Review

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Progress in Preparation And Application of Modified Biochar for Improving Heavy Metal Ion Removal From Wastewater

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Abstract: Modified biochar (BC) is reviewed in its preparation, functionality, application in wastewater treatment and regeneration. The nature of precursor materials, preparatory conditions and modification methods are key factors influencing BC properties. Steam activation is unsuitable for improving BC surface functionality compared with chemical modifications. Alkali-treated BC possesses the highest surface functionality. Both alkali modified BC and nanomaterial impregnated BC composites are highly favorable for enhancing the adsorption of different contaminants from wastewater. Acidic treatment provides more oxygenated functional groups on BC surfaces. Future research should focus on industry-scale applications and competitive sorption for contaminant removal due to scarcity of data.

Keywords: modified biochar; adsorption; heavy metal ion

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1 Introduction

Heavy metals are discharged from different industries including mining, metal finishing, electroplating, glass, textiles, ceramics, and storage batteries. Recently, there have been growing concerns over water pollution by heavy metals released from industrial effluents due to the toxic effects of their ions on organisms and their accumulation in biota. Among these heavy metals, copper and mercury have received considerable attention due to their toxicity. The presence of these metal ions in water endangers human beings and aquatic lives because they accumulate in the food chains (Wang et al., 2012). Therefore, there is the need to purify and recycle wastewater contaminated by heavy metal ions to secure alternative sources of water (Ali, 2010) and to protect our food chains (Wang et al., 2012).

Several treatment technologies have been suggested to remove these heavy metal ions from contaminated wastewater including adsorption, ion exchange, chemical precipitation, membrane technologies, reverse osmosis and electrochemical treatment (Demirbas, 2008). Among these technologies, adsorption is a universal, most convenient and fast method of treating heavy metals contaminated solutions cheaply and efficiently (Bailey et al., 1999; Dupont and Guillon, 2003). The major advantages of this treatment technology are its low residue generation and the potential to recover and recycle the used adsorbent (Yu et al., 2013). Additionally, bio sorbents are not only environmentally friendly but are also readily available in sufficient quantities, and a very well-known bio sorbent is biochar. The biochar is a fine-grained, porous and carbon-rich material produced from the thermal degradation of organic materials under oxygen-limited conditions. Biochar has also been proven to be an effective sorbent for the sorption of a wide variety of inorganic and organic pollutants from aqueous solutions (Xue et al., 2012).

Recent studies have shown that biochar as a bio sorbent can be employed as a useful material to sorb heavy metal ions from contaminated water and also as a remedy for immobilization of metal ions in metal-contaminated soil (Chen et al., 2011; Inyang et al., 2012; Xu et al., 2013).

Their large sorption capacity is connected to their highly-porous structure and surface area which contains various functional groups (e.g. hydroxyl, carboxyl, phenolic groups) hence; it has a very strong affinity for heavy metal ions (Mohan et al., 2007; Cao et al., 2009; Mohamed et al., 2017). Until recently, the traditional and widely used carbon-based adsorbent for wastewater treatment has been activated carbon. The successful application of several bioadsorbents such as chitosan, chitin, wood bark, etc. for wastewater treatment has been published. Therefore, for the biochar to compete favourably for industrial application, researchers are left with the challenge of ensuring that the biochar is the most effective bio sorbents with specific chemical properties. Hence, recent research on the biochar has been focused on their modification and characteristics to satisfy the growing demands for cleaner water (Chingombe et al., 2005). Thus, the aim of this review is to critically examine recently published studies on modified BCs for the removal of heavy metals from aqueous solutions. Specifically this review covers preparation methodologies for modified BCs; improved properties of modified BCs; and suggestions for future studies of modified BCs.

2 Biochar preparation

The physical and chemical properties of biochar depend primarily on the types of feedstock and pyrolysis conditions i.e. temperature, residence time, reactor type and heating rate. Conventional carbonization/slow pyrolysis, fast pyrolysis, flash carbonization, gasification and microwave assisted pyrolysis are the main thermochemical processes that are commonly used to produce biochar (Manyà, 2012). It has been demonstrated that the biochar produced at high temperatures (circa 600℃-700℃) possesses fewer H and O functional groups due to dehydration and deoxygenation of the biomass but shows highly aromatic nature with well organised C layers and has lower ion exchange capabilities (Uchimiya et al., 2011; Ahmad et al., 2014). On the other hand, the biochar produced at lower temperatures (circa 300℃-400℃) shows varied organic characters, including aliphatic and cellulose type structures and contain more C—H and C═C functional groups (Glaser et al., 2002). It is this complex and heterogenous physical and chemical composition of biochar that provides its excellent properties of contaminant removal via sorption (Vithanage et al., 2015).

2.1 Feedstocks

The feedstocks for both conventional and microwave assisted pyrolysis is biomass. During pyrolysis, the proportion of cellulose, hemi-cellulose and lignin content determine the ratios of bio-oil, gas and biochar in pyrolysis products. It has been demonstrated that feedstocks with high lignin content produce the highest biochar yield when pyrolyzed at moderate temperatures (circa 500℃) (Fushimi et al., 2003). Therefore, choice of pyrolysis feedstocks may be determined by the desired balance between the different pyrolysis products (biochar, bio-oil, gas). Biomass is any living or recently living biological material with the potential as a source of energy (Motasemi and Afzal, 2013). Biomass is believed to have the potential to become one of the major sources of energy in the next century (Berndes et al., 2003). The biomass as a source of energy is carbon-neutral, renewable, readily available in nature, relatively lower sulphur content, and have the potential to be the best alternative to fossil fuel resources. Replacing fossil fuel with biomass as a source of energy can lead to reduction in pollution and global warming, alleviate the energy crisis and contribute towards sustainable development (Hall, 1997; Panwar et al., 2011). Biomass resources can be grouped into three major categories: virgin resources, residues and municipal solid waste (Motasemi and Afzal, 2013). The virgin resources include forest resources and oilseed/cereal crops. The residues may be wood residues, agricultural residues and wastes as well as livestock residues. Municipal solid waste (MSW) could be residential or non-residential. With a suitable conversion process, these categories of biomass can be promising sources of energy for the future. The municipal solid wastes, forest and agricultural residues are promising substitutes for microwave pyrolysis processes.

Extensive studies utilising these lignocellulosic feedstocks including virgin resources and residues have been reported. Detailed research using wood, wood pellets, tea waste, coffee hulls, sewage sludge, wheat straw, rice straw, macro- and microalgae, corn Stover demonstrated excellent potentials as feedstocks for pyrolysis process (Miura et al., 2004; Domínguez et al., 2007; Yagmur et al., 2008; Budarin et al., 2009; Huang et al., 2010; Budarin et al., 2011).

2.2 Conventional pyrolysis

This is the traditional heating system in which heat is transferred from an external source to the biomass through conduction, radiation and convection. In this method, the heat/temperature at the surface of the feedstock is very high and decreases towards the centre of the feedstock. In conventional pyrolysis process, the major process variables are that; (1) the heating rate is low (2) the vapour residence time is long (Manyà, 2012). This method has been used to produce charcoal for several years. During this pyrolysis, there are some identified variables that determine the efficiency and yield of the process. These parameters are; pressure and moisture content of the feedstock (Antal and Grønli, 2003).

The maximum temperature attained during conventional pyrolysis process is called the peak temperature. It has been reported that an increase in the peak temperature leads to an increase in the biochar fixed-content ((Manyà, 2012)). The operating pressure of the pyrolysis process has significant impact on the properties of the produced biochar. For a study carried out on the pyrolysis of different biomass feedstocks (eucalyptus wood, radiata pine, sugar cane bagasse) (Cetin et al., 2004), it was found that increasing the operating pressure results in a decrease in the total surface area of the char. Similar results were also reported during a slow pyrolysis of Miscanthus (Melligan et al., 2011). They observed a significant decrease in BET surface area of char from 161.7m^2/g at 0.1MPa to 0.137m^2/g at 2.6MPa. The researchers attribute these observations to the blocking of the char pores by deposits from the tar due to high pressure. Reported studies on the effects of moisture content of the biomass feedstocks indicated that high moisture content enhances the yields of charcoal at high pressures. Hence, most biomass with high moisture contents are particularly attractive for biochar production via conventional pyrolysis (Manyà, 2012). This pyrolysis technique is comparatively inefficient and slow and is also dependent on the biomass' thermal conductivity and the convection current of the system.

2.3 Microwave assisted pyrolysis

Pyrolysis of biomass by microwave involves energy conversion instead of mere heating. In this technique, electromagnetic energy is converted to thermal energy by dielectric heating (Motasemi and Afzal, 2013). Furthermore, the heat is generated throughout the biomass volume instead of an external source. Contrary to the conventional pyrolysis, the temperature at the centre of the feedstock is higher than the materials surface and surrounding as shown in Fig. 1.

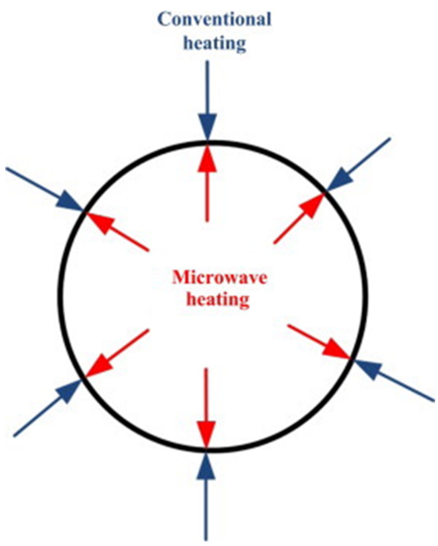

Fig. 1 Microwave and conventional heating nature (Motasemi and Afzal, 2013)

The microwave assisted pyrolysis technique is among the most promising techniques of accelerating and enhancing chemical reactions. Because of the efficient heat transfer profile, the chemical reactions are completed within a shorter time and efficiently as compared with other thermo-chemical processes (Lidström et al., 2001; Salema et al., 2017; Nhuchhen et al., 2018). The advantages of this technique over other methods of pyrolysis are that it speeds up the chemical reactions and reduces the residence time, hence saves energy.

3 Modification of biochar for wastewater treatment

Though the biochar has an excellent capability to adsorb heavy metal ions from metal contaminated solutions, this capacity is relatively lower in comparison with other known bio sorbents such as activated carbon. Hence, despite several scientific researches on the biochar applications, recent researches have been focused primarily on the modification of the biochar with good surface properties and novel structures to enhance its environmental benefits and remediation efficacy. For instance, efforts have been made to increase its porosity, surface area and/or surface functional groups. There are several approaches to modify the biochar which can be divided into four main categories, i.e., chemical modifications, physical modifications, magnetic modifications and impregnation with mineral oxides. This mini review is focused on the chemical and magnetic modifications and their application to the treatment of heavy metal contaminated wastewater.

3.1 Chemical modifications

Biochar modification by chemical methods involves both one-step modification or two-step modification process. In one-step process, both the carbonization and activation are achieved simultaneously in the presence of the activating chemical agent. On the other hand, in two-step process, the biomass feedstock is first carbonized followed by an activation using the relevant chemical agent or pre-treatment of feedstock before the process of carbonization. There are several methods of modifying biochar chemically (Fig. 2). However, for this report, only the major and commonly used methods are identified.

3.1.1 Acid/base treatment and chemical oxidation of biochar

Acidic/alkaline modification of the biochar can cause significant changes to the biochar physico-chemical properties. The biochar modification leads to more acidic functional groups on its surface; for instance, rising percentage of oxygen results in increased O/C and H/C molar ratios with sulfuric acid treatment. The increases in O/C and H/C ratios signified the occurrence of a decrease in hydrophobicity (Vithanage et al., 2015). It has been shown that nitric acid treatment breaks the pore wall and expands micropores into meso- or macro pores, hence the obtained acidic modified biochar possesses more acidic functional groups such as the carboxylic, ketonic, hydroxyl and other moieties containing oxygen (Hadjittofi et al., 2014.). The resulting increase in polarity of acid modified biochar can lead to chemisorption of pollutants from wastewater. Alkaline treatment produces biochar with a larger surface area, a higher ratio of surface aromaticity

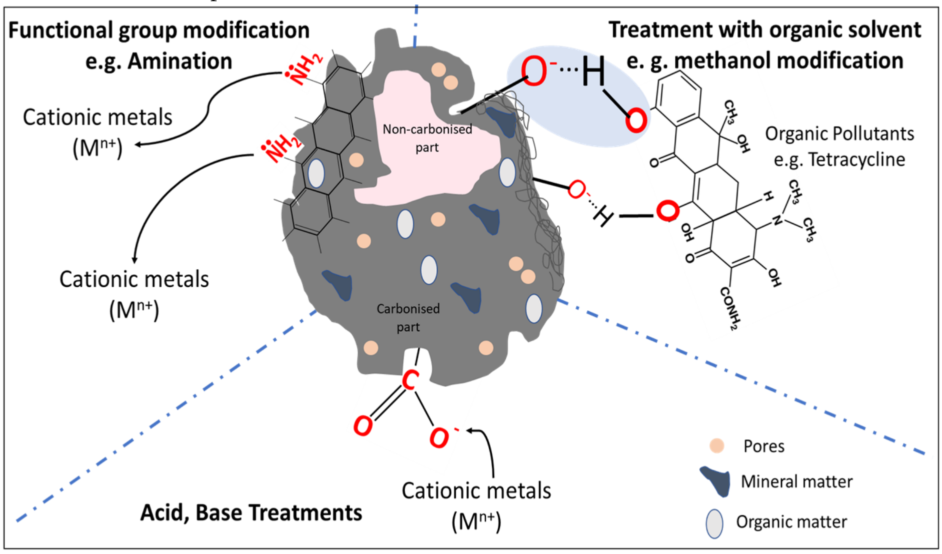

Fig. 2 Chemical modification of biochar

(H/C), higher N/C ratio with lower value of O/C compared to acid modified biochar (Ahmed et al., 2016). Low O/C ratio signifies the decline in the hydrophilic nature of basic modified biochar when aromaticity increased. An increase in oxygen and nitrogen and decrease in carbon in modified biochar results in crosslinking reaction of the biochar surface and the modifying agents (Ma et al., 2014.). The increase N/C ratio signifies that more groups containing nitrogen to which the basic properties of the biochar are attributed are present on the modified biochar surface. This enhances the sorption of negatively charged ions and organic pollutants form wastewater. Furthermore, biochar oxidation using hydrogen peroxide (H_2O_2), Potassium Permanganate ($KMnO_4$), ammonium persulfate [$(NH_4)_2S_2O_8$] and ozone (O_3) have been used to modify surface functional groups (Cho et al., 2010; Tan et al., 2011; Uchimiya et al., 2011).

3.1.2 Modification of functional groups (carboxylation and amination)

The biochar surface functional groups and its hydrophilicity can be modified chemically to meet targeted requirements such as pollutants adsorption from contaminated wastewater and amendment of contaminated soil (Yakout et al., 2015). It has been reported that biochar produced at low temperature (250℃-400℃) has more C═C and C—H functional groups. Furthermore, acidic functional groups such as carbonyl, carboxylic, phenolic and lactonic groups have been introduced onto the biochar surface at relatively low temperature by chemical oxidation using H_2O_2, $KMnO_4$, HNO_3, H_3PO_4 or HNO_3/H_2SO_4 mixture (Shafeeyan et al., 2010; Ahmed et al., 2016; Nhuchhen et al., 2018). Surface carboxylation is mainly achieved by single-step oxidation.

In addition to functional groups containing oxygen, nitrogen-containing functionalities such as (imide, amide, lactane, pyridinic and pyrrolic groups) have significant impact on environmental remediation due to their high affinity for complexation, especially for heavy metal ions such as Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} (Shafeeyan et al., 2010; Rajapaksha et al., 2016). The N-containing functionalities is typically introduced onto the biochar surface by nitration followed by reduction [17, 76] (Yang and Jiang, 2014). The HNO_3 dissociates to form an intermediate nitronium (NO^{2+} ions) which is very active. This attacks the aromatic/benzene rings resulting in nitrated product (-NO_2) on the biochar surface. The nitration of the biochar surfaces is limited by the slow rate of nitration and small quantities of NO^{2+} (Rajapaksha et al., 2016), hence, concentrated H_2SO_4 is usually added simultaneously to enhance the formation of nitronium ions. It has been demonstrated that the nitration occurs via electrophilic aromatic substitution reaction where the nitro group is introduced onto the aromatic rings in biochar (Yang and Jiang, 2014). The nitro functional groups are then reduced to amino groups using acidified sodium dithionite ($Na_2S_2O_4$) as a reducing agent (Chingombe et al., 2005; Yang and Jiang, 2014). The surface amination introduces the amino functional groups that provide the basic properties and strong affinities of biochar to metal ions in contaminated wastewater.

Zhou et al. (2013) used Chitosan to introduce the amine functional groups onto bamboo biochar surfaces to enhance its adsorption capability for heavy metal ions like Pb^{2+}, Cu^{2+} and Cd^{2+}. They demonstrated that coating biochar surface with chitosan can also improve the biochar capacity as a soil amendment or adsorbent and deduced that chitosan-modified biochar can be used as a low-cost, effective and environmental-friendly adsorbent to remediate heavy metal contaminated environment. The amine groups in chitosan forms a very strong chemical bond with heavy metal ions, hence it enhances heavy metal ions uptake from wastewater (Yong et al., 2013).

Xue et al. (2012) modified the surface of peanut hull biochar using hydrogen peroxide (H_2O_2). The study demonstrated an increase in the O-containing functional groups, especially carboxylic group which improves the biochar capacity to adsorb metal ions like Cd^{2+}, Ni^{2+} and Pb^{2+}. It was observed that the modified biochar exhibited improved Pb^{2+} ion adsorption capability with an adsorption capacity of 22.82 mg/g. This adsorption capacity compares with the capacity of commercial bio sorbent such as activated carbon and over 20 times more than the adsorption capacity of pristine biochar (0.88mg/g). The modified biochar was employed in packed column as a filter media, and it was observed that it filters lead even more than a pristine biochar. The modified biochar capacity for lead removal in packed column was found to be nearly 20 times the capacity of unmodified biochar. For a multi-metal solution, the column containing modified biochar was still very efficient in removing lead and other heavy metal ions (i.e., Ni^{2+}, Cu^{2+}, and Cd^{2+}) from water flow. Model results for the multi-metal system showed that the adsorption sequence for the heavy metal ions by the modified biochar were in the order of $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$. They concluded that H_2O_2-modified biochar could be a cheap, effective and environmentally friendly or sustainable sorbent for several environmental applications, especially for heavy metal immobilization.

Yang and Jiang (2014) reported the amino-modification of biochar to improve its adsorption capacity for Cu^{2+} ions from wastewater. The biochar modification was to make it a selective and high efficient adsorbent for Cu^{2+} ions by nitration using HNO_3/H_2SO_4 mixture, followed by reduction using a mixture of $H_2SO_4/N_2S_2O_4$ as a reducing agent. Their characterisation results suggested that the amino-groups were chemically bond to the surface functional groups of the biochar. Their experimental results indicated that the modified biochar was highly efficient in the adsorption of Cu^{2+} ions. The bed volume and adsorption capacity of the amino-modified biochar were eight- and five-folds of the pristine biochar respectively. They concluded that the amino-modified biochar was endowed with high ion selectivity and pH stability due to the strong complexation between the Cu^{2+} ions and the amino functional groups. This is the only published paper where amino-modified biochar from conventional pyrolysis is used to adsorb heavy metal ions from a mono-metal aqueous solution.

Liu et al. (2010) investigated the sorption of tetracycline from aqueous solution using biochar modified with KOH and H_2SO_4. Their characterisation results indicated that the biochar treated with alkali has larger surface area in comparison with those of pristine biochar and biochar treated with acid, and correspondingly shows a better adsorption capacity (58.8 mg/g) than the other two biochars. The KOH modification increased O-containing functional groups (O—H, C—H, C═O and COOH) on biochar surface and thus improved tetracycline adsorption. At neutral pH, O-containing functional groups on the surface of alkali modified biochar facilitated the formation of H_2 bonding with tetracycline molecules thus improved its adsorption by the KOH modified biochar (Rajapaksha et al., 2016). It was concluded that the biochar can remove tetracycline from wastewater effectively. Furthermore, alkali modification of the BC can improve the biochar adsorption capacity. The adsorption is primarily due to hydrogen bonding and π-π interactions.

3.1.3 Treatment with organic solvents

Another method of achieving high carboxylic functional groups on biochar surface is by modifying the biochar using acidified methanol which is inexpensive. The biochar modification by methanol involves esterification, followed by direct reaction involving the biochar carbonyl groups and methanol (Jing et al., 2014).

Jing et al. (2014) investigated the adsorption performance of tetracycline (TC) in aqueous solutions by methanol-modified biochar. They modified rice husk biochar by methanol to enhance the TC adsorption capacities and reduce the inherent organic compound content in the biochar. Their results indicated that methanol-modified biochar showed approximately 45.6% enhancement of adsorption capacity in 12h and 17.2% in equilibrium time compared with pristine biochar. Furthermore, they observed that the hydroxyl and ester functional groups (O-containing groups) were more on methanol-modified biochar than pristine biochar which affects π-π electron-donor-acceptor interactions between the biochar surface and the TC.

3.2 Magnetic modifications

It has been sufficiently demonstrated that biochar has the potential of being an effective sorbent for treating heavy metal contaminated water and wastewater due to its multi-functional properties. However, the separation of the powdered biochar from the aqueous matrix after the contaminant adsorption is very difficult which makes the use of the biochar for wastewater treatment less attractive. Therefore, researchers have made attempts to develop magnetic biochar sorbents to ensure a better and effective separation of the biochar particles after the wastewater treatment process (Chen et al., 2011; Zhang et al., 2013; Mohan et al., 2014; Wang et al., 2015). Furthermore, it is known that the surface of the biochar has a net negative charge (Mukherjee et al., 2011); therefore, adsorption of anionic pollutants, e.g., As (III) or As (V) is somewhat low (Beesley and Marmiroli, 2011; Mukherjee et al., 2011). Hence, researchers have developed several methods for the adsorption of anionic contaminants by magnetically modifying biochar to enhance its adsorption capacities for anionic contaminants (Chen et al., 2011; Zhang et al., 2013; Wang et al., 2015).

Generally, there are some common techniques employed to produce magnetic biochar such as pyrolysis and co-precipitation method. These methods are utilized by many researchers to produce high quality and high yield of magnetic biochar.

3.2.1 Magnetic modification of biochar by pyrolysis

A typical pyrolysis process can be divided into three types such as conventional pyrolysis, fast pyrolysis and flash pyrolysis depending on the operating conditions (Thines et al., 2017). The conventional pyrolysis process takes place under a slow heating rate which allows the production of solid, liquid, and gaseous product in compelling portions. As for laboratory scale, the pyrolysis process is generally done either through conventional heating or microwave heating.

Several papers have appeared where fast or slow pyrolysis (conventional heating) biochars were magnetized, characterized and applied to wastewater treatment (Liu et al., 2010; Chen et al., 2011; Theydan and Ahmed, 2012; Mun et al., 2013; Zhang et al., 2013; Zhu et al., 2014; Wang et al., 2015).

Chen et al. (2011) used orange peel, biomass waste to produce three novel magnetic biochars (MOP250, MOP400, MOP700) by employing the orange peel as the raw material in the presence of $FeCl_3.6H_2O$ and $FeCl_3$ in which the biomass mixture was pyrolyzed under different temperatures (250℃, 400℃ and 700℃) at 5℃/min for 6h. The produced magnetic biochar was used to sorb organic pollutants and phosphate from wastewater. The introduction of Fe_2O_3 as the source of magnet for the biochar was signified by the higher ash contents and lower carbon contents of the produced biochar. The surface areas of the produced magnetic biochar were determined to be 41.2, 23.4 and 19.4 m^2/g with respect of MOP250, MOP400 and MOP700. These results showed that higher temperature leads to a reduction in the surface area due to the destruction of the biochar pores. It was found that the MOP400 consisted of amorphous biochar and nano-size magnetite particles, and hence showed hybrid sorption capacity to adequately sorb phosphate and organic pollutants from water. For adsorption of organic pollutants, MOP400 showed the highest sorption capacity, which was very much higher than the non-magnetic biochar (OP400). For phosphate adsorption, magnetically modified biochars, particularly MOP250, showed much higher adsorption capacity than the unmodified biochars companion. They concluded that the magnetically modified biochar sorbent has the potential to sorb phosphates and organic contaminants from wastewater simultaneously.

Liu et al. (2010) investigated Arsenate sorption from water using Fe_3O_4-loaded biochar prepared from waste biomass (pinewood sawdust) in the presence of $FeCl_3$ as the metallic solution to provide the magnetic effect on the magnetic biochar produced. The important point of the synthetic method was that the carbonization, activation and Fe_3O_4 loading were achieved simultaneously. The pyrolysis process was done in the horizontal pyrolysis reactor in an electrical furnace with the flow of N_2 gas at 600℃ for about 3h. This pyrolysis method was able to produce Fe_3O_4-loaded magnetic biochar that has a spinel structure (maghemite, γ-Fe_2O_3 or magnetite, Fe_3O_4) which signifies that γ-Fe_2O_3 has been reduced to Fe_3O_4. The characteristic of this composite was carried out and used as a sorbent for arsenate sorption from wastewater. Experimental results demonstrated that the Fe_3O_4 particles were deposited uniformly on the composite surface. The surface area of the composite was as high as $349m^2/g$, pore volume of $0.20cm^3/g$ and iron of 39wt% for arsenate adsorption.

Wang et al. (2015) studied Arsenic removal by a magnetically modified biochar produced using natural hematite and pinewood. To prepare this magnetic biochar, a mixture of pinewood biomass and hematite were pyrolyzed in a tube furnace under nitrogen gas flow at 600℃ for 1h. When compared to the pristine biochar, the hematite-modified biochar had both stronger magnetic behaviour and exhibited much higher capacity to adsorb As from water, possibly due to the γ-Fe_2O_3 particles on the surface of the carbon serving as sites for sorption via electrostatic interactions. It was concluded that the magnetised biochar can be used for AS pollutant sorption from aqueous solution since the used biochar can be recovered easily using external magnets.

On the contrary, only a very few articles have been published on the use of microwave assisted pyrolyzed biochar for magnetic modification (Wang W et al., 2013a; Wang Y et al., 2013b; Meng et al., 2015; Ruthiraan et al., 2015).

Meng et al. (2015) used chitosan as the raw material to produce $MnFe_2O_4$-loaded magnetic biochar by a novel single-step microwave assisted hydrothermal method at a microwave heating temperature of 120℃ for 10min. The magnetic biochars were used to sorb Cu^{2+} ions from synthetic wastewater. Several experimental variables such as contact time, pH value and initial Cu^{2+} ions concentration which affect the adsorption behaviour or efficiency of the modified biochars were investigated. Experimental results demonstrated adsorption efficiency increases with solution pH value and contact time. Particularly, it was reported that adsorption efficiency can be as high as 100% and 96.7% after 500min of sorption at pH value of 6.5 for the solutions when the initial Cu^{2+} ions concentration was 50 mg/L and 100 mg/L respectively. In conclusion, this work suggests that magnetic nanoparticles can be helpful for the adsorption of Cu^{2+} ions from wastewater.

Zhang et al. (2013) employed bamboo charcoal (BC) as a raw material to synthesize iron-modified bamboo charcoal (Fe-MBC) by impregnating the BC in HNO_3 and $FeCl_3$ solutions simultaneously. This is followed by micro-wave heating with a frequency of 2.45GHz and an output power of 640 W for 6 minutes under an inert gas (nitrogen) flow of 10mL/min. The magnetic biochar was used to adsorb Pb(II) contaminants from water. When compared to pristine biochar, the Iron bamboo magnetic biochar exhibited rougher surfaces. Furthermore, it was observed that increasing the concentration of $FeCl_3$ created better cluster of iron oxide on the magnetic biochar surfaces. Also, increasing the concentration of $FeCl_3$ produced the maximum BET surface area of $298.732m^2/g$ and a total pore volume of $0.273cm^3/g$ which demonstrated that the pores were well widened and not blocked by the available Fe_2O_3 particles. They concluded these results have vital implications for the design of effective and low-cost adsorbent for the sorption of Pb(II) from aqueous solutions.

Wang et al. (2011) investigated the sorption of Cr(VI) from wastewater using a microwave assisted prepared bamboo charcoal-based iron-containing sorbents. Bamboo charcoal-based, iron-containing adsorbent (Fe-BC) was synthesized by employing bamboo charcoal as a supporting medium for the ferric iron. The impregnation was achieved using a mixture of $Fe_2(SO_4)_3$ and H_2SO_4 simultaneously, before micro-wave heating. The experimental results demonstrated that the iron impregnation led to a decrease of total pore volume, the BET specific surface area and average mesoporous diameter. The microwave heating was carried out with power output of 640W and 2.45GHz frequency for 6 minutes under a nitrogen flow rate of 10mL/min. The Fe-BC was observed to be well-crystallized with a BET surface area of $49m^2/g$ which is relatively lower than that of the pristine biochar ($64m^2/g$) likely due to the pores of the biochar been blocked by iron oxide. It was concluded that Fe-BC can be used as a useful sorbent for Cr(VI) sorption and in fixed bed filtration due to its high affinity toward Cr(VI) because of the iron oxide functional groups.

Wang et al. (2012) used bamboo charcoal as raw material to produce bamboo based-cobalt coated magnetic biochar (Co-MBC). The process utilized $Co(NO_3)_2 \cdot 6H_2O$ as the precursor of cobalt oxide fusion into the biochar pores before the mixture was heated in a modified micro-wave with a power output of 640W and 2.45GHz frequency for 6min under a nitrogen flow rate of 10mL/min. On the other hand, the Co-MBC synthesized via this study have a relatively higher BET surface area of value $263m^2/g$ in comparison with the unmodified biochar ($15m^2/g$) possibly because of the pores that developed from the microwave heating. The desorption study carried out showed that the Co-MBC have a regeneration and reusability.

3.2.2 Magnetic modification of biochar by Co-precipitation

Coprecipitation is a phenomenon whereby impurities in the form of solutes precipitate out from a solution via an agent or carrier that encourages the solutes to attach itself with the agent or carrier rather than remaining dissolved in the solution. This process is widely known as the simplest method in the preparation of magnetic particles (Thines et al., 2017). This method has been widely used by researchers in the preparation of magnetic biochar because it is simple. Researchers have introduced various manipulated variables to achieve the necessary dimension and properties of magnetic particles produced. With this method, researchers have control over the size of the magnetic particles produced and several research works have been published where magnetic biochar was produced using different biomass.

Saravanan et al. (2012) used gum kondagogu (GK) to produce GK-modified magnetic iron oxide particles by co-precipitating Fe^{2+} and Fe^{3+} ions in the ratio of 2:1 using ammonia solution in the presence of GK biomacromolecules. It was observed that the magnetic biochar was stable thermally compared to pristine GK. The magnetic biochars have aggregate structure that is spherical in shape and embedded with iron oxide particles which exhibited ferromagnetic properties with Ms value of 60emu/g. Jiang et al. (2016) produced magnetic chitosan–graphene oxide (MCGO) via the chemical precipitation of Fe^{2+} and Fe^{3+} ions and used it to remove dye (methyl orange, MO) from water. The maximum adsorption capacity of MCGO for MO was 398.08mg/g. This study showed that the MCGO offered enormous potential applications for water treatment. Similarly, Yu et al. (2013) investigated the competitive adsorption of Pb^{2+} and Cd^{2+} ions from solutions using modified sugarcane bagasse modified by magnetic method by two simple steps. The magnetic modified sugarcane bagasse (MSCB) was produced via the chemical precipitation of Fe^{2+} and Fe^{3+} (obtained from $FeCl_3$ and $FeSO_4$). The studies showed that the adsorption capabilities of the modified sorbent for Pb^{2+} and Cd^{2+} ions were 1.2 and 1.1mmol/g respectively. This result demonstrated that Pb^{2+} ions in solution inhibited the adsorption of Cd^{2+} ions. The inhibition was found to be proportional to the initial concentration ratio of $Pb^{2+}$and Cd^{2+}. They concluded that the produced magnetic sorbent can be used in treating heavy metal contaminated water. Devi and Saroha (2014) produced zero-valent iron magnetic biochar composites (ZVI-MBC) using biochar from paper mill sludge. In the synthesis, $NaBH_4$ solution was employed to reduce $FeSO_4$ to Fe (0). The magnetic biochar was used to treat real and synthetic effluent contaminated with pentachlorophenol (PCP). Analysis showed that the BET surface area and micropore volume of ZVI-MBC were found to be 101.23m^2/g and 0.029cm^3/g while the BET surface area and micropore volume of paper mill-based pristine biochar was 67m^2/g and 0.026cm^3/g respectively. This work suggests that the binding of the ZV Iron onto the surface of biochar presented increased surface area for adsorption. Furthermore, Chen and Wang (2011) studied the adsorption capacity of nanoparticles for the removal of Cu(II) from aqueous solution employing magnetic chitosan nanoparticles. They produced a chitosan-based magnetic biochar via a single-step coprecipitation process in the presence of $FeSO_4·6H_2O$ and $FeCl_3·6H_2O$ with a molar ratio of 1:2 with respect of Fe^{2+}:Fe^{3+}. Results analysis showed that the saturation magnetization was 36emu/g with the particles exhibiting super-paramagnetic properties. By using the Langmuir isotherm model, it was determined that the highest adsorption capacity was 35.5mg/g.

4 Application of modified biochar for competitive adsorption of heavy metal Ions from wastewater

The biochar has a great potential for metal sorption from aqueous solutions and has received increased attention during the past decade. However, studies are mostly at a lab scale, focusing on sorption of single metal from spiked solution. In natural waters, different heavy metals may coexist with other pollutant; hence there is competition for sorption sites on biochar surface between metals and other ions or organic pollutants. Presently, only few studies have assessed the competitive sorption of metals by biochar (Harikishore and Lee, 2014.). All the reported studies employed pristine biochar prepared by conventional pyrolysis and not microwave assisted pyrolyzed biochar.

On that note, Park et al. (2016) used sesame straw pristine biochar to sorb multi-metals from synthetic wastewater, showing that sorption behaviours of multi-metals (Pb, Cr, Cd, Cu, and Zn) differed from mono-metal sorption due to competition, especially for Cd, which was reduced the most by other metals. Similarly, Tan et al. (2016) compared the sorption capacity of corn straw pristine biochar for aqueous Hg and/or atrazine, showing that Hg and atrazine inhibited each other's sorption. When phenanthrene and Hg coexisted in solution, Kong et al. (2011) observed direct competitive sorption, each suppressing the other as soybean stalk-based pristine BC was used to sorb Phenanthrene and Mercury(II) from synthetic wastewater. In addition, humic acids coexist with contaminants in aqueous environment, possibly influencing metal sorption by biochar. Zhou et al. (2015) showed that humic acids increased sorption capacities of Pb^{2+} and Cr(VI) by sludge-derived pristine biochar from 197mmol/g to 233mmol/g and from 688mmol/g to 738mmol/g respectively. Due to the adsorbed humic acids, their functional groups offer additional sites for Pb^{2+} ion and supply more reducing agent to facilitate the transformation of Cr(VI) to Cr(III). Furthermore, there is only one reported studies of the use of magnetic biochar to investigate the competitive adsorption of heavy metal ions from aqueous solutions by Yu et al. (2015). Further competitive sorption studies are necessary to accurately estimate metal sorption capacity of biochar in natural environments. At present, there is no report of using the biochar to remove heavy metals from contaminated wastewater for field application (Li et al., 2017). Contaminated water is more complicated than the simulated water used by current studies. To ensure the suitability of the biochar wastewater treatment, employing physicochemical conditions to simulate contaminated water or using actual contaminated water for studies is very necessary. In addition, to support field application, future studies need to address factors related to metal removal efficiency, such as pH, dosing and recovery approaches, and regeneration and disposal of metal-sorbed biochars. Making the biochar magnetic can help recover the biochar following metal sorption.

5 Regeneration of used modified biochar

The adsorption capacity of modified BCs is limited, therefore a prolonged exposure of the BCs with the heavy metal ions eventually results in the formation of thermodynamic equilibrium between the BCs and sorbates. Thus, there is the need to regenerate the BC sorbents for reuse or disposal. It has been demonstrated by Wang et al. (2015) that an economical and effective method of desorption can minimize the BC cost significantly and enhance reusability, because the sorption-desorption cycle could be repeated several times. After the modified BCs are completely saturated with the sorbates, the desorption can be performed with solutions of KNO_3, HNO_3 or $NaNO_3$ at different concentrations. These types of de-sorbents can supply a significant quantity of cations that could displace the heavy metal ions adsorbed. Furthermore, due to low pH, acid solutions desorb heavy metal ions efficiently (Sounthararajah et al., 2015). Additionally, several techniques such as partial pressure reduction, heat treatment, using inert gas or fluid to purge, and altering of chemical state like pH may be used to regenerate fixed bed columns. The solvents that are widely employed for the regeneration of modified BCs include acetic acid, NaOH, HCl, NaCl and EDTA. Heavy metal ions desorption has been described to be favored using acids as the de-sorbents because acidic conditions reduces adsorption of metal ions, as reported Gupta and Ali (2012).

6 Conclusions and perspectives

Studies have shown that the properties of the BC do not only depend on the types of feedstock but also on the methods and production conditions. BCs are produced by pyrolysis of biomass with microwave-assisted pyrolysis being a more efficient thermochemical process for the BC production. The BC produced at high temperatures possesses fewer H and O functional groups but shows highly aromatic nature and has lower ion exchange capabilities. The BC produced at lower temperature shows varied organic characters, including aliphatic and cellulose type structures and contain more C—H and C═C functional groups.

Modification methods especially chemical methods improve the surface properties of the BCs. Acidic modification generates extensive oxygenated functional groups, while alkaline modification produces high ratios of surface aromaticity and N/C. The BCs with impregnated nano-scale materials show enhanced removal of organic and inorganic contaminants, although with reduced pore volumes. A major challenge with the practical wastewater treatment using the BC is the difficulty encountered in isolating and recycling the BC from aqueous solution by the traditional methods (filtration and centrifugation). Magnetic separation method has been demonstrated by few studies to be a potential technique for solid-liquid phase separation. Therefore, substantial studies are needed on how to produce magnetic BCs with excellent adsorption capacity.

Heavy metal ions often coexist in wastewater; hence they compete for adsorption sites. The publications on the competitive adsorption of heavy metal ions from contaminated water using modified biochar is limited. Further competitive sorption studies are necessary to accurately estimate metal sorption capacity of the biochar in natural environment.

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