the biological tank. Increasing PAC concentration to 15 mg/L and with PAC recycling all compounds were removed by more than 80%.

2.3.1.2 Clays

Natural clay minerals are well known from the earliest day of civilization. Because of their low cost, high surface area, high porosity, and abundance in most continents, clays are good candidates as adsorbents. There are many kinds of clay: smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite, sepiolite, bentonite, kaolinite, diatomite, and Fuller's earth (attapulgite and montmorillonite varieties) [6]. The adsorption capacities depend on negative charge on the surface, which gives clay the capability to adsorb positively charged species.

Putra et al. [21] investigated the removal of amoxicillin from aqueous solutions by adsorption on bentonite. A quite high value of initial amoxicillin concentration (300 mg/L) was chosen to represent pharmaceutical wastewater. Adsorption of amoxicillin was strongly affected by pH because it can alter the charge of amoxicillin molecule. In particular, q_e values increased as the pH value decreased. In this study, adsorption capacity of bentonite was compared with a commercial GAC. Both adsorbents were found to be quite effective because removal percentage as high as 88% was achieved. q_e value was comparable (around 20 mg/g for bentonite and 25 mg/g for commercial activated carbon), but adsorption equilibrium time for activated carbon was only 35 min compared to 8 h of bentonite. The main reason could be the different surface area of the two adsorbents: 92 m²/g for bentonite and 1,093 m²/g for GAC.

Bekçi et al. [24, 48] investigated montmorillonite as adsorbent in the removal of trimethoprim, one of the main antibacterial agents used in human and veterinary medicine worldwide. Results showed that the process was exothermic because of adsorption efficiency increased as temperature decreased. As a consequence of thermodynamic studies, the authors demonstrated that physisorption was the main mechanism of adsorption. Another parameter that affected adsorption of trimethoprim was pH. At low pH conditions (in an aqueous solution montmorillonite has a pH value of 3.31), trimethoprim is in the protonated form, so it was strongly adsorbed to the negatively charged surface of the montmorillonite. In the best conditions, the amount of drug adsorbed was 60 mg/g for 1 h of contact time (initial compound concentration was 290.3 mg/L).

2.3.1.3 Minerals

Another class of adsorbents includes natural minerals. Among these zeolite and goethite have been investigated in the adsorption of pharmaceuticals. Zeolite is

typically used for the removal of dyes and heavy metals. Like clay minerals, adsorption capacity is linked to negative charge on the structure.

Ötker and Akmehmet-Balcioğlu [26] investigated the adsorption of enrofloxacin, a fluoroquinolone group antibiotic, onto natural zeolite and subsequent adsorbent regeneration by ozone treatment. The best results were achieved for lower pH values (pH investigated values were 5, 7, and 10) because of enrofloxacin is in the cationic form and so the adsorption onto negatively charged zeolite surface was better. Unlike adsorption clays, the process was endothermic, with higher enrofloxacin removal at higher investigated temperature. However, the results obtained with varying temperature (28, 37, 45, and 50 °C) showed a little change in the adsorbed amount, ranging from 16 to 18 mg/g. Adsorption equilibrium was reached at 200 min and the adsorbed amount at equilibrium was about 18 mg/g. The regeneration process by ozone oxidation (1.4 g/h) was able to decompose enrofloxacin adsorbed onto zeolite as well as to affect zeolite pore structure by decreasing pore size.

Really interesting is the study of Rossner et al. [4] concerning a lake water spiked by a mixture of 25 emerging contaminants at varying concentration (200–900 ng/L). The adsorbents used were one coconut-shell-based GAC (CC-AC), one carbonaceous resin and two high-silica zeolites, Z1 (modernite zeolite) and Z2 (Y zeolite). The order of process efficiency was activated carbon > carbonaceous resins > zeolites. Carbonaceous adsorbents were more effective for micropollutants removal probably because activated carbons exhibit a broader micropore size distribution, in which compounds of different shapes and sizes can be effectively accommodated. High-silica zeolites, on the contrary, have uniform pore sizes, which is effective for the removal of a specific compound but not for a broad mixture of contaminants.

In Fig. 2.2 results were compared with the average removal percentages obtained in four natural waters treated with 5 mg/L of powdered activated carbon (PAC) [42]. Removal values obtained with CC-AC and PAC were comparable also if the brand and the concentration of two adsorbents were different. Z1 allowed to reach high removal percentage of micropollutants but not for all compounds such as activated carbons. Z2 was the worst adsorbent and removal values were really different from Z1 (only fluoxetine, oxybenzone and triclosan were removed by Z2).

Zhang and Huang [19] investigated the removal of seven fluoroquinolones (FQs) and five structurally related model amines with Fe oxides, using two sources of goethite, with a focus on both adsorption and oxidation by Fe oxides. The authors found out that flumequine can be adsorbed more strongly to goethite than other FQs, due to effects of speciation and molecular size. Under investigated conditions (pH 5), adsorbent was positively charged, flumequine in neutral form, and the other FQs in cationic form, thus explaining the lower adsorption for the latter. Furthermore, in terms of molecular size, the other FQs being characterized

Table 2.1 Adsorption capacity (q_e), initial contaminant concentration (C_0), and equilibrium time of some adsorbents investigated

Adsorbent	Adsorbate	C_0 (mg/L)	t_e (min)	q_e (mg/g)	Reference
Bentonite	Amoxicillin	300	≈ 500	20	[21]
Montmorillonite	Trimethoprim	290.3	60	60	[24]
Natural zeolite	Enrofloxacin	200	200	18	[26]

by a larger molecule structure than flumequine may obstruct adsorption active sites.

In Table 2.1 are shown initial concentration of some emerging compounds and adsorption capacities (reached at a fixed equilibrium time) of some adsorbents.

2.3.2 Low Cost Adsorbents

Although, activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse kinds of pollutants from water, its widespread use is sometimes restricted due to the high costs [8, 9, 49]. Attempts have been made to develop low-cost alternative adsorbents which may be classified in two ways (Fig. 2.3) either (i) on basis of their availability, i.e., (a) natural materials (wood, peat, coal, lignite etc.), (b) industrial/agricultural/domestic wastes or by-products (slag, sludge, fly ash, bagasse flyash, red mud etc.), and (c) synthesized products; or (ii) depending on their nature, i.e., (a) inorganic and (b) organic material [6, 8, 10, 11].

2.3.2.1 Agricultural Waste

The basic components of the agricultural waste materials include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch, containing a variety of functional groups [10]. In particular agricultural materials containing cellulose show a potential sorption capacity for various pollutants. If these wastes could be used as low-cost adsorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low-cost adsorbent, if developed, can reduce the treatment of wastewaters at a reasonable cost [9, 50]. Agricultural waste is a rich source for activated carbon production due to its low ash content and reasonable hardness [51].

The agricultural solid wastes from cheap and readily available resources such as almond shell, hazelnut shell, poplar, walnut sawdust [52], orange peel [53, 54], sawdust [55], rice husk [56], sugarcane bagasse [57], coconut burch waste [58], and papaya seed [59] have been investigated for the removal of pollutants from aqueous solutions.

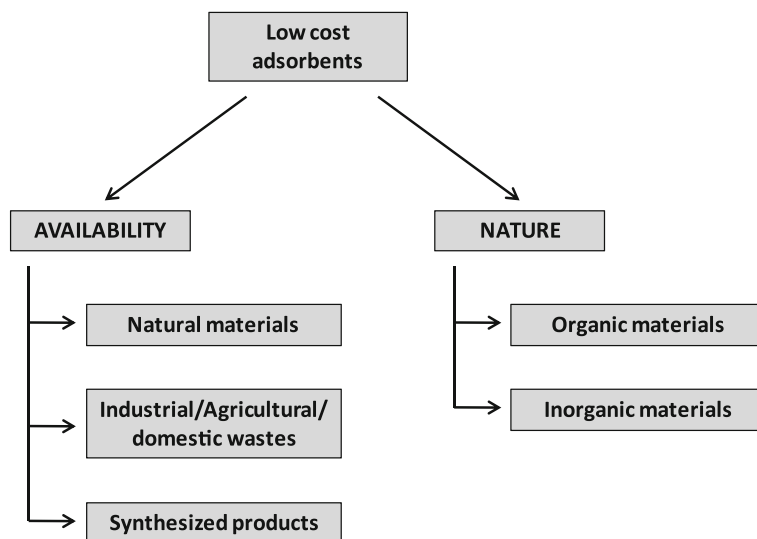


Fig. 2.3 Possible classification of low-cost adsorbents

Sawdust [55] is one of the most appealing materials among agricultural waste materials, used for removing pollutants, such as, dyes, salts, and heavy metals from water and wastewater. The material consists of lignin, cellulose, and hemicellulose, with polyphenolic groups playing important role for binding dyes through different mechanisms. Generally the adsorption takes place by complexation, ion exchange and hydrogen bonding.

The agricultural waste materials have been used in their natural form or after some physical or chemical modification. Pretreatment methods using different kinds of modifying agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), and dyes for the purpose of removing soluble organic compounds, color and metal from the aqueous solutions have been performed.

Shells of almond and hazelnut, poplar, and walnut sawdust were investigated by Aydin et al. [52] for the removal of acid green 25 and acid red 183 from aqueous solution. Equilibrium isotherms were determined and analyzed using the Freundlich equation. Capacities of adsorbent were found to be in the order: walnut > poplar > almond > hazelnut for acid green 25 and almond > walnut > poplar > hazelnut for acid red 183, respectively.

Orange peel as adsorbent has also been studied by Arami et al. [53] for the removal of direct dyes: direct red 23 and direct red 80. The authors investigated the effects of initial dye concentration (50, 75, 100, 125 mg/L), pH, mixing rate,

contact time, and quantity of orange peel at 25 °C. The adsorption capacity was found to be 10.72 and 21.05 mg/g at initial pH 2 (15 min), for direct red 23 and direct red 80, respectively.

Hamdaoui [23] studied the removal of methylene blue, from aqueous solution (40 mg/L) onto cedar sawdust in order to explore their potential use as low-cost adsorbents for wastewater dye removal. Adsorption isotherms were determined at 20 °C and the experimental data obtained were modeled with the Langmuir, Freundlich, Elovich, and Temkin isotherm equations. The authors concluded that equilibrium data were well represented by a Langmuir isotherm equation with maximum adsorption capacity of 142.36 mg/g.

Rice husk as obtained from a local rice mill grounded, sieved, washed and then dried at 80 °C was used by McKay et al. [60] for removal of two basic dyes: safranin and methylene blue and adsorption capacity of 838 and 312 mg/g was found.

Batzias and Sidiras [61] studied beech saw dust as low-cost adsorbent for the removal of methylene blue and basic red 22 (1.4–14, 2.1–21 mg/L). In order to know the effect of chemical treatment and to improve its efficiency the authors also tested the potential of the adsorbent by treating it with CaCl₂ [61], using mild acid hydrolysis [62] and found it to increase the adsorption capacity. Further studies to evaluate the effect of pH were also carried out by Batzias et al. [63].

Shi et al. [64] improved the adsorption capacity of sunflower stalks by chemically grafting quaternary ammonium groups on them. The modified sunflower stalks exhibited increased adsorption capacity for anionic dyes, due to the existence of quaternary ammonium ions on the surface of the residues. The maximum adsorption capacities on modified sunflower stalks were found to be 191.0 and 216.0 mg/g for Congo red and direct blue, respectively, which were at least four times higher than that observed on unmodified sunflower stalks. Further, the same authors observed that adsorption rates of two direct dyestuffs were much higher on the modified residues than on unmodified ones. A comparison of various low-cost adsorbents derived from different agricultural wastes for the removal of diverse types of aquatic pollutants is summarized in Table 2.2.

2.3.2.2 Industrial Waste

Widespread industrial activities generate huge amount of solid waste materials as by-products. Industrial wastes such as sludge, fly ash, and red mud are classified as low-cost materials, locally available and can be used as adsorbents for removal of pollutant from aqueous solution [65].

Fly ash is a waste material originating in combustion processes. Although it may contain some hazardous substances, such as heavy metals, it has been showing good adsorption qualities for phenolic compounds [66]. The maximum phenol adsorption capacity has been found to be 27.9 mg/g for fly ash and 108.0 mg/g for granular activated carbon at initial phenol concentration of 100 mg/L.

Wang et al. [67] used fly ash as adsorbent for the removal of methylene blue from aqueous solution reporting an adsorption capacity of 4.47 mg/g. The effect

Table 2.2 Adsorption capacities (q_e), initial contaminant concentration (C_0), and equilibrium time of different agricultural wastes for removal of pollutants from aqueous solutions

Adsorbent	Adsorbate	C_0 (mg/L)	t_e (min)	q_e (mg/g)	Reference
Rice husk (water washed)	Cd(II)	50	600	8.58	[68]
Rice husk (sodium hydroxide)		50	240	20.24	
Rice husk (sodium bicarbonate)		50	60	16.18	
Rice husk (epichlorohydrin)		50	120	11.12	
Rice husk ash	Methylene blue			690	[69]
Jack fruit peel	Methylene blue	50	180	285.713	[70]
Papaya seed	Methylene blue	50	180	555.557	[71]
Bael fruit shell (Ortho-phosphoric acid)	Cr (VI)	75	240	17.27	[72]
Tea waste	Cu	100	90	48	[73]
	Pb			65	
Hazelnut shell	Ni (II)			10.11	[74]
Sugarcane bagasse	PAHs	15		0.345	[75]
Green coconut shells		15		0.553	
Orange peel	Direct red 23	50	15	10.72	[53]
	Direct red 80	50	15	21.05	
Rice husk	Safranine			838	[60]
	Methylene blue	312	360	312	
Cedar sawdust	Methylene blue	40		142.36	[23]
Beech sawdust	Methylene blue	14		9.78	[61]
	Basic red 22	21		20.2	
Beech sawdust (H ₂ SO ₄)	Methylene blue	14		30.5	[62]
	Basic red 22	21		24.10	

of physical (heat) and chemical treatment was also studied on as-received fly ash. The heat treatment was reported to have adverse effect on the adsorption capacity of fly ash but acid treatment (by nitric acid) resulted in an increase of adsorption capacity of fly ash (7.99 mg/g).

Bhatnagar and Jain [9] investigated steel and fertilizer industries wastes, as an adsorbent for the adsorption of cationic dyes. It was found that the adsorbents prepared from blast furnace sludge, dust and slag have poor porosity and low surface area, resulting in very low efficiency for adsorption of dyes.

Smith et al. [76] reported that chemical activation using alkali metal hydroxide reagents, especially KOH, was found to be the most effective technique for producing high BET surface area sludge-based adsorbents (in excess of 1,800 m²/g).

Red mud is a waste material formed during the production of alumina [77]. Red mud has been explored as an alternate adsorbent for arsenic. An alkaline aqueous medium (pH 9.5) favored As(III) removal, whereas the acidic pH range (1.1–3.2) was effective for As(V) removal [78, 79]. A comparison of various low-cost adsorbents derived from different industrial wastes for the removal of diverse types of aquatic pollutants is summarized in Table 2.3.

2.4 Adsorption as Green Technology

The literature studies showed above highlighted that adsorption process can be considered an efficient treatment for the removal of emerging compounds from water. It allows to reach good removal percentage and, furthermore, being a physical process, does not imply by-products formation, which could be more toxic than parent compounds. It is obvious that adsorption process is encompassed in an integrated treatment system which involves many factors, such as available space for the construction of treatment facilities, waste disposal constraints, desired finished water quality, and capital and operating costs. All these factors imply the achievement of the optimal operating conditions for low-cost high efficiencies [10, 80].

The most used and studied adsorbents are certainly activated carbons both for synthetic and real water (surface water and wastewater). In spite of large use of them, the overall idea is to reduce the use of activated carbon because of high costs. Therefore, scientific world is looking for low-cost adsorbents for water pollution. In addition to cost problem, another important factor pushing toward low-cost adsorbents is the use of agricultural and industrial waste products in order to extend the life of waste materials without introducing into the environment new materials as adsorbents and to reduce costs for waste disposal therefore contributing to environmental protection. Anyway a suitable non-conventional low-cost adsorbent should:

- (1) be efficient to remove many and different contaminants,
- (2) have high adsorption capacity and rate of adsorption, and
- (3) have high selectivity for different concentrations.

Table 2.3 Adsorption capacities (q_e), initial contaminant concentration (C_0), and equilibrium time of different industrial wastes for removal of pollutants from aqueous solutions

Adsorbent	Adsorbate	C_0 (mg/L)	t_e (min)	q_e (mg/g)	Reference
Carbon slurry of fertilizer industry	Ethyl orange	5.10^{-4} M	45	198	[50]
	Metanil yellow	5.10^{-4} M	45	211	
	Acid blue 113	5.10^{-4} M	45	219	
Exhausted olive cake ash	Ni (II)	100	120	8.38	[81]
	Cd (II)	100	120	7.32	
	Cr(VI)	50	120	26.31	[82]
Clarified sludge		50	180	25.57	
Activated alumina		50	180	23.86	
Fly ash				4.47	
Raw fly ash	Methylene blue			7.99	[67]
Fly ash (acid treatment)				19.46	[83]
Fertilizer industrial waste (carbon slurry waste)	As (V)	50	480	40.7	[84]
	4-bromophenol	4.10^{-4} M	480	170.4	
	2-bromophenol	4.10^{-4} M	480	190.2	
	2,4-dibromophenol	4.10^{-4} M	480	76	[85]
Modified basic oxygen furnace slag	Reactive blue 19	100	180	60	
	Reactive black 5	100	180	55	
	Reactive red 120	100	180		

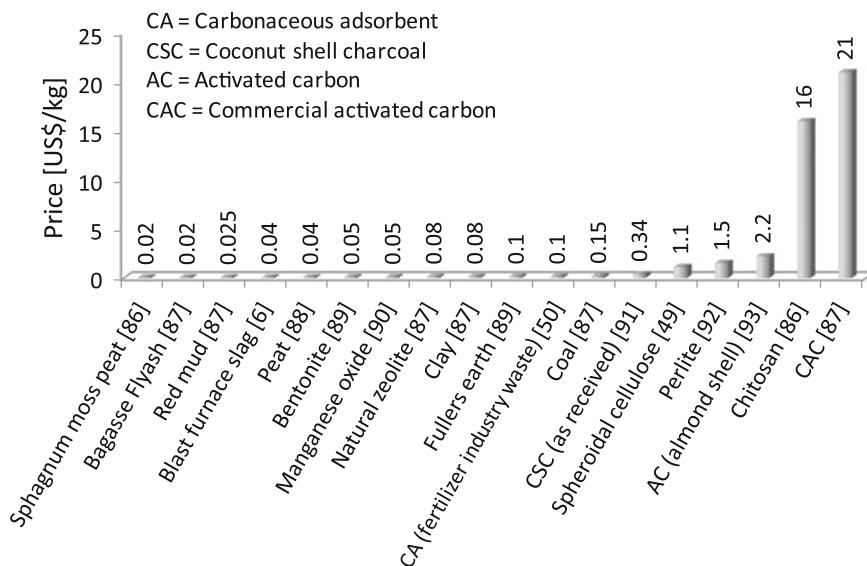


Fig. 2.4 Cost of several adsorbents. The image contains the references to the respective adsorbents in square brackets [6, 49, 50, 86–93]

It is very difficult to understand which adsorbent is better because they have different properties (porosity, surface area, and physical strength) as well as different adsorption capacities related to experimental conditions [94].

Adsorbent cost is an important parameter to compare different materials. In Fig. 2.4 costs of several low-cost and commercial adsorbents are shown.

They should be considered indicative because of adsorbent costs depend on many factors such as its availability, its source (natural, industrial/agricultural/domestic wastes or by-products or synthesized products), treatment conditions, and recycle and lifetime issues. Furthermore, the cost also depends on when adsorbents are produced in (or for) developed, developing, or underdeveloped countries [95]. Finally, a right cost evaluation is related to the application scale and, although many studies about non-conventional low-cost adsorbents are available in the literature, they are limited to laboratory scale. Thus, cost estimation is not strictly right and pilot-plant studies should also be conducted utilizing low-cost adsorbents to check their feasibility on commercial scale.

2.5 Concluding Remarks

The economical and easily available adsorbent would certainly make an adsorption-based process a viable alternative for the treatment of wastewater containing pollutants. Selection of an appropriate adsorbent is one of the key issues to achieve the maximum removal of type of pollutant depending upon the adsorbent and

adsorbate characteristics. The effectiveness of the treatment depends not only on the properties of the adsorbent and adsorbate, but also on various environmental conditions and variables used for the adsorption process, e.g. pH, ionic strength, temperature, existence of competing organic or inorganic compounds in solution, initial adsorbate and adsorbent concentration, contact time and speed of rotation, particle size of adsorbent, etc.

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