2 Utility of Surface-Modified Biochar for Sequestration of Heavy Metals in Water

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Abstract

Increased industrial growth in the world serves a significant role in the water contamination with heavy metals. Heavy metals such as arsenic, copper, lead, chromium, mercury, nickel, and cadmium impart several health hazards to humans, plants, and animals. Moreover their accumulation potential disturbs the food chain. Freshwater demand is higher in the world which may lead to a severe water crisis in the upcoming years. Hence feasible water treatment technologies must be identified and its efficiency must be concentrated. Heavy metals bear the risk of biodegradation and transformation. Hence adsorption is found to be an attractive method nowadays for sequestration of such metals. It is an economically feasible and eco-friendly method. Biochar is advantageous over other adsorbents such as activated carbon, graphene, silica, etc. It is the product of a thermochemical process which possesses better adsorption capacity. It reduces the production time and in addition provides fuel. Different pyrolysis conditions influence the quantity and yield of char. The degree of biochar adsorption is mainly focused on the type of biomass used, metal species concentrated, functional groups, and surface area of the biochar. Regeneration of biomass is also an important phenomenon to be considered as the adsorbed biochar may cause secondary pollution if not disposed in a proper manner. In order to improve the surface properties, physical structure, and regeneration capacity of biochar, various modification technologies have been adopted. It will also pave way for

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the effective utilization of waste biomaterials in wastewater treatment. The modification may be carried out before pyrolysis or after pyrolysis. It is categorized under physical, chemical, magnetic, and mineral impregnation methods. This review focuses on the mechanism and improvements of the treated biochar in comparison to the pristine biochar for heavy metal sequestration.

Keywords

Biochar · Surface modification · Biosorbent · Heavy metals

2.1 Introduction

Water is an essential commodity for which our entire life relies on. Save water to save the earth and to secure future generation are what the human aims and needs. With the improvement in scientific works, our earth is attaining newfangled spheres, but the amount that the people are giving and will give in upcoming years will be surely too high putting the people in appalling situation. One of the upshots is environmental pollution which hits our country both economically and ecologically. The demand for water has increased tremendously with the production of huge quantities of wastewater with manifold pollutants. Among the innumerable pollutants known so far, the heavy metals have drawn a special concern considering its carcinogenicity, and it causes serious threat to the aquatic ecosystem. Among the variety of industries in operation, tanneries drain effluent rich in chromium which in turn reaches the human through the biomagnification processes. Therefore, a suitable cleanup technology is needed for making our environment pollution-free. To overcome the aforesaid lacuna and to justify a suitable technology, the literature pertinent to the sources of contamination, environmental impact, available conventional methods, suitable technology, and its impact on crop growth are reviewed and presented below.

2.2 Water Contamination

"When the well's dry, we know the worth of water." Water is an asset to be carried over for the future generation benefits. But nowadays water has been polluted anthropogenically in many ways. The industries play a prime role comprising metals like cadmium, zinc, nickel, chromium, arsenic, lead, iron, etc. (Debnath et al. 2020). These heavy metals enter into food chain and bioaccumulate in the body of humans and animals (Salam et al. 2011). Among various inorganics, chromium is an egregious contaminant released by the industries comprising leather tanning, pigment manufacturing, metal finishing, and wood preservation.

A recent study estimated that wastewater generated from municipal and urban centers is about 61,754 million of liters per day (MLD) out of which 62% is left untreated due to insufficient facilities and dispersed into the water and groundwater sources (Kamble et al. 2019). Because the treatments vary with financial status of the nation where 70%, 38%, and 8% of the wastewater are treated by high-income, middle-income, and low-income countries, respectively. As a result, water availability is much reduced, for example, per capita availability of water in India had decreased from 5177 m^3/year in 1951 to 1545 m^3/year in 2011 given by the Ministry of Water Resources (2011). Although the industries came after various pavements for the metal contamination eradication, huge volume of discharge is carried out annually into the environment which is the gateway for diverse impairment to the life forms on the earth.

2.2.1 Leather Industries and Its Production

Among the different industries, the highest activity is recorded by the leather industries where the discharge contains about 4–5% of Cr in 15% of mineral components. Here, 70–80% of the input in the industry acts upon hides and the remaining expelled as waste. They consume water of about 15–20 m^3/ton of raw skin. Wastewater expelled by the tanneries lies within 1500–3000 mg L^{-1}. Worldwide production of leather is around 2108.94 Mmt^2. It exceeds 551,000 tons/year affecting 1.8 million people (Rafique et al. 2019; Tamersit and Bouhidel 2020).

India is one of the major exporters of leather-related products which ranks fifth in the world. It contributes about 15% of the world leather production capacity (Alam et al. 2007). In Tamil Nadu, Dindigul and Vellore are the preponderant districts in tannery industries which release enormous volume of wastewater that affects major parts and causes several diseases (Princy et al. 2020).

2.2.2 Chromium and Its Toxicity

Chromium (III) and Cr (VI) are the two major forms present in nature. Chromium (III) persists in two forms as Cr $(OH)_3$ and Cr_2O_3. They are less soluble, immobile, and less toxic. In contradiction, hexavalent chromium leads to serious damages to human beings due to its carcinogenic and mutagenic properties as it is highly mobile, toxic, and rapidly soluble. They prevail in terms of anions such as $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-}. Hexavalent ions show comparatively 10–100 times more toxicity than the trivalent ions (Sarkar et al. 2019; Qin et al. 2020).

According to the World Health Organization, the admissible limit of total chromium in drinking water is 50μgL^{-1} although chromium (III) was found to be an essential nutrient. But potable water has been reported to have as high as 120μgL^{-1} (WHO 2011). The maximum contaminant level (MCL) for chromium is 5×10^{-2} mgL^{-1} reported by USEPA (Bej et al. 2020). In human, chromium exposure is contributed more by the oral uptake, whereas 1.9–7% by means of water and role of air is trivial. Once ingested, the hexavalent chromium is reduced to trivalent and binds to the macromolecules. Hilar lymph nodes and lungs registered higher concentrations. Those Cr (III) ions result in producing more reactive oxygen species and reactive chromium intermediates causing apoptosis. In addition, they cause lung cancer, nephrotoxicity, DNA damage, and intravascular hemolysis. Ongon'g et al. (2020) found that children who consume vegetables cultivated in Cr (VI) soils are more prone to health risks than the adults. The major route for crops is by means of growing in the chromium-contaminated soil. The vegetable crops uptake, translocate, and accumulate Cr (VI) in the edible parts and roots which results in the decline of carbohydrates, sugars, amino acids, and proteins. Stambulska et al. (2018) had specified that these hexavalent Cr ions will disturb the pigment and cellular function. It also has impact on nodular formation affecting their symbiosis and gets accumulated there. Other effects on plants were inhibition of seed germination, protein modification, and damage to DNA.

2.2.3 Treatment Methods

There are various physicochemical and biological methods for the treatment of wastewater such as precipitation, filtration, flocculation, adsorption, membrane separation, and ion exchange. The suitable treatment method is chosen based on the factors such as treatment energy, cost, environmental effects, and influent and effluent quality. The physical methods have certain complications including high cost of equipment, toxic sludge generation, and high space requirements and time. Chemical methods also beneficial in terms of higher pollutant removal efficiency but have some disadvantages like secondary waste production, higher operational cost etc. Other drawbacks are incomplete removal, continuous checking, and higher energy requirement (Crini 2005; Siyal et al. 2020). Among them adsorption was found to be an effective one compared to others as the amount of secondary waste generated is comparatively less (Renu et al. 2017). Adsorption mostly relies on the surface characteristics of adsorbents particularly their surface area and porous structure (Wu et al. 2017).

The frequently used adsorbents for metal removal are silica gel, activated carbon, biochar, and alumina (Ahmed et al. 2016). Activated carbon is found to have higher cost in commercial purpose and poor regeneration capacity, and hence its usage is foreshortened. Hence biochar prepared by exploiting agricultural and industrial wastes have been widely utilized.

2.2.4 Adsorption

Adsorption has been in practical use for longer time. It is used for the purpose of separation or purification. Adsorption and absorption differ with the fact that adsorption takes place on a two-dimensional matrix, whereas absorption occurs on a three-dimensional matrix. Adsorption takes place at the interface of two phases. Usually, it happens on a pore-filled solid matter in which the other phase liquid or gas is attracted. There are two types of sorption based on the interaction of adsorbate and adsorbent: physisorption and chemisorption. The physisorption is due to the forces such as dipole-dipole forces, London forces, and van der Waals interaction. On the other hand, covalent bond forms between the adsorbent and adsorbate by transferring of electrons in case of chemisorption. Physisorption has low enthalpy and it is reversible, while the chemisorption is irreversible and has high enthalpy (Sims et al. 2019; Ghouti and Da'ana 2020).

The main advantage of adsorption process is regeneration potential of the adsorbent. Isosteric heat is also considered as an important factor in this study. It is calculated by dividing the infinitesimal change of the adsorbate enthalpy by change in the infinitesimal of the adsorbed amount. The most important thing for gaining knowledge on adsorption process is adsorption equilibria. This helps in understanding how much components can fit on the biosorbent (Ayawei et al. 2017). Isotherms of adsorption give the equilibrium of the adsorbents. It depends on various properties like pH, temperature, initial ion concentration, adsorbent, dosage, and adsorbate.

2.2.5 Biochar Production

Biochar is a finely grained porous, stable, and carbon-rich material produced by thermal decomposition (pyrolysis, gasification, and torrefaction) of biomass at a temperature of about 300–700 °C with limited or no supply of oxygen (Ahmed et al. 2015). Thines et al. (2017) reported that their production dates back to the past history as native Indians produced char by burning the wood stocks piled up in the pits which resulted in fertile soil known as terra preta. It has an excellent application in pollutant removal as it is simple to produce, eco-friendly, economic, and efficient compared to other methods of heavy metal remediation. In addition, they possess unique properties such as high microporosity, higher ion exchange, larger surface area, and high adsorption capacity (Mohanty et al. 2013). Apart from adsorption they possess multiple applications comprising soil remediation, carbon sequestration, and bioenergy production.

Biochar production is influenced by temperature. For instance, at elevated temperature it possesses high aromatic nature but due to deoxygenation possesses fewer functional groups and lesser ion exchange capability. In case of lower temperature of about 300–400 °C, the biochar shows more functional groups (C–H and C=C) and contains numerous organic characters.

Such biochar are prepared nowadays from various feedstocks including rice husk, pomelo peel, water hyacinth, *Lantana camara*, pinewood, sugar beet tailings, pineapple peel, sugarcane bagasse, sewage sludge, peanut straw, wood bark, and dairy manure at different temperature for adsorption of the specific inorganics from effluent (Nithya et al. 2020). Those nonliving biomass by producing biochar remove the inorganic contaminants by means of passive binding over their surface. Amid different sources, water hyacinth is a poisonous and dreadful weed found ubiquitously in the water bodies globally. The weed was brought as ornamental plant in India from Brazil. IUCN (International Union for Conservation of Nature and Natural Resources) has classified it as one of the most aggressive invasive species. Its growth is vigorous as it could increase its size twofold within 5 days. It is an urgent need to get rid of this serious issue. It creates the way for evapotranspiration rate increase and greenhouse gas emissions. It has high cellulosic carbon and high biomass yield. The conversion into biochar happens by the transformation of cellulose carbon into aromatic carbon, which is more stable.

2.2.6 Water Hyacinth as a Biosorbent

Water hyacinth (*Eichhornia crassipes*), belonging to Pontederiaceae family, is a rooted aquatic macrophyte. The leaves of the weeds accumulate higher concentration of heavy metals followed by stem and roots. This pickerel weed leads to several adverse effects because of their vigorous growing ability. They affect the biodiversity of water body by reducing the dissolved oxygen concentration as they block the pavement for sunlight penetrance. Moreover, they interfere in the activities of fishing, irrigation, and power generation and lead to navigation jam. Besides these disadvantages, they also possess some of the properties such as improved pores, mineral components, functional groups, and larger surface area. Hence, they are utilized as "low-cost" adsorbents of heavy metals. Absence of natural enemies in the newly introduced places paves way for them to grow exponentially. In a hectare of water, 270–400 tons of *Eicchornia* are noticed present. Utilization of this widespread species for wastewater treatment is very suitable as it is an eco-friendly, economic, and efficient technology. This abundant weed gives good biomass yield, and it is a rich source of cellulose (64.51%), lignin (7.69%), and ash (12%). In addition, they acquire both the cationic and anionic binding sites. Though raw biochar is a good adsorbent, they are less efficient compared to the modified char. It involves functional modification and surface oxidation that enhances the adsorption potential. For instance, acid or alkali treatment will increase the metal uptake. In case of chromium, Cr^{6+} uptake was improved, whereas Cr^{3+} uptake is lowered in acidic enhancement.

2.2.7 Mechanism of Adsorption

There are mainly five different mechanisms (Fig. 2.1) for removal of heavy metals from industrial washouts which are as follows (Inyang et al. 2016):

1. Physical sorption
2. Ion exchange
3. Complexation
4. Electrostatic interactions
5. Precipitation

Hexavalent chromium follows the mechanism of electrostatic attraction and reduction where they are converted into trivalent which forms complex with the functional groups. Heavy metals form complex with the biochar due to the occurrence of special O-containing functional groups including carboxylic, hydroxyl,

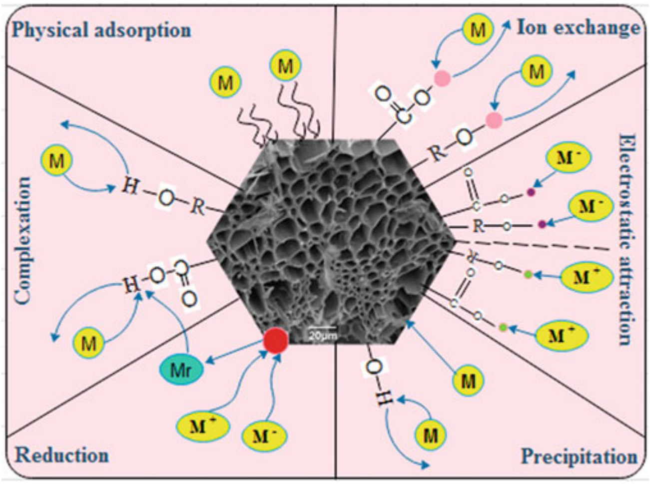


Fig. 2.1 Various mechanisms for sorption of metal ions on biochar (Shaheen et al. 2018)

amine, alcohol, etc. The O-containing functional groups such as catechol, diols, and unsaturated anhydro sugars on the adsorbent surface reduce Cr (VI) into Cr (III)). Xu et al. (2018) found out that besides reducing the ions, they also aid in adsorbing the reduced metal ion. The authors also quoted that at lower pH the biochar acts as electron donors, whereas at higher pH acts as electron shuttle (O-centered radicals).

2.2.8 Impact of Surface Properties

Surface properties highly affect the adsorption process of biochar. It is based on the type of biomass used, pyrolysis temperature, and pretreatment/posttreatment handling. Biochar is an amorphous and honeycombed structure. They have heterogeneous adsorption sites. If pore size is too narrow for the ions to bind and diffuse into the surface, steric hindrance occurs. The criteria for hindrance lie in the fact that the ratio of pore size to the minimum critical diameter is less than 10^{50}. The pore aperture of the surface varies. The different sizes include nanostructures, micropores (<2 nm), and mesopores (2–50 nm). The micropores are produced on the surface of biochar due to dehydration during the pyrolysis process. Composition of biochar predicts the pore aperture. Plant biochar shows higher porosity than biochar from biosolids. Cellulose-rich biochar produces micropores, whereas macropores are developed from lignin-rich material.

Another surface factor influencing sorption is surface charge. As the biochar added for wastewater treatment, surface charge is controlled by the pH of the solution. Point of zero charge is the pH where net charge of the surface is zero. When $pH > pH_{pzc}$, negative charges dominate the surface so it attracts cations and vice versa. At higher pyrolysis temperature, pH_{zpc} is increased where positively charged functional groups increased resulting in less negative charges.

Organic content is an important surface property. It is determined by aromaticity and polarity. Aromaticity is represented by ratio of aromatic to total carbon content in the biochar. Polarity is subjected to the aliphatic portion of the biochar. The overall polarity is increased by the oxygen-containing functional groups. The organic content can be carbonized and non-carbonized due to improper carbonization which influences isotherm. Carbonized and non-carbonized fractions represent isotherm with curvature and linear isotherm, respectively.

Another surface property of biochar is elemental composition. When the feedstock is pyrolyzed, chemical composition of the biomass gets changed. When the temperature increases, the detachment of oxygen- and hydrogen-containing functional groups occurs and leads to increase in carbon groups. Hence, the carbon can increase for about 90% and greater reduction in oxygen and hydrogen. Modified biochar assists in amelioration of the surface properties. Chemical oxidation of the biochar increases the hydrophilicity as the functional groups (Table 2.1) such as –OH and –COOH are increased. It also enhances pore size and structure of biochar. On the other hand, chemical reduction decreases the oxygen-containing groups and improves the nonpolarity of biochar. In addition, it expands the surface area and strengthens the pore volume (Yang et al. 2019).

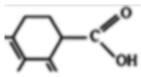
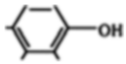
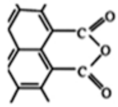
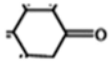
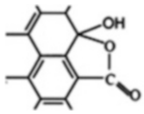
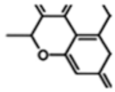
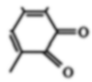
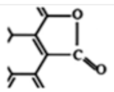
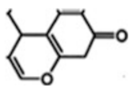
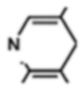
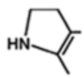
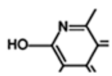
2.2.9 Factors Affecting Adsorption Process

2.2.9.1 Effect of pH

The pH is a significant factor influencing adsorption. The pH differs not only for the different metals but also for different kinds of biomass. As aforesaid, anion adsorption is facilitated more at $pH_{pzc} > pH$. On the other hand, $pH_{pzc} < pH$ favors cationic sorption. Chromium prevails in $HCrO^{4-}$ form at pH 1.0 and as $Cr_2O_7^{2-}$, $HCrO_4^-$, and $Cr_3O_{10}^{2-}$ at pH 2–6, while the dominant species is $HCrO_4^-$. At pH greater than 6–11, CrO_4^{2-} dominates. Hexavalent chromium adsorption is higher at lower pH and decreases as the pH increases. Because at lower pH, the biosorbent surface is dominated by H ions and hence the surface becomes positively charged which improves the Cr (VI) adsorption onto surface, while at higher pH, OH ions influences the surface which causes electrostatic repulsion between the adsorbent surface and the negatively charged Cr (VI) species. The Cr (VI) adsorption at pH below 2 is administered by reduction to Cr (III). The pH is also varied due to changes in acidic groups on adsorbent surface.

Modified biochar surface also shows variations in different pH range due to changes in the chemical nature of the adsorbent functional group. Those modified char adsorb Cr (VI) more efficiently because they have low surface net negative charge compared to the unmodified biochar. In addition to higher acidic conditions, modified biochar could remove the ions at high rates even in the wide range of pH up to 7.0. Adsorbate solution pH influences the solution chemistry of ions such as redox reactions, hydrolysis, and precipitation which in turn influences biosorption

Table 2.1 Functional groups on the surface of biochar (Tomczyk et al. 2020)

Functional groups	Structural formula
Acidic groups	
Carboxyl	
Phenol	
Ether	
Anhydride	
Carbonyl	
Lactol	
Chromene	
Quinone	
Lactone	
Pyrone	
Basic groups	
Pyridine	
Pyrrole	
Pyridone	

availability and speciation of ions. Finally, increase in pH resulted in negative charges on the surface and therefore decreased the sorption. In addition, more number of protons is required for hexavalent reduction.

2.2.9.2 Effect of Dosage

Amount of biochar added is a vital parameter affecting the biosorption. It is studied by fixing other factors constant. Usually, the adsorption increases with increase in dosage. This fact is due to increase in surface area of the adsorption resulting in large number of active sites. But in many cases, lower amount of adsorbent shows higher uptake of heavy metals. This is due to overlapping of Cr (VI) ions on surface of the biosorbent decreased the unit adsorption. It also increased the diffusion path length. Thus, increase in dosage of biochar increased the removal efficiency but decreased the biosorption per unit weight of biochar. There may be interference in binding sites due to deficiency of solute for all the exchangeable sites present on the biochar. The removal efficiency stays constant after reaching the optimum level. Adsorbent functional group and their concentration influence the adsorption of different adsorbents (Singha and Das 2011).

2.2.9.3 Effect of Reaction Time

Chromium (VI) adsorption increases with increase in time. Equilibrium time is determined by the adsorbent nature and its sorption sites (Singha and Das 2011). The adsorption is higher at the initial stage and then it decreases near the equilibrium. Presence of more number of binding sites increases the surface area which is later occupied by the Cr (VI) and gets saturated. The initial metal ion concentration facilitates the monolayer formation on the surface. Hexavalent chromium ions are adsorbed within short period to reach equilibrium in physical adsorption. When the contact time increases, the chemical binding of species with the surface of biochar also increased.

2.2.9.4 Effect of Temperature

Temperature also plays a crucial role in adsorption process. The adsorption potential increases with increase in temperature indicating that the process is endothermic. This is because the rise in temperature results in higher diffusion rate of the metal ions on the adsorbent internal pores and outer surface. Equilibrium capacity is varied by the temperature for various absorbents. Hence, the adsorption is favored by lower temperature for some cases. For example, biochar made from peanut hull have higher potential for Cr (VI) removal at lower temperature as the functional groups containing "O" are more at this condition which favor metal ion interaction. But when this biochar is treated with magnetic property (γ-Fe_2O_3), it is favored by higher temperature.

2.2.10 Isotherm Study for Adsorption

In order to enhance the adsorption process, isotherms must be studied well. These equilibrium relationships are essential for the assessment of effective adsorption system and how the adsorbate interacts with the surface of adsorbents. As a result, isotherm explains the mobility of heavy metal ion from aqueous solution into the porous solid adsorbent. It also describes the degree of affinity, surface properties, and capacity of adsorbent used. The isotherms are classified as one-, two-, three-, four-, and five-parameter isotherms. One-parameter isotherm is the simplest isotherm model where the adsorbate is directly proportional to the partial pressure of the gas. The most commonly used isotherm models are Langmuir and Freundlich isotherms.

Langmuir isotherm is used to quantify the adsorption potential of various adsorbents though it was initiated for gas-solid phase. It is a monolayer adsorption that occurs at a fixed number of sites. It follows a dynamic equilibrium which balances the rate of adsorption and desorption. This theory has arrived that rise of distance results in rapid decrease of the intermolecular forces. In contrast, Freundlich isotherm is based on the multilayer adsorption between the liquid and solid phase. It occurs on a heterogeneous surface. In this model stronger binding sites are filled first and then the energy of adsorption decreases exponentially. Temkin isotherm takes into account the indirect interactions of the adsorbate and adsorbent. Increase in surface coverage leads to decrease in the heat of adsorption of molecules. Though nonlinear regression analysis is used by the researchers, linear analysis is frequently used for analyzing adsorption performance. Therefore, the successful adsorption isotherm modeling influences the accuracy of sorption process (Ayawei et al. 2017).

2.2.11 Kinetic Models for Adsorption of Heavy Metals

Kinetic study is used to express the rate of chemical processes that governs the residence time in adsorption process. It is used to determine the performance and mechanism of adsorption. The rate of kinetics depends on the species concentration, and the law is expressed as follows (Gupta and Bhattacharyya 2011):

$$R = K\,[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}} \ldots\ldots\ldots\ldots$$

where K is the kinetics coefficient and A, B, etc. are the species involved in adsorption which have the order a, b, etc.

The rate-limiting step and kinetics have been portrayed by different kinetic models. They are pseudo-first-order, pseudo-second-order, Adam-Bohart-Thomas model, Elovich model, Ritchie's equation, intraparticle diffusion, and external mass transfer model. Pseudo-first-order rate equation was first presented by Lagergren in 1898. He explained the oxalic and malonic acid adsorption by the charcoal, i.e., liquid-solid phase adsorption. Though it is the earliest model, it was found that it is not suitable for whole contact time, whereas appreciable only for about initial

20–30 min. Pseudo-second-order kinetic model was introduced by Ho which involves the divalent metal ion adsorption on peat. This model is interpreted as special kind of Langmuir kinetics that gives two assumptions. They are (1) amount of ion species determines the total number of sorption sites at equilibrium and (2) ion concentration is constant with time. Intraparticle diffusion model is found to be a suitable model in case of diffusion of ions into the pores for porous substance. It is a rate-limiting factor but not for the whole process where other models control the rate simultaneously. Homogeneous solid diffusion model (HSDM) is the typical intraparticle diffusion model. Elovich rate equation was initially introduced by Zledowitsch for chemisorption of gases onto solids, whereas it has expanded to the aqueous phase adsorption. Elovich model states that adsorption takes place on particular sites and the energy is directly proportional to surface coverage in adsorption.

2.2.12 Response Surface Methodology

Biosorption is a multifactor-dependent process which impacts the sorption performance. Hence, optimization is a best method to find the specific condition that results in best efficiency. The response surface methodology (RSM) is one of the excellent methods for optimization of parameters. It will help in reducing the number and cost of experiments. The RSM is a set of mathematical and statistical tools developed by Box and Wilson. It defines the interaction and relation between the dependent and independent variables. The results will be in the form of 2-D contours and 3-D plots (Nair et al. 2014).

Optimization in RSM is carried out by the following six steps. They are (1) independent variable selection, (2) suitable design selection, (3) carrying out the experiment and data generation, (4) the results were fitted with model equation, (5) verification of the obtained response graphs, and (6) graphical representation and determination of optimal conditions. The popular experiment designs involved are Box-Behnken design, central composite design, full three-level factorial design, and Doehlert matrix. The full factorial design includes three levels such as maximum, mean, and minimum which are represented by +1, 0, and −1, respectively. It includes all possible combinations. The disadvantage is second-order and higher-order polynomials. Hence to overcome this, Box and Wilson (1951) have introduced the central composite design (CCD). This CCD is highly efficient up to six factors and then decreases. The CCD is applied for parallel experiments instead of sequential experiments. In order to produce an alternative to the full factorial design, Box and Behnken developed the incomplete block design. It includes only two-level factorial (+1, −1) which is less labor extensive and more economical in industrial research. Apart from these advantages, RSM find difficulty over wide range. Hence the selection of domain must be concentrated by the experimenter (Nair et al. 2014).

2.2.13 Significance of Column Experiment

The contact between adsorbate and adsorbent is brought out by various techniques such as batch, column, continuous fluidized bed, and pulsed bed experiment. For adsorption of heavy metals, batch experiment is widely used in the laboratory scale, while column setup will facilitate treatment of large quantities of wastewater in commercial scale (Parameswari et al. 2020). The adsorption performance of the column study is explained by the breakthrough curve analysis. The determining factors for operation of column are time to attain breakthrough point and shape of the breakthrough curve. The effect of variables on the adsorption efficiency is described by various models. Among them, Adam-Bohart, Yoon-Nelson, and Thomas models are widely utilized. Thomas model predicts the breakthrough curves and it follows second-order reversible kinetics. It describes the column performance and predicts the monolayer adsorption. It is applied in adsorption process where internal and external diffusion limitations are absent. Yoon-Nelson model is a simple assumption which states that decreasing rate of probability of adsorption is directly proportional to breakthrough and adsorbate adsorption. Adam and Bohart model is based on the assumption that adsorption rate depends upon the residual capacity and sorbate concentration. Column experiment is better, fast, and feasible for industrial scale. Further studies are required to overcome the challenges of column study (Patel 2019).

2.2.14 Activation of Biochar

Tailoring the properties of biochar to improve the surface properties is an emerging technology for efficient removal of both organic and inorganic pollutants. Surface enhancement of biochar can be achieved by different methods (Fig. 2.2). They are as follows:

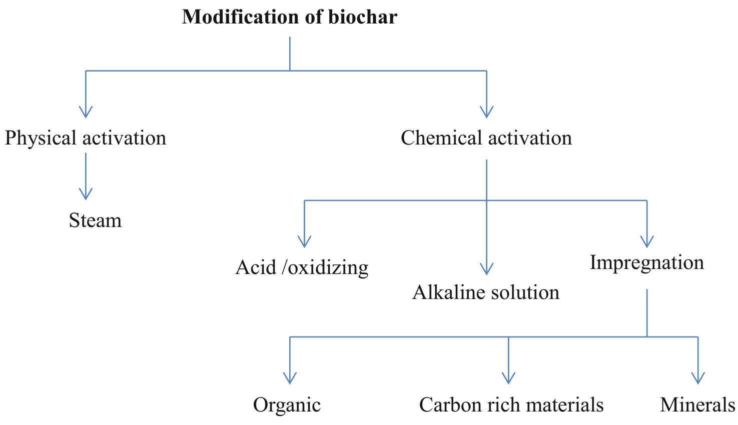


Fig. 2.2 Different methods of biochar modification (Shakoor et al. 2020)

1. Steam activation
2. Heat treatment
3. Acid modification
4. Alkali modification
5. Impregnation methods

Steam activation is the widely used method where improvement is obtained by exposure of biochar to steam for partial gasification which enhances the surface pores and surface area. Bardestani and Kaliaguine (2018) found an increase in BET surface area by steam activation from 50 to 1025 m^2/g.

The disadvantage of this process was found out that it does not have significant impact on the functional groups. Heat treatment increases the surface hydrophobicity and functional groups of biochar by exposing to heat at temperature of about 800–900 °C.

Acidic modification by introducing the oxidants improves the surface area due to increase in porosity. The expansion of micropores leads to increase in the oxygen-containing functional groups such as carboxylic, ketonic, and hydroxyl groups. Due to the presence of these groups, there is an increase in O/C and H/C molar ratios which leads to decrease in hydrophobicity. Sulfuric acid, oxalic acid, phosphoric acid, and nitric acid are the common oxidizing agents used for the biochar amelioration. Sarkar et al. (2019) in his study reported that acid modification enhanced the active sites 10 times and 25.29% increase in carbon content. It has also improved BET surface area of about $142.78 \pm 2.57\ m^2g^{-1}$.

The phosphoric acid treatment increases the micropores enhancing the specific surface area. The micropores were formed by two mechanisms: (1) H^+ catalysis process generates the micropores, utilizing H^+ ions from H_3PO_4, and (2) the organic PO_4^{3-} bridge ensured the carbon skeleton from collapse of micropores by means of phosphate radical cross-linking.

Enhancement of biochar with alkali like potassium hydroxide and sodium hydroxide offers additional positively charged sites which assist in absorbing negatively charged species. Alkali treatment increases the surface area as it increases the surface basicity. For example, potassium hydroxide-tailored biochar has improved surface area from 14.4 to 49.1 m^2g^{-1}. Sun et al. (2015) reported that effect of alkali modification depends on the preparation methods and feedstock nature. In addition to surface area, there is an increase in the surface aromaticity (H/C). When compared to acid treatment, alkali modification showed lesser O/C and higher N/C ratio. Mahdi et al. (2019) suggested that alkali pretreatment can consume long time and is performed at low temperature and high concentration. In case of acid pretreatment, it can be at lower temperature and long retention time, otherwise at higher temperature in a short retention time. Hence, time is one of the important factors to be considered during surface modification of the biosorbent.

Impregnation is accompanied by different materials such as metal oxides, minerals, organic compounds, nano-materials, clay, and carbonaceous materials. This method is quite different from the physical method as it introduces new functional groups which are absent on the surface earlier. It involves two methods of impregnation pre-pyrolysis and post-pyrolysis. The mineral impregnation is mostly carried out using $FeCl_3$, FeO, and $MgCl_2$ which introduces positive charge favorable for the removal of inorganics like chromium. The γ-Fe_2O_3 nanoparticles on surface enhance the sorption sites through electrostatic interactions. The major mechanisms for sorption on the biochar impregnated with magnetic material are electrostatic attraction, surface complexation, ion exchange, and O-containing groups. Coating with carbon-rich material is mostly assisted by the introduction of graphene oxide for effective sorption of heavy metals.

Treatment with polyethylenimine solution increases the sorption sites by introduction of primary and secondary amine groups (Table 2.2). In nanocomposite, establishment of particles such as MnO_x and ZnO reduces the overall O/C ratios which shoot up the metal uptake capacity. The nZVI has been utilized for reduction and adsorption of Cr (VI). The removal efficiency of 98.35% was recovered wherein the virgin biochar tends to remove only 64.04%. Wang et al. (2019) had modified the bamboo biochar with polyethylenimine for adsorbing U(VI) and compared with the unmodified biochar. As a result, PEI (polyethylenimine)-alkali/acid biochar showed 9–10 times higher adsorption capacity.

2.2.15 Regeneration of Adsorbents

As the biochar can undergo several adsorption-desorption cycles, it is a good option to go for effective desorption and regenerating the adsorbent from the adsorbate. The desorption process helps in reducing the biochar cost in treatment and also the environmental risk of secondary pollutant. The eluted metal can also be used for various purposes. It should be noted that the desorbents used are cheap and nonpolluting. The adsorbate must be easily readsorbed and the desorbing agent should not damage the structure of adsorbent. The elutant used may be of varying concentration from 0.01 to 5 M (Table 2.3). The efficiency increases with increase in molarity. For instance, Pb (II) ions adsorbed on the surface have been regenerated with 0.01 M at 77.7% efficiency and 0.5 M HCl at 98.3% efficiency. However, in some cases biochar structure may be degraded at higher concentration.

The best desorbent is chosen from the first desorption cycle. Double-distilled water is found to express worst behavior in detachment of bounded metal ions. Hence, adsorbed heavy metals are desorbed by undergoing multiple washes with various desorbents such as strong acids (HNO_3, HCl, H_2SO_4), strong alkali (NaOH), salts ($NaNO_3$, KNO_3), and chelating agents. These elutants provide cations which could replace the adsorbed metal ions on the surface of adsorbent. However, the metal ions regeneration cannot be 100% as they may be tightly bonded in the porous space and hence cannot be removed easily.

Acid favors regeneration process as acidic condition prevents the metal ion sorption. Desorption with alkali has less efficiency compared to the acids. The acid condition provides a space for the surface to be protonated by H_3O^+ ions desorbing the ions of positive charge. The sorbents were washed with distilled water after desorption followed by treating with 1 M $CaCl_2$. The use of calcium

Table 2.2 Adsorption capacity of various surface-modified biochar

Sl. no	Modifications	Feedstock	Adsorption capacity (mg/g)	Significance/effect	Reference
1.	Polyethylenimine	Rice husk	435.7	Introduced more amino groups, good stability in the adsorption-desorption cycles. Adsorption is very effective than pristine biochar, i.e., 18%	Ma et al. (2014)
2.	H_2SO_4	Sugarcane harvest residue	62.89	Promising adsorbent, releases less amount of trivalent Cr and less secondary sludge	Xiao et al. (2018)
3.	H_3PO_4	Pomelo peel	57.64	Electrostatic interaction followed by ion exchange enhanced the adsorption	Wu et al. (2017)
4.	$FeCl_3$	Sugarcane bagasse	13.37	At lower pH and higher temperature, the removal percentage is found to be higher at 99.89%	Zhu et al. (2012)
5.	Ca and Fe modification	Rice husk		Removal rate is 95%. The adsorption increased due to the mechanism of metal precipitation and electrostatic interactions	Agrafioti et al. (2014)
6.	Chitosan + Fe modifications	Water hyacinth	120	The adsorption is influenced by pH and found to be maximum at pH 2	Zhang et al. (2013)
7.	HCl	Willow residue	217.39	Removal efficacy is 97.40%, whereas in the pristine biochar found to be 64.04%	Zhu et al. (2018)
8.	H_2SO_4	Plum	14.024	High efficiency is attributed to the occurrence of surface complexation of sulfur-containing functional groups with the heavy metal ions	Pap et al. (2018)
9.	H_3PO_4	Jute fibers		Removal efficiency of Cr (VI) is about 98%, and also reduction percentage of Cr (VI) to Cr (III) is in the range of 86–97%. It could remediate the pollutant at the inherent pH	Chen et al. (2015)

(continued)

Table 2.2 (continued)

Sl. no	Modifications	Feedstock	Adsorption capacity (mg/g)	Significance/effect	Reference
10.	$FeCl_3$	Corncob	25.94	Fe^{2+} ions on the surface oxidized to Fe^{3+} and hence enhanced the hexavalent Cr reduction	Wang et al. (2019)
11.	Polydopamine-polyethylenimine	Rice husk	42.8	It has more stability and recyclability. However it loses the stability slightly only after eight cycles	
12.	Zn nanocomposite	Bagasse	102.66	The adsorption is twofold increased than the pristine biochar, and the ability withstands even after six desorption cycles	

chloride removes the excess protons and repairs the damage caused by the acid creating the new sites for binding. It also reduces the loss of sorbent mass and hence decreased by 18%. It has been recorded that even after three sorption cycles, the change in sorption and desorption efficiency is negligible. Hence the acid elutants have been used for better regeneration. But it fails in one or two cases. In case of recovery of Pb (II), sulfuric acid should not be used because of the lower solubility of lead sulfate resulting in lower pore volume (Abdolali et al. 2015).

Alkaline salts such as NaOH, $NaHCO_3$, and Na_2CO_3 were utilized as elutants. Alkaline desorbents can elute the metal ions based on the pH. The pH responsible for elution is alkaline condition (pH 8–10) because the adsorption forces weaken and the bounded Cr ions get eluted into the aqueous solution. Desorption of fixed bed column is carried out by purging with inert fluid, change in pH, and heat treatment.

Chelating agents desorb the heavy metals from the surface of adsorbents and produce the water-soluble compounds. Chatterjee and Abraham (2019) had reported that commonly used chelation agents are ethylenediaminetetraacetic acid (EDTA) and [*S*,*S*]-ethylenediamine disuccinic acid (EDDS). Without altering the nature of the adsorbent, 0.1 M EDTA showed good removal of chromium and copper. The EDDS also effectively desorbed the contaminants mainly Cu (II), Zn, and PB. In addition, it is also economic because it can be reused in several cycles.

2.2.16 Chrome Tanning from Recovered Chromium

As aforesaid chromium discharged from the tannery would cause serious damage to the environment. Hence chromium in the discharge must be treated and disposed. The used chrome liquor must be filtered and precipitated as chromium hydroxide

Table 2.3 Desorption of adsorbents using various desorbents

Adsorbent	Elutant	Adsorbate	Removal efficiency	Reference
Wheat straw biochar	HNO_3	Cr (VI)	79%	Tytłak et al. (2015)
Bagasse	0.1 M HNO_3	Pb^{2+}	90%	Kumari (2017)
Seaweed	4 N H_2SO_4	Cr	47%	Aravindhan et al. (2004)
Aminated chitosan bead	EDTA	Hg	95%	Jeon and Park (2005)
Titanium dioxide nanoparticles	0.1 M NaOH	Se (IV)	95%	Zhang et al. (2009)
Nano-zerovalent iron	0.1 M NaOH	As	100%	Zhu et al. (2009)
Alkali-treated apricot shells	0.1 M HCl	Fe, Pb, Cu, Cr, Ni, Zn	95%	Šoštarić et al. (2018)
Sulfonated expanded graphite	0.1 M HCl	Pb (II)	90.8%	Jiao et al. (2017)
Spirulina sp.	0.1 M EDTA	Cr	60%	Chojnacka et al. (2005)
Cellulose acetate membrane	1 M H_2SO_4	Cu (II)	32.1%	Kamaruzaman et al. (2017)
Cladosporium cladosporioides	0.1 M H_2SO_4	Cu	43%	do Carmo et al. (2013)
Titanium dioxide nanoparticles	0.01 M $NaNO_3$	Zn (II)	88%	Hu and Shipley (2012)
Mesoporous γ-Fe_2O_3	0.1 M NaOH	Cr	90%	Wang and Lo (2009)

using alkali. When required quantity of sulfuric acid was added to the precipitate, basic chromium sulfate is regenerated. Thus recovered chromium can be utilized in tanning process.

2.3 Conclusion

The prevailing purification technologies used to remove contaminants are too costly and not eco-friendly. As the research is oriented toward economically sound and environmentally safe technology for contaminant removal, it has paved the way for the present investigation for the use of water hyacinth biochar as a suitable adsorbent to bind the metallic ions. The biosorbent is renewable in nature and have more binding sites towards heavy metals which adds strength to the development of a viable biological system for adsorption of heavy metals from industrial effluent. Besides this, the possibility of metal recovery and reuse of desorbed chromium in tanning process will reduce approximately 10–20% of production cost incurred through the process of chrome tanning. Hence, this proposed study can be a viable green technology which is highly useful for the industry to treat their wastewater effectively and economically ensuring the socioeconomic status of the people besides protecting the environment.

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