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Pb(II) removal from water using Fe-coated bamboo charcoal with the assistance of microwaves

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Abstract
Bamboo charcoal (BC) was used as starting material to prepare iron-modified bamboo charcoal (Fe-MBC) by its impregnation in FeCl₃ and HNO₃ solutions simultaneously, followed by microwave heating. The material can be used as an adsorbent for Pb(II) contaminants removal in water. The composites were prepared with Fe molar concentration of 0.5, 1.0 and 2.0 mol/L and characterized by means of N₂ adsorption-desorption isotherms, X-ray diffraction spectroscopy (XRD), scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS), Fourier transform infrared (FT-IR) and point of zero charge (pHₚzc) measurements. Nitrogen adsorption analyses showed that the BET specific surface area and total pore volume increased with iron impregnation. The adsorbent with Fe molar concentration of 2 mol/L (2Fe-MBC) exhibited the highest surface area and produced the best pore structure. The Pb(II) adsorption process of 2Fe-MBC and BC were evaluated in batch experiments and 2Fe-MBC showed an excellent adsorption capability for removal Pb(II). The adsorption of Pb(II) strongly depended on solution pH, with maximum values at pH 5.0. The ionic strength had a significant effect on the adsorption at pH < 6.0. The adsorption isotherms followed the Langmuir isotherm model well, and the maximum adsorption capacity for Pb(II) was 200.38 mg/g for 2Fe-MBC. The adsorption processes were well fitted by a pseudo second-order kinetic model. Thermodynamic parameters showed that the adsorption of Pb(II) onto Fe-MBC was feasible, spontaneous, and exothermic under the studied conditions, and the ion exchange mechanism played an significant role. These results have important implications for the design of low-cost and effective adsorbents in the removal of Pb(II) from wastewater.

Key words: adsorption; bamboo charcoal; microwave assistance; kinetics; adsorption isotherms
DOI: 10.1016/S1001-0742(12)60144-2

Introduction
The presence of heavy metal ions in the aquatic environment has been a big issue for scientists and engineers (Bulut and Tez, 2007). Pb(II) is one of the most useful of all metals because of its wide distribution and its ease of extraction (Xing et al., 2011). It is also the metal that causes the most organ damage in children, even at extremely low concentrations (0.01–5.0 mg/L) (Ahmedna et al., 2004). The permissible limit of Pb(II) in drinking water is 0.01 mg/L, according to the current Chinese Standards (GB5749-2006) for Drinking Water Quality. The treatment of heavy metal-bearing effluents has been studied by several methods, such as reduction precipitation, ion exchange, electro-chemical reduction, evaporation, reverse osmosis, adsorption and direct precipitation (Terry, 2004; Ólmez, 2009; Alguacil et al., 2003). The process of activated carbon adsorption was found to be a promising technique that can remove trace amounts of adsorbate from aqueous solution due to its extremely high surface area, micropore structure, large adsorption capacity, rapid adsorption behavior and relatively easy regeneration (Wang et al., 2006; Lin et al., 2010).

In general, carbon adsorption is not nearly as effective at removing metals and inorganic pollutants as it is in removing organic compounds. Recent studies have placed emphasis on the surface modification of carbons to enhance Pb(II) removal from wastewater (Fan et al., 2011). Iron oxide has been proven to be an excellent adsorbent with high affinity toward inorganic lead species and selectivity in the adsorption process (James and Healy, 1972). However, iron oxide is very bulky in nature, highly amorphous, and flocculant, which limits its widespread application for Pb(II) removal. To improve the adsorption efficiency, recent research has focused on creating media to support iron oxide (Bulut and Teg, 2007). Activated
carbon was proven to be an ideal support because of its stable and variable pore structure, and promising results for Pb(II) removal have been obtained using iron oxide-loaded activated carbon. It has been shown that the effectiveness of Pb(II) removal is closely related both to the amount of iron loading and to the dispersion and surface accessibility of this iron within the activated carbon.

However, the biggest barrier in the application of this process by industry is the high cost of activated carbons presently available for commercial use (Liu et al., 2010). In recent years, the development of new inexpensive adsorbent materials has been focused on the production of activated carbon from agricultural or agro-industrial waste materials. This has led many workers to search for cheap and efficient alternative materials (Yang et al., 2004). Bamboo belongs to the grass family and is an enduring, versatile and renewable material. It can be carbonized in a furnace at high temperature in the absence of oxygen to produce carbon chars. It was estimated that the throughput of bamboo charcoal (BC) in China has been approximately 40,000 tons a year. However, its utilization has not been fully explored. Therefore, the use of BC as a potential adsorbent for the removal of toxic pollutants from waters would enlarge its application and help to deal with the emergent wastewater treatment challenge in China.

In this study, we used bamboo charcoal as a low-cost supporting material for Fe oxides coated by a novel and simple synthetic approach. The approach was based on the hypothesis that BC is a good microwave absorber, which receives microwave energy directly through dipole rotation and ionic conduction. As a consequence, the bulk temperature of iron-impregnated BC rises rapidly and uniformly under microwave irradiation, so that the pyrolysis process is able to induce ferric species to cross-link with various functional groups in a dispersive way on the BC. Our objective was to explore the feasibility of using such an adsorbent for the removal of Pb(II) in water solutions.

1 Materials and methods

1.1 Adsorbent

The BC used in this study was manufactured by Suichang Mingkang Charcoal Enterprise Co. Ltd. (Zhejiang, China) with a particle size of 1–2 mm. Iron trichloride (FeCl$_3$) was employed as a precursor for oxide incorporation into the pores of the granular-size porous BC.

The following procedure was developed to achieve homogeneous impregnation: 100 mL of FeCl$_3$ solutions at concentrations of 0.5 mol/L, 1.0 mol/L and 2.0 mol/L in acid media (9 mol/L HNO$_3$) were dispersed over 10 g of BC and mixed for 24 hr at room temperature, followed by ultrasonication for 2 hr to achieve full penetration and saturation of the metal ions into the BC pore. Then, the BC was separated from the mixture and placed in a modified microwave heating apparatus, and heated with continuous output 640 W power and a frequency of 2.45 GHz for 6 min under a nitrogen flow of 10 mL/min. After cooling, the composite was washed thoroughly using deionized water until the filtrates were close to neutral and dried at 333 K for 24 hr, then stored in a desiccator for use (designated as xFe-MBC, where x represents the molar concentration of the FeCl$_3$ solution).

1.2 Characterization methods

The pore structures and surface areas of xFe-MBC and BC samples were characterized using a nitrogen adsorption/desorption analyzer (ASAP 2020, Micrometrics, USA). Their structure and phase composition were studied in detail by X-ray diffraction (XRD) with an X-ray diffractometer (X’pert Pro, Bruker, Germany), which was equipped with CuK$_\alpha$ radiation (40 kV, 40 mA) and scanned with a 0.01° step and 2.5 sec step time over the range 10° < 2θ < 90°. The micro-image and chemical constituents were obtained using a scanning electron microscope (SEM) (S4700, Hitachi, Japan) coupled with an energy dispersive X-ray spectrometer (EDS) (JSM-6500F, JEOL, Japan). Infrared absorption (IR) spectra was measured at room temperature on a Fourier transform infrared (FT-IR) spectrometer (5700, Nicolet, USA) using the KBr Pellet technique. The point of zero charge measurements were carried out using the pH drift method (Li et al., 2008).

1.3 Adsorption studies

Batch sorption studies were carried out by agitating 50 mL of Pb(II) solution of the desired concentration and a known weight of BC and xFe-MBC in 250 mL conical flasks. The pH and ionic strength effect were studied within the range of 1.0–7.0 (adjusted with 0.1 mol/L HNO$_3$ or NaOH) and ionic strength was investigated at non-fixed ionic strength, 0.01 mol/L, and 0.1 mol/L NaNO$_3$ solution. Sorption kinetic experiments were conducted by analyzing the residual concentration of Pb(II) at predetermined time intervals. Batch isothermal studies were conducted by varying the concentration of Pb(II) solution and shaking for 24 hr to ensure equilibrium was reached. All samples were mixed in a rotary shaker at 150 r/min and (25 ± 0.5)℃. Before analysis, samples were filtered through a 0.45 μm membrane. The residual Pb(II) concentrations in solutions were measured using graphite furnace atomic adsorption spectroscopy (AAAnalyst 600, Perkin Elmer, USA).

2 Results and discussion

2.1 Properties of the adsorbents

XRD patterns of the BC and xFe-MBC are shown in Fig. 1. The results were assessed using the powder diffraction file
with increasing loading of iron oxide indicated a significantly increased content of hydroxyl groups on the carbon, which might be due to the increase of carboxylic groups. This clearly indicated that the formation of iron oxides generated a large number of surface functional groups such as carbonyl, carboxyl, and nitrate groups. Another band was found at 1640 cm\(^{-1}\), which was associated with the C=O stretching vibration. The strong band of at 1062 cm\(^{-1}\) could be assigned to the bending vibration of hydroxyl groups on the surface (M–OH) (Zhang et al., 2005). For \(x\)Fe-MBC (Fig. 2), there were peaks assignable to the Fe–O group at 630 cm\(^{-1}\) (Namduri and Nasrazadani, 2008; Tang et al., 2007), which are diagnostic of hematite. At the same time, the spectra of \(x\)Fe-MBC displayed absorption peaks at 1120 cm\(^{-1}\) related to the C–O stretching vibration of alcholic, phenolic and carboxylic groups (Gu et al., 2005).

SEM images showed that pores with different sizes and different shapes existed on the external surface of BC and \(x\)Fe-MBC. Unlike the smooth surface of the BC (Fig. 3a), \(x\)Fe-MBC (Fig. 3b, c, d) exhibited comparatively rougher surfaces. The observation suggested that the particulates observed might be iron oxide (Fe\(_2\)O\(_3\)), which was in good agreement with the XRD analysis. In 0.5Fe-MBC (Fig. 3b), there was a small amount of Fe\(_2\)O\(_3\) particles covering on the surface. However, as the concentration of FeCl\(_3\) increased, the iron oxide particles grew in number or quantity and agglomerated together (Fig. 3c). With the continued increase of FeCl\(_3\), abundant iron oxide particles appeared and dispersed uniformly on the surface of 2Fe-MBC (Fig. 3d). Furthermore, together with the elemental analysis determined by the energy dispersive spectroscopy (EDS) (Table 1), where intense peaks at 0.65, 6.38 and 7.05 keV characteristic of Fe could be observed for \(x\)Fe-MBC, this indicated that the impregnation of BC in FeCl\(_3\), followed by microwave heating, resulted in iron oxides coating the BC through redox reactions (Zhang et al., 2008). The atomic percentage of iron increased with increasing FeCl\(_3\) concentration. Nitrogen was also identified in the coating, which might originate from HNO\(_3\). The high intensity of the oxygen peak was another evidence of the presence of an iron oxide coating.

The nitrogen adsorption-desorption isotherms of BC and \(x\)Fe-MBC are shown in Fig. 4. The shape of the N\(_2\) adsorption/desorption isotherms of BC was indicative of type V and the \(x\)Fe-MBCs were a mixture of types I and IV, according to the International Union of Pure and Applied

![Fig. 1](image1.png)

Powder XRD of bamboo charcoal (BC), 0.5Fe-MBC, 1Fe-MBC and 2Fe-MBC.

![Fig. 2](image2.png)

FT-IR spectra of BC, 0.5Fe-MBC, 1Fe-MBC and 2Fe-MBC.

### Table 1

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>C (%)</th>
<th>N (%)</th>
<th>O (%)</th>
<th>Fe (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>59.52</td>
<td>3.48</td>
<td>18.46</td>
<td>N.A.</td>
</tr>
<tr>
<td>0.5Fe-MBC</td>
<td>59.05</td>
<td>14.27</td>
<td>17.41</td>
<td>1.95</td>
</tr>
<tr>
<td>1Fe-MBC</td>
<td>46.75</td>
<td>6.68</td>
<td>41.38</td>
<td>5.09</td>
</tr>
<tr>
<td>2Fe-MBC</td>
<td>3.87</td>
<td>8.73</td>
<td>45.93</td>
<td>41.29</td>
</tr>
</tbody>
</table>

BC: bamboo charcoal; N.A.: not available.
Chemistry (IUPAC) classification. These results indicated the simultaneous presence of microporous and mesoporous structure in the materials. The surface physical parameters obtained from the N₂ adsorption isotherms of BC and xFe-MBC are shown in Table 2. In comparison with BC, the BET surface area and total pore volume of xFe-MBC increased, and the pore size decreased. Among the three Fe-MBCs, 2Fe-MBC had the largest surface area of 298.732 m²/g. The results showed that the introduction of iron promisingly promoted the pore formation or prevented the pores from being blocked by the presence of Fe₂O₃ (Ania et al., 2005; Ji et al., 2007).

Table 2  Physical properties of different materials

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BC</th>
<th>0.5Fe-MBC</th>
<th>1Fe-MBC</th>
<th>2Fe-MBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (m²/g)</td>
<td>15.000</td>
<td>198.619</td>
<td>249.906</td>
<td>298.732</td>
</tr>
<tr>
<td>Total pore volume (cm³/g)</td>
<td>0.140</td>
<td>0.242</td>
<td>0.208</td>
<td>0.275</td>
</tr>
<tr>
<td>Pore size (nm)</td>
<td>12.900</td>
<td>4.463</td>
<td>3.230</td>
<td>3.691</td>
</tr>
<tr>
<td>Particle size (mm)</td>
<td>5.86</td>
<td>2.95</td>
<td>2.64</td>
<td>2.55</td>
</tr>
<tr>
<td>pH_zpc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3  SEM images of BC (a), 0.5Fe-MBC (b), 1Fe-MBC (c) and 2Fe-MBC (d).

Fig. 4  N₂ adsorption/desorption isotherms of BC, 0.5Fe-MBC, 1Fe-MBC and 2Fe-MBC.

The pH_zpc values of BC, 0.5Fe-MBC, 1Fe-MBC and 2Fe-MBC were measured as 5.86, 2.95, 2.64 and 2.55, respectively. The high concentration Fe-MBC was more acidic than low concentration Fe-MBC owing to the acidity of the iron species (Hines et al., 2004). The decrease
in pH_{zpc} after iron loading indicated that protonated surface functional groups on the carbon were neutralized or blocked by the polymer layer coating (Fang et al., 2007). Another reason for the increased acidity might be due to nitric acid residues on the surface of xFe-MBC which could not be removed by thorough washing with distilled water (Xua et al., 2010).

### 2.2 Effect of pH and ionic strength on Pb(II) removal

Sorption of Pb(II) on BC and 2Fe-MBC in 0 mol/L, 0.01 mol/L and 0.1 mol/L NaNO₃ solutions, respectively, at pH in the range 1.0–7.0 are shown in Fig. 5. As can be seen from Fig. 5, it was clear that sorption of Pb(II) was strongly dependent on pH, and also dependent on ionic strength. Pb(II) uptake increased quickly with an increase in pH up to 5.0, then increased slightly with further increase of pH. At pH higher than 7.0, the precipitation of Pb(II) ions took place, therefore studies of the adsorption of Pb(II) ions were conducted below pH 7.0 to ensure that the mechanism for Pb(II) ion removal only depended on adsorption (Fan et al., 2011).

The surface charge of the prepared adsorbent was positive at pH < pH_{zpc} due to an excess of protons on the surface, and negative at pH > pH_{zpc}. At lower pH, the surface of the adsorbent was surrounded by H⁺ ions which could compete with Pb(II) ions for surface adsorption sites, thereby preventing the Pb(II) ions from approaching the binding sites on the adsorbent (Kadirvelu et al., 2000). However, when the pH increased too much, Pb(II) adsorption to the adsorbent was mainly dominated by the exchange of protons and some Na⁺ ions, with the increasing negative charge increasing Pb(II) adsorption until a plateau was reached. The combined effect of these factors caused the adsorption capacity for metal ions to reach its maximum value at pH 5.0.

The adsorption of Pb(II) on both adsorbents at pH < 6.0 was clearly influenced by ionic strength, whereas no significant difference of Pb(II) adsorption was found at pH > 6.0 as a function of ionic strength. From the above results, one should draw a conclusion that the ionic strength-dependent adsorption indicated that ion exchange or outer-sphere complexation contributes to Pb(II) adsorption at pH < 6.0 (Fan et al., 2011; Chen et al., 2007; Wang et al., 2009), while the ionic strength-independent adsorption suggested that inner-sphere complexation was the main adsorption mechanism of Pb(II) on the adsorbents at pH > 6.0 (Eren et al., 2010).

### 2.3 Adsorption kinetics

The effect of contact time on adsorption of Pb(II) onto 2Fe-MBC and BC is shown in Fig. 6. The equilibrium was attained by an initial rapid process followed by a slow process. Under the experimental conditions of this study, adsorption equilibrium was achieved within about 360 min for 2Fe-MBC. However, the adsorption of Pb(II) on BC took about 600 min to reach equilibrium.

The nature of the adsorption kinetics is one of the most important characteristics governing the solute uptake rate and adsorption efficiency of an adsorbent, knowledge of which is important for design, operation and optimization (Sreejalekshmi et al., 2009). To investigate the adsorption kinetics of Pb(II) on BC and 2Fe-MBC, both pseudo first-order (Eq. (1)) and pseudo second-order (Eq. (2)) kinetic models were used to correlate the adsorption data (Wang et al., 2006):

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where, \(q_t\) (mg/g) and \(q_e\) (mg/g) are the amounts of Pb(II) adsorbed at time \(t\) (min) and at equilibrium, respectively, and \(k_1\) (1/min), \(k_2\) (g/(mg·min)) and \(k_3\) (mg/(g·min^{1/2})) are the rate constants of first-order, second-order and intraparticle diffusion models, respectively. The product
Table 3 Pseudo first-order and pseudo second-order kinetic parameters of Pb(II) adsorption onto BC and 2Fe-MBC

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>qe,exp (mg/g)</th>
<th>Pseudo first-order</th>
<th>Pseudo second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>qe (mg/g)</td>
<td>k1 (1/min)</td>
<td>R²</td>
</tr>
<tr>
<td>BC</td>
<td>9.60</td>
<td>6.82</td>
<td>4.606 × 10⁻³</td>
</tr>
<tr>
<td>2Fe-MBC</td>
<td>21.03</td>
<td>15.56</td>
<td>13.818 × 10⁻³</td>
</tr>
</tbody>
</table>

$k_2q_e^2$ is the initial sorption rate, represented as $h = k_2q_e^2$. Kinetic parameters of these plots of log($q_e$-qe) versus t and t/qe versus t are given in Table 3. It also illustrates the comparison between the calculated and observed values of qe versus t for the adsorption of Pb(II). The R² values in Table 3 show that the experimental data fit the pseudo second-order model for the adsorption of Pb(II) and the calculated values of qe also agreed with the experimental values. This indicated that the rate-limiting step was a chemical adsorption process. The values of the initial adsorption rates h were significantly higher for Fe-MBC compared to BC, which indicated that, the removal rate of Fe-MBC was faster than that of BC.

The kinetic results were further analyzed by the intraparticle diffusion model (Eq. (3)) to determine if the intraparticle diffusion was the rate-limiting step:

$$q_t = k_1t^{1/2} + c$$  \hspace{1cm} (3)

The intraparticle diffusion constant was computed from the plot of $q_t$ vs. $t^{1/2}$ (Fig. 8). All plots in Fig. 7 present three separate regions with different slopes, indicating that more than one process affected the Pb(II) adsorption on both BC and 2Fe-MBC. The first sharper linear portion (I) was the instantaneous adsorption or external surface adsorption stage, while the second region (II) was the gradual adsorption stage where intraparticle diffusion was rate-limiting, and the third flat region (III) was the final equilibrium stage where intraparticle diffusion started to slow down due to the extremely low adsorbate concentrations left in the solutions (Wu et al., 2005). For Pb(II) adsorption on both adsorbents, the plots for the initial linear segment did not pass through the origin ($c \neq 0$), implying that intraparticle diffusion was not the only rate-controlling step and boundary layer control might affect the adsorption (Kannan and Sundaram, 2001; Chen et al., 2003; Zhu et al., 2010).

2.4 Adsorption isotherms

The adsorption isotherms of Pb(II) on BC and 2Fe-MBC at three different temperatures are shown in Fig. 8. It can be seen that Pb(II) adsorption onto 2Fe-MBC was much higher than BC, and the adsorbed amounts both decreased with the increase of temperature, indicating that the process was exothermic in nature. The adsorption data were analyzed with Langmuir and Freundlich isotherm models.

The Langmuir isotherm equation, which is most commonly used for monolayer adsorption onto a surface with a finite number of identical sites, is represented by the following Eq. (4) (Ghanizadeh et al., 2012):

$$q_e = \frac{q_{max}bC_e}{1 + bC_e}$$  \hspace{1cm} (4)

where, $C_e$ (mg/L), is the equilibrium concentration of metal ions, $q_e$ (mg/g) is the amount of metal ions adsorbed, $q_{max}$ (mg/g) is the maximum adsorption capacity of metal ions, and $b$ (L/mg) is the Langmuir adsorption equilibrium constant related to the affinity of the binding sites.

The Freundlich isotherm equation, the most important multilayer adsorption isotherm for heterogeneous surfaces, is described by the following Eq. (5) (Velmurugan et al., 2010):

$$q_e = K_iC_e^{1/n}$$  \hspace{1cm} (5)
Comparison of the maximum adsorption capacities of Pb(II) onto various adsorbents is shown in Table 5. The maximum adsorption of Pb(II) for 2Fe-MBC was comparable to or higher than that of the other reported adsorbents. Taking into account its considerable adsorption capacity and cost-efficiency, the 2Fe-MBC developed in the present study has great potential for application in Pb(II) removal.

Table 4 Langmuir isotherm parameters for adsorption of Pb(II) onto BC and 2Fe-MBC at different temperatures

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temperature (K)</th>
<th>$q_m$ (mg/g)</th>
<th>$b$ (L/mg)</th>
<th>$R^2$</th>
<th>$K_L$ (mg/g)</th>
<th>$1/n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>288</td>
<td>31.25</td>
<td>0.023</td>
<td>0.9992</td>
<td>1.875</td>
<td>0.657</td>
<td>0.9438</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>25.03</td>
<td>0.012</td>
<td>0.9989</td>
<td>0.826</td>
<td>0.702</td>
<td>0.9657</td>
</tr>
<tr>
<td>2Fe-MBC</td>
<td>308</td>
<td>20.41</td>
<td>0.001</td>
<td>0.9995</td>
<td>0.479</td>
<td>0.736</td>
<td>0.9639</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>166.67</td>
<td>0.018</td>
<td>0.9994</td>
<td>4.207</td>
<td>0.577</td>
<td>0.9738</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>125.21</td>
<td>0.018</td>
<td>0.9995</td>
<td>3.673</td>
<td>0.627</td>
<td>0.9625</td>
</tr>
</tbody>
</table>

where, $K_L ((\text{mg/g})(\text{L/mg})^{1/n})$ and $n$ are the Freundlich adsorption isotherm constants, which are indicators of adsorption capacity and adsorption intensity, respectively (Aksu and Akpinar, 2000). The parameters of the isotherm models determined from regression analysis of the experimental data are summarized in Table 4. As seen from the isotherms in Fig. 8 and the $R^2$ values in Table 4, the Langmuir isotherm fitted better than the Freundlich isotherm under the concentration range studied, which might be due to a homogeneous distribution of active sites onto BC and 2Fe-MBC surfaces, since the Langmuir equation assumes that the surface is homogenous. A steady decrease in $q_m$ and $b$ values with increasing temperature in Table 4 proves that the affinity of Pb(II) for both 2Fe-MBC and BC decreased with the rise in temperature from 288 to 308 K, also indicating that the process is exothermic in nature.

2.5 Adsorption thermodynamics

The thermodynamic parameters, such as change in standard free energy ($\Delta G^0$, kJ/mol), enthalpy ($\Delta H^0$, kJ/mol) and entropy ($\Delta S^0$, J/(mol·K)) are determined using the following equations (Du et al., 2008):

$$\Delta G^0 = -RT\ln K_L$$

(6)

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

(7)

where, $R$ (8.314 J/(mol·K)), is the ideal gas constant, $T$ (K) is Kelvin temperature and $K_L$ (L/mol) is the Langmuir constant. The values of $\Delta H^0$ and $\Delta S^0$ can be calculated from the slope and intercept of the van’t Hoff plot of $\ln K_L$ versus $1/T$.

The calculated values of $\Delta H^0$, $\Delta S^0$ and $\Delta G^0$ for adsorption of Pb(II) on 2Fe-MBC and BC are given in Table 6. The negative values of $\Delta G^0$ increased with the increase in temperature, indicating that the spontaneous nature of the adsorption processes and the decrease in temperature favored them (Daifullah et al., 2007). The negative values of $\Delta H^0$ further confirmed the exothermic nature of the processes. The positive values of $\Delta S^0$ suggested increased randomness at the solid/solution interface, with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent (Tan et al., 2009; Gupta et al., 2005).

Table 5 Comparison of the maximum adsorption capacities of Pb(II) onto various adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_m$ (mg/g)</th>
<th>pH</th>
<th>Temperature (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidized MWCNTs</td>
<td>2.05</td>
<td>5.9</td>
<td>298</td>
<td>Rao et al., 2011</td>
</tr>
<tr>
<td>Oak bark char</td>
<td>13.05</td>
<td>6.0</td>
<td>298</td>
<td>Boudrahem et al., 2011</td>
</tr>
<tr>
<td>H2O2-oxidized activated carbon</td>
<td>37.92</td>
<td>5.0</td>
<td>303</td>
<td>Acharya et al., 2009</td>
</tr>
<tr>
<td>Mg2Al LDH</td>
<td>66.16</td>
<td>5.7</td>
<td>303</td>
<td>Sari et al., 2007</td>
</tr>
<tr>
<td>Sewage sludge activated carbon</td>
<td>70.30</td>
<td>5.4</td>
<td>–</td>
<td>Fan et al., 2011</td>
</tr>
<tr>
<td>Phosphoric acid activated carbon</td>
<td>89.30</td>
<td>5.8</td>
<td>298</td>
<td>Boudrahem et al., 2011</td>
</tr>
<tr>
<td>Spartina alterniflora activated carbon</td>
<td>99.50</td>
<td>5.6</td>
<td>298</td>
<td>Li and Wang, 2009</td>
</tr>
<tr>
<td>Activated carbon-chitosan complex adsorbent</td>
<td>125.40</td>
<td>5.0</td>
<td>303</td>
<td>Ge and Fan, 2011</td>
</tr>
<tr>
<td>BC</td>
<td>31.25</td>
<td>5.0</td>
<td>288</td>
<td>Present study</td>
</tr>
<tr>
<td>2Fe-MBC</td>
<td>200.38</td>
<td>5.0</td>
<td>288</td>
<td>Present study</td>
</tr>
</tbody>
</table>
2.6 Mechanism study

SEM images of 2Fe-MBC before and after Pb(II) adsorption are presented in Fig. 9. Compared with the original 2Fe-MBC, the surface morphology of 2Fe-MBC after Pb(II) adsorption was found to change little except for some additional substances which might be the adsorbed lead species. This indicated that the as-prepared adsorbent provides feasibility for regeneration and reuse.

The EDS analysis (Table 7) revealed that the oxygen content on the 2Fe-MBC surface significantly increased after Pb(II) adsorption, indicating the formation of Fe-Pb complexes. Lead was found to be evenly distributed on the surface, which indicated the uniform distribution of adsorption sites for Pb(II) on the surface of 2Fe-MBC. Metal hydroxyl groups existing on a large number of metal oxides play an important role on the adsorption of metal ions, such as lead.

Interactions between lead and the functional groups on the surface of the adsorbents was determined by FT-IR, which is acknowledged as a direct means for studying the mechanism of Pb(II) adsorption. The FT-IR spectra of 2Fe-MBC and Pb-saturated 2Fe-MBC are represented in Fig. 10. After Pb(II) adsorption, the band intensity of –OH (3430 cm\(^{-1}\)) significantly decreased and the M–OH bending bands (1062 cm\(^{-1}\)) almost disappeared, implying that the Pb(II) adsorbed on the surface of 2Fe-MBC through the substitution of hydroxyl groups. On the other hand, a new band at 400 cm\(^{-1}\) representing the covalent Pb-O bond appeared in the spectra of 2Fe-MBC after the adsorption of Pb(II) (Chen and Ferraris et al., 2003).

According to the above analysis, it can be concluded that ion exchange and coulombic forces are simultaneously responsible for Pb(II) adsorption.

3 Conclusions

The iron-bamboo charcoal (Fe-MBC) composites reported in this work can be prepared with a high adsorption capacity activated carbon by a very simple procedure using available and low-cost materials. The results suggested that a coating of iron could improve the porosity of the bamboo
charcoal-based material after a short duration microwave heating. The Pb(II) adsorption onto BC and 2Fe-MBC were dependent on time, initial metal ion concentration, solution pH, ionic strength and temperature. The maximum adsorptions of metal ions on both adsorbents were at pH 5.0. The adsorption kinetics were well explained by pseudo second-order kinetics rather than first-order kinetics. The equilibrium of adsorption was suitably described by the Langmuir model with a maximum adsorption capacity of 200.38 mg/g. The adsorption processes were exothermic in nature, the addition of iron oxide (Fe₂O₃) was advantageous to the spontaneous process, and the ion exchange mechanism played an significant role. Therefore, the Fe-MBC is promising for application in the removal of Pb(II) from large volume solutions for practical application in wastewater treatment.

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References


Aims and scope

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