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Sorption of Heavy Metals onto Biochar

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Abstract

Biochar is a stable carbon-rich product synthesized from biological materials through different heating methods above the decomposition temperature. The potential uses of biochar in various fields include soil fertility improvement, C sequestration, pollutant removal and waste minimization/reuse. In recent years, large number of research has confirmed that biochar can be used successfully for the removal of heavy metal ions from aqueous solutions. The main aim of this chapter is to summarize and assess the sorption capacity of biochar toward various heavy metal ions. Considering that sorption is a surface phenomenon, the key parameters controlling the formation of biochar including pyrolysis temperature, residence time, and feedstock type will be discussed in detail. In addition, the mechanism associated with remediation of heavy metal ions and the physicochemical factors affecting the sorption potential will be discussed. Mathematical models employed in the sorption studies will be given special importance. The modification procedures used to enhance the sorption capacity of biochar will also be highlighted.

Keywords: biochar, adsorption, heavy metals, water quality, pyrolysis

1. Introduction

Water usage has been rising immensely with growing population and industrial activities in both developed and developing countries [1]. This resulted in deterioration of water sources as various contaminants such as dyes [2], toxic heavy metals [3], organic compounds like detergents, phenols, dyes, pesticides in addition to the other persistent organic pollutants [4] are increasingly being dumped into the water bodies [5]. Among these contaminants, heavy metals are of high priority because they persist in soils and do not undergo biodegradation [6]. This might affect significantly the suitability and sustainability of the water resources [7]. These contaminants reach water bodies through various industrial activities, including mining, electrolysis, metallurgy, battery manufacture, metal finishing, electroplating, electro-osmosis, pigment manufacture, tanneries, etc. [8, 9]. Heavy metals are then taken up by the biological systems through food intake and thereby cause major hazardous health impacts [10, 11]. Owing to this, different biological and physico-chemical treatment techniques have been proposed to remediate heavy metal-bearing contaminated waters. These remediation technologies include adsorption, biosorption, ion-exchange, electrocoagulation, membrane technologies and precipitation [12]. Adsorption is one of the widely used remediation

approaches, which has its unique advantages including cost-effectiveness, high performance toward metal ion of interest, flexibility and ease in operation. [13]. Some of the widely used adsorbents for heavy metal remediation include fly ash, activated carbon, sorbents prepared from agricultural, industrial and biological waste materials [14]. Recently, char derived from biological materials under oxygen free condition, popularly known as “biochar” has been recently been introduced as an effective sorbent for various toxins [4, 15].

Biochar is a stable carbon-rich product synthesized from biological materials through different heating methods above the decomposition temperature. Biochar is produced through thermal degradation of organic components in absence of O_2 or under limited oxygen conditions (pyrolysis) [16]. In recent years, owing to the inherent biochar properties such as surplus surface binding sites (hydroxyl, carboxyl, phenolic hydroxyl and carbonyl groups), porous surface, high cation exchange capacity and its surface area, this organic amendment be utilized as an efficient and practical sorbent for remediation [17]. Biochars from different feed stock materials were prepared and successfully examined for their adsorption potential toward various metal ions [3] and nutrients [18]. The pyrolysis conditions such as temperature, rate of heating and residence time are all critical factors influencing the potentiality of metal sorption on biochar. In addition, changes in sorption potential can also be obtained through physico-chemical techniques. Thus through this chapter, we critically explore the state of knowledge on different methods to modify biochar with preferred properties. We focused on various aspects including biochar preparation methods, factors affecting the biochar sorption potential and metal removal mechanisms.

2. Production of biochar and the factors influencing the properties

Biochar has been receiving considerable attention in recent years as an important material for sorption of contaminants from polluted waters [16, 19]. Carbon-rich materials are established adsorbents for inorganic and organic contaminants. For instance, activated carbon (AC) is a well-known adsorbent extensively used for removal of heavy metal ions [20]. It is worth noting that the preparation of AC requires high temperature, costly and an additional activation step (activated carbon, sorbents prepared from agricultural, industrial and biological waste materials) [14]. Hence the cost of remediation is high. Alternatively, biochar is a recommended cost-effective alternative sorbent because of its binding sites, high permeable structure and extensive surface area [21]. Its preparation is comparatively cheaper while considering its fewer requirements for energy [21, 22]. In addition, biochar consist of non-carbonized portion that may react with soil pollutants [19]. Uchimiya et al. [23] also indicated that degree of O-comprising hydroxyl, phenolic and carboxyl binding sites on the biochar surface can play crucial roles to immobilize soil pollutants.

The sorption potential of biochar is critically dependent on the pyrolysis conditions (temperature and residence time) as well as chemical composition of the feedstock. Overall, pyrolysis temperature markedly affects the functional groups and surface area of biochar. Jung et al. [24] recorded that the pores of biochar were blocked at pyrolysis temperatures greater than $400^{\circ}C$. Similarly, Gai et al. [25] examined the effects of feedstock (wheat-straw, corn-straw and peanut-shell) and pyrolysis temperature ($400-700^{\circ}C$) on the properties and adsorption potential of biochar and found that yield of biochar as well as composition of H_2 , O_2 and N_2 decreased as pyrolytic temperature surges from 400 to $700^{\circ}C$. Xiao et al. [26] studied influence of pyrolysis temperature during synthesis

of biochar from crayfish shell for adsorption of Pb(II) ions from aqueous solutions. The authors observed that pyrolysis temperature exhibited varied effects on active functional groups, surface area and elemental composition of the produced biochar. Also, the sorption performance of biochar increased with increase in pyrolysis temperature, with biochar produced at 600°C exhibited maximum Pb(II) uptake of 190.7 mg/g.

Biochar are generally synthesized from cheap and copiously available waste biomaterials [27]. To be specific, biochar feedstocks are primarily produced from solid wastes and biomasses of agricultural activities. The agricultural residues are generally available in vast quantities and frequently pose disposal challenges [3]. For instance, preparing biochar from invasive plant can resolve challenges posed during disposal as well as help in waste management. Similarly, marine algae are generally abundant and can clog waterways; therefore other usages such as biochar synthesis can be beneficial to the local people. In recent years, a wide range of biomaterials were proposed as feedstocks for biochar, including animal manure, plant waste, seaweed, municipal solid waste and wood chip [27]. The type of feed stock strongly influences the biochar attributes and subsequently its further applications. Sohi et al. [28] indicated that the size of pores, surface area and functional groups in biochars are strongly influenced by the feedstock type. Hodgson et al. [29] examined the feasibility of different feedstocks (*Salix viminalis*, *Lolium perenne* fiber, *Lolium perenne*, *Picea sitchensis*, *Fraxinus excelsior* and *Miscanthus x giganteus*) as adsorbents for zinc. Their results pointed out to the efficiency of the synthesized biochar from *L. perenne* to remove Zn from water and its removal potential ranged from 83.27 to 92.96%. Zhao et al. [30] tested the impacts of feedstock type on properties of biochar by assessing several organic wastes, including various aquatic plant, waste wood, municipal waste, crop residue, animal manures and food wastes. The results indicated that type of feedstock affected the biochar properties, such as carbon sequestration capacity, cation exchange capacity, biochar C-content, fixed C, ash content and mineral composition. Therefore, preparing biochar with desired characteristic for a specific application may require careful screening and correct choice of a feedstock.

3. Sorption of heavy metals and associated mechanisms

Biochar has been investigated for adsorption of pesticides, heavy metals, nutrients, and organic compounds. Several researchers explored the adsorption capacity of biochar and confirmed favorable results for heavy metal ions [3, 31], nutrients [15], and organic pollutants [4]. Shakya and Agarwal [32] derived biochar from pineapple peel at different pyrolysis temperatures and investigated its efficiency for Cr(VI) sorption from aqueous solution. The results indicated that biochar synthesized at 350°C exhibited maximum sorption potential of 41.7 mg/g. Liu et al. [33] prepared biochar from corn stalk to test its capability of removing Pb(II) from aqueous solutions. Using X-ray diffraction, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy and Scanning electron microscopy with energy dispersive spectrometer analyses, the authors identified combined complexation, mineral precipitation and ion exchange mechanisms contributed to Pb(II) sorption onto corn stalk-derived biochar. The maximum Pb(II) adsorption capacity of biochar was identified to be 49.7 mg/g.

Biochar sorption experimental trials are generally performed in continuous/batch operational modes. In most batch trials, the researchers aim at examining the effects of initial metal concentration, adsorbent dosages, temperatures, and solution pH. On the other hand, continuous trials aimed at understanding the continuous contaminant removal potential of biochar.

3.1 Solution pH

Solution pH is a vital operating factor influencing the adsorption process and usually plays a critical part in overall success of adsorption. Precisely, the solution pH influences the surface properties of the sorbent, as well as the metal speciation and finally the extent of metal sorption. The pH also decides the extent of adsorbent protonation, thereby affecting the specific charge of functional groups and finally the adsorption capacity of adsorbent [13]. In general, under acidic (low pH) conditions, the uptake of cationic metal ions is low owing to strong competition from H^+ ions. As the pH surges, the amount of H^+ ions declines and sorption of cationic metal species increases [13]. In order to endorse the effect of pH on the adsorption potential, few researchers investigated the impact of pH on sorption capacity of biochar. Liu et al. [33] witnessed that Pb(II) sorption capacity of corn stalk derived biochar surged as the solution pH increased. The removal performance was improved within the pH ranges of 4–6. The authors suggested that under acidic conditions, the existence of H^+ inhibited the sorption of Pb cations. On the other hand, Senthilkumar et al. [34] observed that remediation of As(V) by *Ulva reticulata* derived biochar enhanced from 55 to 93% as the pH surged from 2 to 4. Further increase in pH decreased the adsorption potential of biochar. The authors indicated that As(V) oxyanion mostly occurs as $HAsO_4^{2-}$ and $H_2AsO_4^-$ species under acidic conditions (pH 4 to 6). Thus, relatively high As(V) sorption in low pH conditions by seaweed derived biochar was due to high protonated positively charged binding sites on biochar surface owing to saturation of excess H^+ ions, thereby enhancing the sorption of As(V) through electrostatic attraction.

3.2 Temperature

Temperature tends to affect the kinetics rate and adsorption capacity of any adsorbent. The increase or decrease of the adsorption capacity upon varying the temperature will be useful to establish the type of the sorption process. On the basis of change in temperature, the process is identified to be endothermic when the adsorption capacity rises with the increase in temperatures; whereas the process is exothermic when the sorptional capacity decreases with temperature [13]. Several research studies have confirmed that temperature plays a critical part during adsorption of heavy metal ions by biochar [33, 35].

3.3 Biochar dosage

In an attempt to determine the optimum adsorbent dose essential to attain maximum adsorption, many researchers have performed adsorbent dosage optimization experiments during metal removal studies [36, 37]. In general, the % metal removal is directly linked with the adsorbent dosage. Precisely, the increase in adsorbent dosage generally increases the % metal removal of the adsorbent. This general trend can be explained as follows: as the sorbent dose increases, the total number of binding groups present on the surface of the adsorbent increases which, in turn, increases the overall binding of metal ions [38]. On the other hand, the sorptional capacity decreases with increasing adsorbent doses [39]. This is due to nature of interaction between sorbent and sorbate. The important factor being at high biochar dose, the metal ions in the solution are less compared to the exchangeable groups on the biochar, typically results in less metal uptakes [13].

3.4 Initial solute concentration

Initial solute concentration is a critical parameter that influences the adsorption potential of any adsorbent. Past studies have shown that increase in initial metal concentration generally resulted in decline in the % metal removals [33, 34]. However, the sorptional uptake normally improves with the increase in the initial metal concentration. This was because at lower initial metal concentration, the ratio of the initial moles of metals in the solution to the biochar surface area was low and consequently, the adsorption became independent of initial concentration. Nevertheless, at higher metal concentration the accessible binding groups of sorbent become fewer in comparison to the moles of metal ions available in solution and hence, the percentage metal removal would be severely impacted by the initial metal ion concentration. During adsorption of arsenic(V) by *Ulva reticulata* derived biochar, Senthilkumar et al. [34] observed that augmentation of initial concentration of arsenic(V) from 10 to 25 mg/L produced enhancement of As(V) uptakes from 4.65 to 7.40 mg/g, whereas % removal decreased from 93.0 to 59.2, respectively.

3.5 Parameters influencing column sorption of metals

In comparison to batch sorption research, very little background literature is available about the possibility of utilizing column sorption in the removal of metal ions from aqueous solutions. Packed column sorption refers to feeding contaminated solution into the column packed with sorbent for continuous treatment. Of these little continuous-flow studies, it was identified that column adsorption potential strongly depends on operational parameters such as flow rate, influent metal concentration and bed depth [13]. The batch experimental trials are helpful in elucidating the fundamental information about the characteristics of adsorbent and the factors affecting the adsorption process [38]. Nevertheless, the batch experimental results cannot be utilized for accurate scale-up in real industrial wastewater systems [40]. This is due to the fact that in industrial wastewater systems, continuous adsorption column setup are generally used [13]. For cyclic adsorption/elution processes, packed columns are effective and practical arrangement, as they efficiently utilizes the concentration difference which is known to be the driving force for sorption of heavy metals [41]. Also, the column assembly allows more efficient utilization of the adsorbent capacity and generally results in superior effluent quality. Thus, adsorption using packed columns has important advantages including fast and high yield operations as well as easy scaling up [42]. Additionally, packed columns permit large amount of wastewater to be continuously remediated using a small amount of sorbent loaded inside the column [43]. Regeneration and subsequent reuse of sorbent is also possible using appropriate elutant. After adsorption, metal ions loaded-adsorbent can be eluted using suitable desorbent, or otherwise can be contained/disposed [44].

Vilvanathan and Shanthakumar [45] conducted continuous column adsorption experiments using biochar prepared from *Tectona grandis* leaves to remediate Co(II) and Ni(II) ions from aqueous solutions. The breakthrough curves were generated by fluctuating the inlet metal ion concentration, flow rate and bed depth. The results confirmed that the column exhaustion time prolonged with increasing bed depth and/or reducing each of the metal ion concentrations and flow rate. The metal-loaded column was desorbed using HCl, which indicates the possible regenerated and reuse of column bed for subsequent sorption cycles. Senthilkumar et al. [34] utilized 2 cm internal diameter and 35 cm depth column loaded with *U. reticulata* biochar to perform

column experiments for arsenic(V) remediation from aqueous solutions. At a flow rate of 0.3 L/h, initial arsenic(V) concentration of 25 mg/L and bed depth of 25 cm, the column recorded breakthrough and exhaustion times of 3.25 and 13 h, respectively. Around 3.9 L of arsenic(V) solution was remediated by the column. The %As(V) removal and adsorption capacity of column were calculated as 59.5% and 8.12 mg/g, respectively. The bed was successfully eluted using 0.01 M sodium hydroxide with 99.5% elution efficiency.

As indicated before, very limited research studies focused on column applications compared to batch applications. Thus, serious efforts are needed to explore the adsorption capacity of adsorbent in continuous operational mode to elucidate the adsorbent compatibility in real wastewater plants.

3.6 Biochar modification

Although biochar exhibits good sorption properties; however, it can be additionally altered to improve its sorption efficiency. The modification procedures employed include acid/base modification, functional group modification and impregnation with mineral oxides.

Through acid/base modification, alteration of surface acidities and porous nature of biochar can be obtained [15]. After exposure to chemicals including HNO₃, H₂SO₄, HCl, KOH and NaOH, El-Hendawy [46] identified that HNO₃ exposure resulted in improved adsorption and pore diffusion of hydrated Pb²⁺ with O₂ groups, and therefore improved the hydrophilic nature of biochar. Li et al. [31] evaluated lead adsorption capacity of two biochar materials (low mesopore char (AC1) and high mesopore char (AC2)) derived from bagasse modified using nitric acid. The results indicated that the adsorption capacities of AC2 and AC1 toward lead ions were recorded by 27 and 15 mg/g, respectively, due to high mesopore volume of AC2. Precisely, the lead removal rate of by AC1 surged from 46 to 99% after treatment with HNO₃. Liu et al. [47] investigated the influence of KOH and H₂SO₄ modifications onto biochar during sorption of tetracycline. The results indicated that the KOH-exposed biochar showed high porosity, larger specific surface area, and high C and O composition than the H₂SO₄-exposed and virgin biochars. The remediation of inorganic constituents during alkali treatment allowed the biochar to sorb more pollutant.

The biochar hydrophilicity and surface functional sites can be chemically modified for remediation of specific pollutants at a specific rate from solutions [48]. It is well-known that carboxyl, amine, hydroxyl, phosphonate, and phenolic groups are functional groups often responsible for adsorption of different dyes/metals [49]. The biochar material exhibit low pollutant uptake capacities if the amount of these binding sites is low. Nevertheless, several modification techniques are present to improve the number of these functional sites on the surface of biochar. Xue et al. [50] highlighted that modification using H₂O₂ for peanut hull-derived biochar enhanced the oxygen-comprising functional groups particularly carboxyl groups on surface of biochar, which caused enhanced Pb(II) adsorption potential of over 20 times compared to raw biochar.

Biochar can also be prepared for particular applications through mineral impregnation methods. Yao et al. [51] improved the biochar functionality by distributing clay particles in biochar matrix. The authors mixed the biomaterial (bamboo, bagasse and hickory chips) with clay and consequently pyrolysed at 600°C without O₂ for 1 h. The adsorption potential of clay-biochar composite was enhanced five times compared to virgin biochar due to highly porous structure and presence of clay. Magnetic biochar can be prepared through chemical coprecipitation of Fe²⁺/Fe³⁺ onto biomass and subsequent pyrolysis [17]. The hybrid nature of magnetic biochar permits enhanced adsorption of various organic and

inorganic toxins. Through exposure of peanut hull biochar to FeCl_3 , Han et al. [52] synthesized magnetic biochar for removal of Cr(VI) ions. The prepared magnetic biochar showed improved adsorption potential toward Cr(VI) , around 1–2 times compared to raw biochar. The study also identified the removal mechanism through XPS, XRD and SEM and revealed that Cr(VI) was interacted electrostatically to the protonated $-\text{OH}$ onto the surface of $\gamma\text{-Fe}_2\text{O}_3$.

4. Mathematical modeling

Adsorption isotherm is the mathematical representation of adsorption capacity (Q) versus equilibrium concentration of the solute (C_e). Modeling adsorption isotherm data is important for prediction/comparison among adsorption performances. Two, three and four-parameter isotherm models are suggested to model the sorption data. Some of the important sorption isotherm models used in the sorption studies include, the Langmuir, Freundlich, Toth and Sips models.

The Langmuir model [53] was fundamentally derived to define the sorption (gas-solid phase) of activated carbon. However, in later years, it was employed to assess and calculate the adsorption behavior of various adsorbents. In its formulation, binding to the surface was primarily by physical forces and implicit in its derivation was the assumption that all sites possess equal affinity for the sorbate. Its use was extended to empirically describe equilibrium relationships between a bulk liquid phase and a solid phase [53]. The model can be expressed as

$$Q = \frac{Q_{\max} b_L C_e}{1 + b_L C_e} \quad (1)$$

where Q is the sorptional capacity (mg/g); C_e is the equilibrium concentration (mg/L); Q_{\max} is the maximum uptake of toxin by the adsorbent (mg/g) and b_L is the equilibrium coefficient of the Langmuir model (L/mg).

The Freundlich model [54] was empirically derived equation; however it can be applied to adsorption onto diverse surfaces or surfaces with sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation. It can expressed as,

$$Q = K_F C_e^{1/n_F} \quad (2)$$

where n_F is the exponent of the Freundlich model and K_F is the Freundlich model coefficient (L/g) ^{$1/n_F$} ,

The Sips model [55] is based on the assumption that binding sites on the adsorbent have varied strengths and each active binding site interact with one sorbate molecule. The constant K_S represents sorptional uptake of the adsorbent, whereas a_S denotes affinity of adsorbent toward metal ions. At high metal ion concentrations, the model ultimately takes the Langmuir form, whereas at low metal concentrations reduces to the Freundlich model [56]. The model can be expressed as

$$Q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}} \quad (3)$$

where a_S is the Sips model coefficient (L/mg) ^{β_S} , β_S is the Sips model exponent and K_S is the Sips model isotherm coefficient (L/g) ^{β_S} .

The Toth model [57] is the other three parameter model frequently employed to describe metal-adsorbent isotherms. The model assumes quasi-Gaussian energy distribution and is derived from the potential theory. The Toth model can be expressed as

Toth model:

$$Q = \frac{Q_{max} b_T C_e}{[1 + (b_T C_e)^{1/n_T}]^{n_T}} \quad (4)$$

where b_T is the Toth model constant (L/mg) and n_T is the Toth model exponent.

For any practical applications, the process design, operation control and sorption kinetics are very important [13]. The sorption kinetics can be described using several models.

The most commonly used method to identify the contribution of intraparticle diffusion during adsorption is through fitting the kinetic data to an intraparticle diffusion plot, as presented by Weber and Morris [58] as below:

$$Q_t = k_i t^{1/2} \quad (5)$$

where Q_t is the sorptional capacity at any time t (mg/g) and k_i is the intraparticle diffusion constant. This involves plotting the sorptional capacity at a given time vs. the square root of that time. If the plot passes through the origin, then intraparticle diffusion is the rate determining step.

The pseudo-first-order model assumes that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time. The model can be expressed as,

$$Q_t = Q_e (1 - \exp(-k_1 t)) \quad (6)$$

where Q_e is the equilibrium uptake (mg/g) and k_1 is the pseudo-first-order constant (1/min). In an attempt to understand the Cd(II) adsorption mechanism of rice straw-derived biochar from aqueous solutions, Fan et al. [59] fitted Cd(II) kinetics data using pseudo-first-order and pseudo-second-order kinetic models. The results indicated that Cd(III) adsorption kinetics by rice straw biochar was better described by the pseudo-first-order kinetic model.

The pseudo-second-order kinetics is framed to predict adsorption capacity over entire experimental conditions (ranges) as the model based on the adsorption capacity of the solid phase.

$$Q_t = \frac{Q_e^2 K_2 t}{1 + Q_e K_2 t} \quad (7)$$

where k_2 is pseudo-second-order constant. Xiao et al. [60] prepared biochar using cow bone meal for adsorption of Cd(II), Pb(II) and Cu(II) ions. On analyzing the kinetics data, the authors identified that pseudo-second-order model fitted the kinetics data well compared to the pseudo-first-order model based on the correlation coefficients and calculated equilibrium uptake values.

5. Conclusions

Biochar represents an effective class of sorbent for remediation of heavy metals from solutions. Several studies recognized superior adsorption potential of biochar compared to other established sorbents. The pyrolysis temperature and feedstock

type strongly influences the sorption capacity of biochar. In addition, the process operating parameters such as pH, temperature, initial solute concentration and biochar dosage strongly influences the extent of metal sorption by biochar. Despite the application of biochar as sorbents is increasing as indicated through published literatures, more knowledge needed especially in the area of column sorption and real effluent clean-up.

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