

Biosorption of Heavy Metal Ions from Aqueous Solution on Chinese Fir Bark Modified by Sodium Hypochlorite

Wenpeng Su, Yiqin Yang,* Hongqi Dai,* and Linyu Jiang

The oxidation conditions and adsorption ability of Cu (II), Cd (II), and Pb (II) from an aqueous solution of sodium hypochlorite-oxidized fir bark powder were investigated. The optimum amount of NaClO was 9.6%, the pH was 9, and the oxidation time was 120 min. Batch adsorption experiments were carried out with various times, pH values, and initial metal ion concentrations. The adsorption isotherms and kinetics of adsorption were also studied. The maximum adsorption capacity of oxidized fir bark was 0.983, 1.223, and 0.966 mmol/g for Cu (II), Cd (II), and Pb (II), respectively, within 30 min at pH 5, higher adsorption capacity than that of unoxidized fir bark. The isothermal adsorption of heavy metal ions in aqueous solution was a good fit to the Langmuir equation, with a coefficient of determination, R^2 , above 0.99. The adsorption of fir bark on metal ions can be appropriately approximated by a pseudo-second order adsorption kinetics model. Results indicate that the fir bark powder modified with sodium hypochlorite can adsorb large amounts of metal ions and could be a good adsorbent for the removal of Cu(II), Cd(II), and Pb(II) from aqueous solution.

Keywords: Modified fir bark; Sodium hypochlorite; Adsorption; Heavy metal ions; Adsorption kinetic; Isothermal adsorption model

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INTRODUCTION

With the acceleration of industrialization, and especially the rapid development of the electroplating, battery manufacture, and metallurgy industries (Liu *et al.* 2013), wastewater containing large amounts of heavy metal ions is produced and discharged into the environment, potentially causing environmental hazards and adversely impacting the environment and living organisms (Salehi and Madaenim 2010). This negative influence on the whole biological chain is attributed to the poor biodegradability, accumulative tendency in living organisms, and extreme toxicity of heavy metal ions such as Pb, Cd, Hg, and Zn (Wu *et al.* 2010; Padilla-Ortega *et al.* 2011; Kilic and Kirbiyik 2013). In particular, heavy metals can damage the human body *via* absorption pathways such as ingestion, inhalation, and skin contact (Saliva and Gauthier 2002; Kanazawa *et al.* 2004; Leone *et al.* 2007). Heavy metal ions can cause physical illnesses such as neurological impairment, liver disease, and various types of cancer, even at very low concentrations (Reddad *et al.* 2002). Reducing the content of heavy metal ions in wastewater is therefore necessary and urgent.

Numerous treatments have been developed to remove heavy metal ions from industrial wastewater, including chemical precipitation, ion exchange, ultrafiltration, reverse osmosis, and electrodialysis (Unlu and Ersoz 2006; Kalaivizhi *et al.* 2011;

Mahmoud and Hoadley 2012; Borklu 2013; Mandel and Hutter 2013). However, many of these methods are ineffective or uneconomical, especially when used to reduce heavy metal ions to very low concentrations (Liao *et al.* 2006). Disadvantages such as long processing times, high costs, and secondary pollution exist in practical applications, restricting the popularization of these processes (Zhao and Mitomo 2008; Huang and Zhu 2013). Adsorption seems to be a preferable method for removing heavy metal ions from wastewater. Adsorption of heavy metal ions (HMI) by activated carbon is more expensive than adsorption by plant material (bio-adsorbents) from forestry and agricultural residues (Bulut and Tez 2007; Hubbe *et al.* 2011). Bio-adsorbents are readily available, simple to use, and have extensive adaptability (Xu *et al.* 2013), so they may have a lower cost of implementation (Bailey *et al.* 1999). Most studies have focused on untreated plant wastes. Bhattacharya *et al.* (2006) studied the adsorption of Zn(II) from aqueous solution using neem bark. Ronda *et al.* (2014) studied the adsorption of lead using pine bark in batch systems. Mishra *et al.* (2012) studied the adsorption of Zn(II) using eucalyptus bark saw dust. Su *et al.* (2014) studied adsorption using fir bark. However, several problems with the application of untreated plant wastes as adsorbents exist, such as low adsorption capacity and high COD and BOD as a result of the release of soluble organic compounds contained in the plant material (Nakajima and Sakaguchi 1990). Plant wastes must be modified for use in the removal of HMI. Liang *et al.* (2014) explored the removal of Cr(VI) with various modified spruce bark adsorbents. Gaballah *et al.* (1997) studied the recovery of Cu(II) using modified barks.

Pretreatment of plant wastes can enhance their chelating efficiency (Gaballah *et al.* 1997). Various physicochemical steps to modify bark adsorbents, such as covalent grafting with oligogalacturonans (Astier *et al.* 2010), periodate oxidation (Martin *et al.* 2004), and phosphoric acid treatment (Patnukao *et al.* 2008), have been reported. Oxidation with sodium hypochlorite, to develop an adsorbent from fir bark, was studied in this paper. Chinese fir is one of the most important plantation tree species in China and has a thousand years of cultivation history. It is a fast-growing species prized for its wood quality and is widely planted for timber production in southern China. At present, this species accounts for 30% of all plantations in the country. Efficient use of fir bark has realistic significance. The objective of this study was to discuss the suitable oxidation conditions of sodium hypochlorite and the adsorption performance of modified fir bark powder for heavy metal ions. Adsorption conditions were investigated, and the isothermal adsorption equation and adsorption dynamics were simulated and discussed. The results provide theoretical guidance for the effective use of fir bark.

EXPERIMENTAL

Chemicals and Raw Material

All chemicals were of analytical reagent grade, purchased from Nanjing Chemical Reagent Co., Ltd., and used as received. The pH of the dispersed fir bark powder suspension and each metal solution were adjusted using NaOH (0.1 M) or HCl (0.1 M) solutions. Sodium hypochlorite was used to chemically modify the fir bark. Sodium salts of standard ethylenediaminetetraacetic acid (EDTA) solution were used to determine the concentrations of Cu(II), Cd(II), and Pb(II). Heavy metal ion (HMI) solutions for adsorption were made by dissolving CuSO₄·5H₂O, Cd(NO₃)₂·4H₂O, and Pb(NO₃)₂ in deionized water from a Millipore-Q™ water system. Fir bark was air-dried and ground,

and the 250- to 830- μm -sized powders were collected and stored in desiccators operating at room temperature.

Modification of Fir Bark

The sodium hypochlorite solution was used for the modification process. At first, each oxidizing agent was prepared as about 8% solutions. An accurately weighed ($\pm 0.001\text{g}$) 6 g sample of oven-dried fire bark was washed several times to remove any water-soluble particles, and then the material was oven-dried again at 65 °C. The modification of fir bark with sodium hypochlorite was performed in three-necked round-bottom flasks immersed in a warm bath. Different volumes of sodium hypochlorite solution were added to 100 mL of water containing fir bark powder to make sure that the ratio of hypochlorite dosage to fir bark powder dosage ranged from 0.6% to 11%. Then the fir bark was exposed with oxidizing agent at 200 rpm. The mixture was filtered. The fir bark powder after modification was washed and vacuum-dried at 40 °C. The effect of oxidation pH values, oxidation time, and the dosage of sodium hypochlorite on the absorption capacities of heavy metal ions by the oxidized fir bark powder was evaluated. Suitable oxidation conditions were determined. Chemical structure and composition of fir bark before and after oxidation was analyzed according to previous works (Argun *et al.* 2007; Argun and Dursun 2008; Su *et al.* 2014).

Characterization of Fir Bark

Weight percent loss (wpl)

The weight percent loss (wpl) was calculated according to Eq. 1,

$$\text{wpl, \%} = \frac{w_1 - w_2}{w_1} \times 100 \quad (1)$$

where w_1 is the weight of unmodified fir bark, and w_2 is the weight of modified fir bark.

Level of free carboxylic acid groups (n_{COOH})

The level of free carboxylic acid groups (n_{COOH}) in fir bark before and after the oxidation was determined by acid-base back titration of the carboxylic acid functions (Yu *et al.* 2013). The number of free carboxylic functions per gram of adsorbent material was calculated using Eq. 2 as follows,

$$n_{\text{COOH}}, \text{mmol/g} = \frac{C_{\text{NaOH}}V_{\text{NaOH}} - C_{\text{HCl}}V_{\text{HCl}}}{m} \times 100 \quad (2)$$

where C_{NaOH} (mmol/L) and C_{HCl} (mmol/L) are the concentrations of the NaOH and HCl solution, V_{HCl} (L) is the volume of HCl spent in the titration of excessive non-reacted NaOH, and m (g) is the weight of adsorbent material.

BET surface area

The experiments to obtain the surface area of adsorbents before and after oxidation were carried out using a NOVA[®] Surface Area Analyzer model 1000 (Quantachrome Instruments).

FTIR analysis

The samples were prepared by mixing 1mg of each material with 100 mg of spectroscopy grade KBr. The FTIR spectra were recorded using Nicolet Impact 410

equipment with the detector at a resolution of 4 cm^{-1} from 500 to 3500 cm^{-1} and 32 scans per sample.

Scanning electron microscopy (SEM)

The morphology of the adsorbents before and after oxidation was examined with scanning electron microscopy, using a filament voltage of 20 keV. Dry powder samples were dispersed on a graphite ribbon fixed on an aluminum sample holder. The powders were sputter-coated with gold in a modular high-vacuum coating system Q150R ES (Quorum Technologies).

Adsorption Experiments

Adsorption studies were conducted using a batch adsorption method within Erlenmeyer flasks at various pH values (2, 3, 4, 5, 6, 7, and 8), contact times (1 to 30 min), and initial HMI concentrations (0.5 to 10 mM) to obtain the equilibrium and kinetic parameters. A known amount of oxidized fir bark powder was added to each flask with 100 mL of the relevant Cu(II), Cd(II), or Pb(II) solution at $30\text{ }^{\circ}\text{C}$ and shaken (180 rpm) in a thermostatic shaker for specified times. After adsorption, solutions were filtered using a sand core crucible, and the residual HMI concentration was determined by direct titration with EDTA at pH 4.6 using xylenol orange as an indicator. Sodium acetate buffer solution was used to adjust the pH in the titrations. During the titration, 25 mL portions of ion solutions were pipetted into a clean Erlenmeyer flask, and 10 mL buffer and two drops of indicator were added. The burette was filled with EDTA solution, and the titration was carried out. The initial color was red, and the endpoint was indicated by a change to blue. The residual HMI concentration was calculated using Eq. 3. All batch isotherm experiments were replicated twice, titration was recorded in triplicate, and the average values were reported. The deviation of each value was less than 2%. The amount of adsorbed metal ions was calculated using the following equation (Yin *et al.* 2010),

$$C'_e = 40 \times C_{EDTA} V_{EDTA} \quad (3)$$

$$C_e = C'_e M \quad (4)$$

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (5)$$

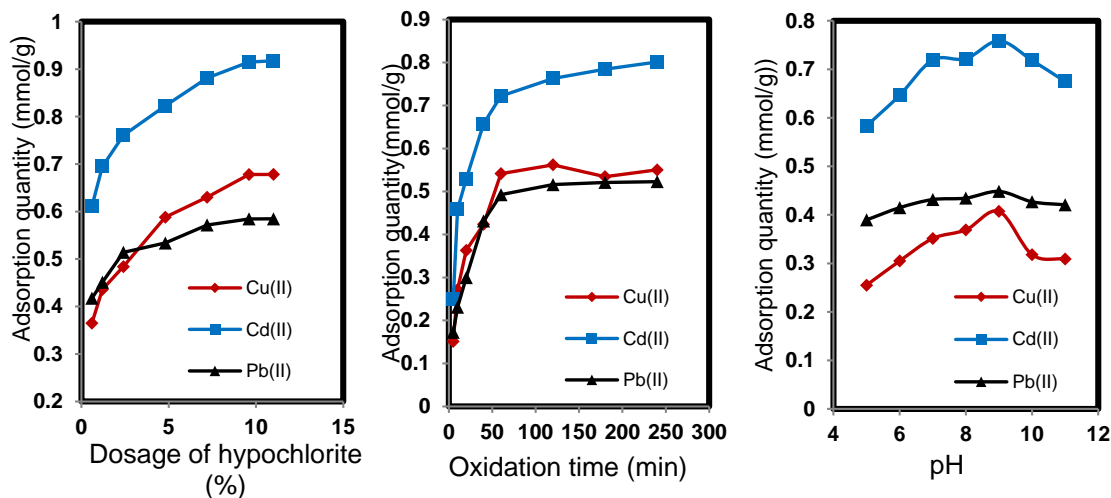
where C_{EDTA} (mmol/L) is the concentration of EDTA solution; V_{EDTA} (L) is the titrant's volume; C'_e (mmol/L) is the equilibrium molar concentration of metal ions. M is the relative atomic mass of Cu(II), Cd(II), or Pb(II); Q_e (mg/g) is the equilibrium adsorbance; C_0 and C_e (mg/L) are the initial and equilibrium concentrations of Cu(II), Cd(II), or Pb(II) in the aqueous solution, respectively; V (L) is the aqueous volume; and m (g) is the mass of adsorbent.

RESULTS AND DISCUSSION

Oxidized Modification of Fir Bark vs. Adsorption Capacity for Metals

The effects of the oxidation conditions on the absorption quantity of HMI on oxidized fir bark are shown in Figs. 1, 2, and 3. The effect of hypochlorite dosage on the absorption capacity of oxidized fir bark powder is shown in Fig. 1. The uptake of metal

ions increased when the dosage of sodium hypochlorite increased. Sodium hypochlorite oxidization produced more carboxyl groups and carbonyl groups on the fir bark, increasing the probability of contact between metal ions and active sites such that more heavy metal ions could be quickly adsorbed. The number of free carboxylic group per gram of fir bark was increased from 4.07 mmol/g to 5.31 mmol/g after modification. However, an overly strong dose of the oxidant could cause damage to both the structure and adsorption capacity of the fir bark powder. Aldehyde groups produced during the modification progress may enhance the cellulose degradation rate of fir bark powder (Sangseethong *et al.* 2010). Heavy oxidation could reduce the adsorption capacity of fir bark powder because part of the cellulose could be dissolved into the reaction solutions *via* severe degradation and separated out by later centrifugation (Ma *et al.* 2014). The optimum dosage of sodium hypochlorite for the oxidization of fir bark powder in adsorbing metal ions was 9.6%. Figure 2 shows that the best reaction time for the NaClO modification of fir bark was 120 min and that the major functional group produced in hypochlorite oxidation, depending on the pH of the oxidation medium, was either carboxylic acid or some other carbonyl species, which increased with the reaction time (Zhao and Xia 2003). The oxidation process occurs rapidly and can be accomplished within 120 min; only a slight improvement in the oxidation effect can be obtained with prolonged reaction times (Hullinger and Whistler 1951). The effect of pH on the oxidation of the adsorbent is shown in Fig. 3. The adsorption capacity of oxidized fir bark powder reached a maximum at pH 9. It was found that the pH of the system decreased as the reaction progressed. The pH value had a significant influence on the production of functional groups during the modification progress (Isbell and Frush 1987). The best sodium hypochlorite oxidation results were achieved under mildly alkaline conditions (pH 8 and 9) (Sangseethong *et al.* 2013). Research on the oxidation conditions showed that the highest uptake of heavy metal ions occurred when fir bark was modified using 9.6% sodium hypochlorite at pH 9 for 120 min.



Absorption experiments were conducted at 30 °C, 60 min, pH 5, 180 rpm, and initial concentration 8 mmol/L.

Fig. 1. Effect of NaClO dosage (based on fir bark powder) on the absorbed quantity of HMI by oxidized fir bark powder (oxidation for 120 min at pH 9)

Fig. 2. Effect of oxidation time on the absorbed quantity of HMI by oxidized fir bark powder. (oxidation at pH 9 with 9% NaClO)

Fig. 3. Effect of pH on the absorbed quantity of HMI by oxidized fir bark powder. (oxidation for 120 min with 9% NaClO)

Characterization of Adsorbent

Results of chemical and physical analyses of this material before and after oxidation were studied. Several changes occurred in the structure of fir bark after modification. The weight loss was found to be 13.27% when the dosage of oxidant was 9.6%. The number of free carboxylic group per gram of fir bark increased from 4.07 mmol/g to 5.31 mmol/g under the same condition. The proportions of lignin increased from 43.57% to 48.34%, and cellulose, hemicellulose decreased from 23.61%, 19.92% to 20.12% and 17.73%. These changes were mainly because the solubility of the reaction products of cellulose and hemicellulose were greater than those from lignin. What's more, chemical structures of cellulose and hemicellulose have more affinity to react and dissolve in the oxidants.

Figure 4 presents the FTIR spectra of raw fir bark and oxidized fir bark. The band at 3400 cm^{-1} corresponds to O-H stretching of polymeric compounds, especially polysaccharides (cellulose). The 2931 cm^{-1} absorbance can be attributed to the symmetric vibration of CH_2 , and 1602 cm^{-1} is stretching vibration of COO and C=O . The 1270 cm^{-1} band is from the vibration of a carboxylic acid group.

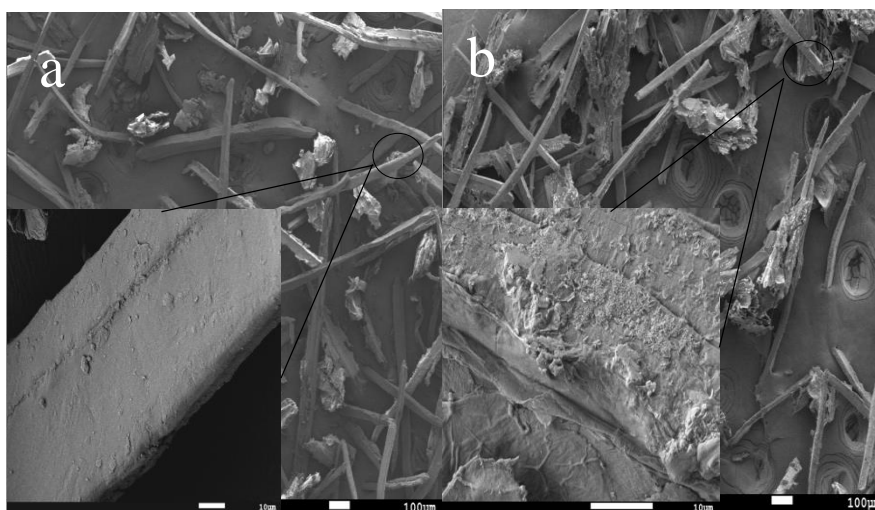


Fig. 4. SEM micrographs of fir bark(a) and modified fir bark (b)

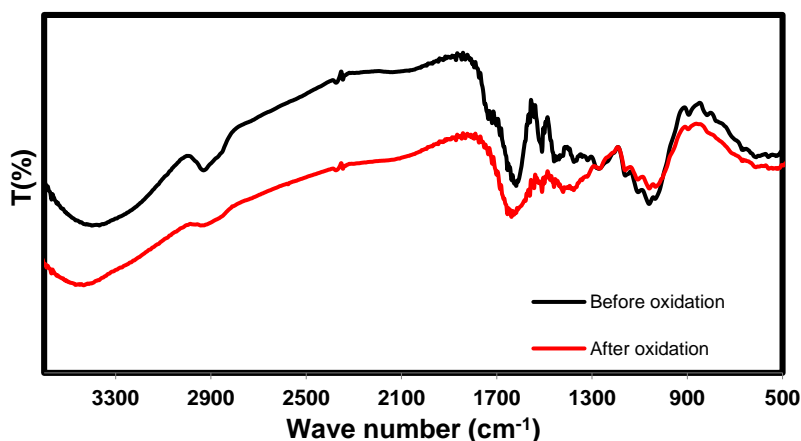


Fig. 5. Fundamental FTIR spectra of raw fir bark and oxidation of fir bark

It should be noticed that the higher percentages of transmittance mean the lower amount of functional groups. So, it could be concluded from Fig. 5 that COO groups or other C=O groups increased with sodium hypochlorite modification.

The SEM images (Fig. 4) reveal that the surface of fir bark without oxidation was smooth. The surface of modified fir bark was porous and rough. The BET surface area of adsorbent before and after modification was $1.822 \text{ m}^2\text{g}^{-1}$ and $2.761 \text{ m}^2\text{g}^{-1}$, respectively. The surface area of fir bark was lower than other commercial adsorbents such as active carbon, which indicates that the adsorption of heavy metal ions by fir bark was due to the chelation between function groups on adsorbents and the heavy metal ions.

Effect of Adsorption Conditions on Adsorption Capacities of Oxidized Fir Bark Powder of HMI

Effect of aqueous solution pH on adsorption capacity of oxidized fir bark powder of HMI

The pH of the solution is an important factor in the adsorption of heavy metal ions (Mohsen and Aboulghazi 2013). Batch adsorption experiments were carried out using aqueous HMI solutions to evaluate the effects of pH on the adsorption capacity of oxidized fir bark powder. The pH value was adjusted by 0.1 M HCl or NaOH. The influence of pH on the adsorption of Cu(II), Cd(II), and Pb(II) is shown in Fig. 6.

Figure 6 clearly indicates that the pH of the HMI solution has a significant influence on the adsorption capacities of the oxidized fir bark powder. The best pH range for metal adsorption was 4 to 5. At higher pH values, the formation of metal hydroxides, the surface structure of adsorbent, and the interaction between adsorbent and metal ions influenced the adsorption behavior of the adsorbent (Nguyen *et al.* 2013). The formation of soluble hydroxylated metal ion complexes at higher pH values (above 5.5) with higher volumes combined with the active sites and decreased the metal ion adsorption capacities (Garcia *et al.* 2014). However, when the pH was lower than 4, high concentrations of H^+ in solution competed with metal ions for the active sites of the adsorbent, reducing the metal ion adsorption efficiency.

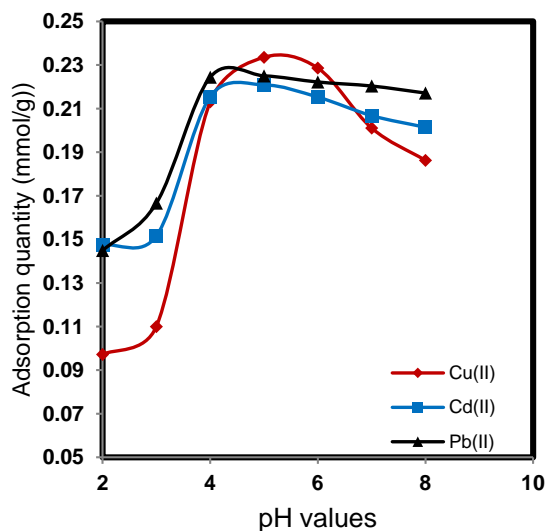


Fig. 6. Effect of pH of HMI aqueous solution on adsorption of oxidized fir bark at $C_0 = 1 \text{ mmol/L}$ and 120 min

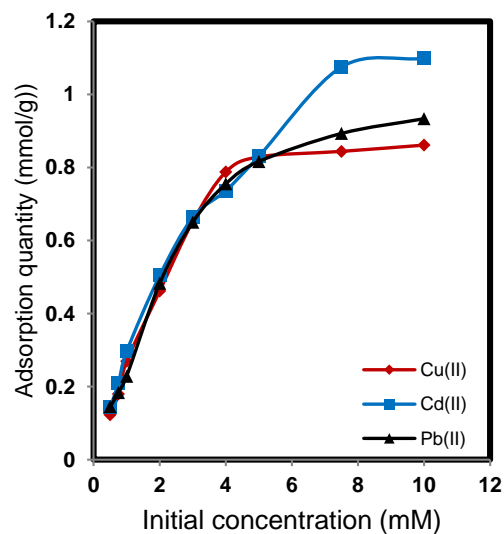


Fig. 7. Effect of initial HMI concentration on adsorption of fir bark at pH 5 and 120 min

Effect of metal ions initial concentration on adsorption quantity

The initial concentration of metal ions is an important factor that greatly affects the effective adsorption of metal ions (Koby *et al.* 2005). The adsorption process simultaneously includes liquid-phase diffusion and solid-phase adsorption processes. With increasing the initial metal ion concentration, the probability of contact between metal ions and active sites is improved and a greater adsorption capacity is achieved. The effect of the initial metal ion concentration on the batch adsorption of oxidized fir bark powder is shown in Fig. 7. When further increasing the initial concentration of metal ions, the rate of increase in the adsorption capacity slowed. As the metal ion concentration was increased, the active sites became saturated and the exchange sites were filled (Jia *et al.* 2002).

The adsorption behavior in a solid-liquid system is complex and affected by many factors such as the interaction of ions in the solution, the properties of the adsorbent, contact time, and others. Isotherm models can be used to explain the phenomena occurring during the adsorption process. The equilibrium between metal ions adsorbed on the active sites of the adsorbent and those retained in the aqueous phase is usually presented by adsorption isotherms (Dastgheib and Rockstraw 2002). This equilibrium is most frequently described using either the Langmuir or Freundlich isothermal adsorption models (Tan *et al.* 2001).

The Langmuir isotherm is derived to model the monolayer coverage of the adsorption surface (Cay *et al.* 2004), and it can be expressed by the following equation,

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}} \quad (6)$$

where C_e (mg/L) is the equilibrium concentration of metal ions in solution, K_L (L/mg) is the Langmuir constant, and Q_{max} (mg/g) is the quantity of metal ions needed to form a monolayer on the surface of adsorbent. The plot of C_e/Q_e vs. C_e gives a linear relation. K_L and Q_{max} values can be calculated and are given in Table 1.

The Freundlich isotherm models multilayer adsorption and can be expressed by the following equation,

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \quad (7)$$

where K_F ($[\text{mg/g}][\text{L/mg}]^{1/n}$) is the Freundlich constant and $1/n$ is an empirical constant. The plots of $\ln q_e$ vs. $\ln C_e$ give linear relations. The values of K_F and $1/n$ can be calculated and are given in Table 1.

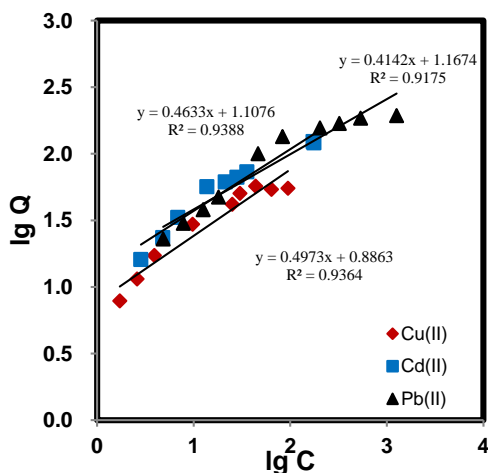


Fig. 8. Freundlich model of HMI on fir bark

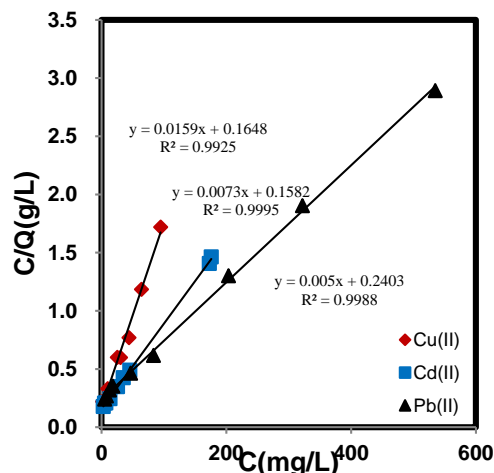


Fig. 9. Langmuir model of HMI on fir bark

Linear regression analysis was applied to each set of adsorption data. The coefficient of determination (R^2) of the isotherm adsorption process of heavy metal ions in aqueous solution is shown in Figs. 8 and 9 and Table 1, showing that the Langmuir model fit the data well. This suggests that the adsorption behavior of heavy metal ions is like that of a monolayer adsorption reaction. The Langmuir parameter Q_{\max} was 0.983, 1.223, and 0.966 mmol/g for Cu(II), Cd(II), and Pb(II), respectively. $1/n$ values were less than 1, indicating that the oxidized fir bark powder exhibited strong adsorption ability on these three heavy metal ions (Yu *et al.* 2013).

Table 1. Isotherm Adsorption Constants for the Adsorption of HMI on Oxidized Fir Bark Powder

Heavy Metal Ions	Freundlich Isotherm Adsorption			Langmuir Isotherm Adsorption		
	K_F	$1/n$	R^2	Q_{\max} (mmol/g)	K_L (L/mg)	R^2
Cu(II)	7.70	0.4973	0.9364	0.983	0.096	0.9925
Cd(II)	12.81	0.4633	0.9388	1.223	0.046	0.9995
Pb(II)	14.70	0.4142	0.9175	0.966	0.021	0.9988

Furthermore, the modified fir bark powder had higher K_L (Su *et al.* 2014), indicating a greater affinity to the metal ions. A larger number of ion exchange sites were introduced to the fir bark powder surface by the oxidizing modification (Vimal *et al.* 2006). Modifying fir bark powder with sodium hypochlorite increased the HMI adsorption capacity significantly. The Q_{\max} of fir bark for heavy metal ions adsorption using the Langmuir model were found to be 0.983, 1.223 and 0.966 mmol/g, respectively. The adsorption capacity of adsorbents was affected by the interaction between the heavy metal ions and the $-\text{COOH}$ group. The presence of ligands strongly controls the adsorption isotherm and the uptake capacity mechanism (Bulut and Tez 2007). Thus the adsorption capacity of adsorbents can be enhanced by a chemical modification of the adsorbent surface by introducing new functional groups (Aparecida and Gurgel 2014). Oxidized fir bark powder could be used as an adsorbent for heavy metal ion removal from water.

Effect of contact time on adsorption capacity and kinetics of adsorption

The adsorption of metal ions by modified fir bark powder was affected by the contact time. The effects of contact time on the adsorption quantity are shown in Fig. 10.

The amounts of adsorbed metal ions increased rapidly during the initial 5 min and reached equilibrium at about 10 min. At the beginning of adsorption, large numbers of active sites were available on the surfaces of the bark powder, providing a great probability of contact between metal ions and active sites such that the heavy metal ions in solution could quickly be adsorbed. As the adsorption process continued, the adsorption of Cu(II) reached equilibrium quickly, whereas the adsorption of Cd(II) and Pb(II) continued after 10 min before stabilizing. More and more metal ions were adsorbed by the active sites on the surface of the bark powder. The active sites became saturated, and the exchange sites became filled. In the later stages of the adsorption process, the repulsive forces between the solute molecules in the bulk phase and the solid surface can be expected to hinder the occupation of the remaining vacant active sites (Astier and Chaleix 2012). The metal ion adsorption process was complicated but fast and could be mainly completed within 30 min.

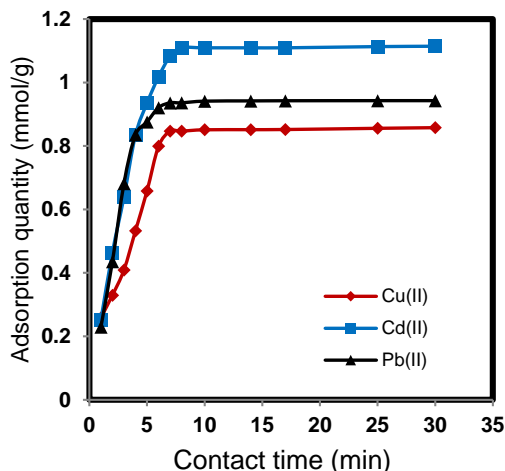


Fig. 10. Effect of contact time on adsorption of HMI on fir bark at pH 5

To gain insight as to how quickly the heavy metal ions can be transferred from the aqueous phase to the solid phase, the kinetics of adsorption were studied. Adsorption kinetics can be described using Lagergren pseudo-first order adsorption kinetics, pseudo-second order adsorption kinetics, or Webber & Morris intraparticle diffusion models.

The Lagergren pseudo first-order adsorption kinetics model can be expressed as,

$$\ln(q_e - q_t) = \ln q_e - \frac{K_f t}{2.303} \quad (8)$$

where q_t (mg/g) is the amount of adsorption at time t (min), q_e is the sorption capacity at equilibrium (mg/g), and K_f (min^{-1}) is the rate constant for a pseudo-first order reaction. The plot of $\ln(q_e - q_t)$ vs. t should yield a straight line, according to this equation.

The pseudo-second order adsorption kinetics model can be expressed as,

$$\frac{t}{q_t} = \frac{1}{K_s q_e^2} + \frac{t}{q_e} \quad (9)$$

where K_s (mg/g·s) is the rate constant for a pseudo-second order reaction. The plot of t/q_t vs. t gives a straight line. The values of K_s and q_e can be calculated and are given in Table 3.

The Webber & Morris intraparticle diffusion model can be expressed as,

$$q_t = K_{id} \sqrt{t} + C \quad (10)$$

where K_{id} ($\text{mg/g} \cdot \text{min}^{0.5}$) is the apparent diffusion rate constant and C is the diffusion constant.

The fits of each model to the experimental data are shown in Figs. 11, 12, and 13. According to the fitting results of the different models, the adsorption of metal ions on oxidized fir bark can be approximated most appropriately by the pseudo-second order adsorption kinetics model. The coefficients of determination were all greater than 0.9. Similar results were reported for the adsorption of ether amine on kaolinites by Magriotis *et al.* (2010). The differences in the adsorbance between heavy metal ions may relate to some relevant metallic properties such as the atomic weight, ionic radii, hydrolysis constant, electronegativity, and electron-shell structure of the metal. The difference in the ionic size is not the only dominant factor in the adsorption process metal ions, and the adsorption

process may be affected by the density of the ion charge and by the orbital energy valence (Heidari *et al.* 2013).

According to the fitting results of Weber and Morris intra-particle diffusion model, the plot can be divided into two consecutive steps: (1) the external diffusion stage depicting macro-pore diffusion; and (2) the gradual adsorption is controlled by micro-pore diffusion. The rate constants K_{id} and C are shown in Table 2. K_{id1} was larger than K_{id2} . This indicates that micro-pore diffusion was the main rate-limiting step in the adsorption process, but not the sole rate-limiting step (Ma *et al.* 2015).

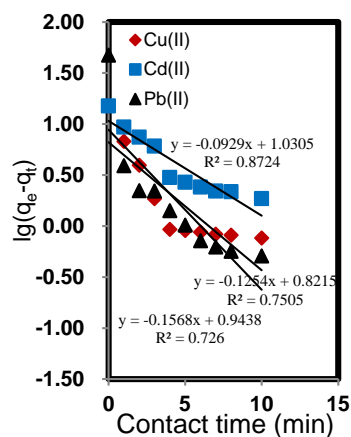


Fig. 11. Lagergren pseudo-first order adsorption kinetics of HMI on fir bark

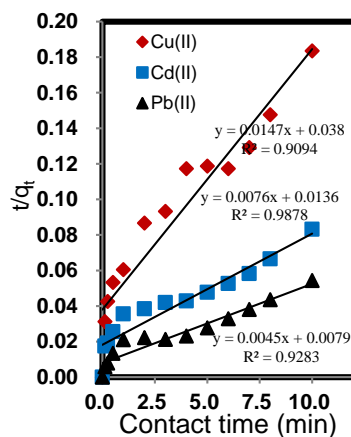


Fig. 12. Pseudo-second order adsorption kinetics of HMI on fir bark

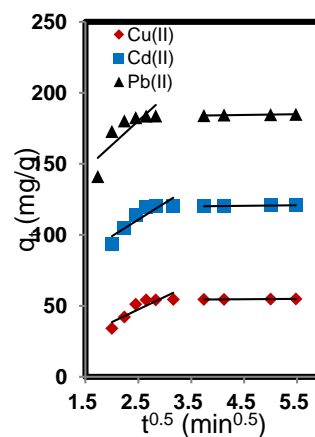


Fig. 13 Weber and Morris intra-particle diffusion of HMI on fir bark

Table 2. Adsorption Kinetic Parameters of HMI on Modified Fir Bark

Metal Ions HMI	Pseudo First-order Adsorption Kinetics			Pseudo Second-order Adsorption Kinetics			Weber and Morris Intra-particle Diffusion		
	$q_{e, cal}$ (mmol/g)	K_f	R^2	$q_{e, cal}$ (mmol/g)	K_s	R^2	K_{id1}	C	K_{id2}
Cu(II)	0.048	0.29	0.7505	0.941	0.0073	0.9094	17.75	3.04	0.24
Cd(II)	0.056	0.21	0.8724	1.175	0.0042	0.9878	23.36	52.31	0.35
Pb(II)	0.014	0.36	0.7260	0.929	0.0034	0.9283	33.95	95.44	0.50

As can be seen in Table 2, the theoretical q_e value for modified fir bark powder, calculated according to the pseudo-second order adsorption kinetics model fitting results, was closer to the experimental q_e values ($q_e = 0.983, 1.223, \text{ and } 0.966$ mmol/g). The lower equilibration time is a significant advantage of the sodium hypochlorite-modified fir bark powder. Modified fir bark powder can remove metal ions more efficiently than unmodified powder. The suitability of the pseudo-second order rate equation in representing the adsorption of Cu(II), Cd(II), and Pb(II) by pristine and modified fir bark powders agrees well with the findings of previous studies of other adsorbents. As seen in Table 3, the adsorption capacity (q_e) of Cu(II), Cd(II), and Pb(II) were higher for modified fir bark powder than that of unoxidized powder. The values of R^2 are closer to unity for the pseudo second-order model. The pseudo second-order model can describe metal ions adsorption by both materials very well and adsorption by fir bark is controlled by a chemical process.

Table 3. Kinetic Parameters for the Adsorption of Heavy Metal Ions on Unmodified Powder and Modified Powder

Heavy Metal Ions	Modified fir bark		Unmodified fir bark (Su <i>et al.</i> 2014)	
	Pseudo Second-order		Pseudo Second-order	
	$q_{e, cal}$ (mmol/g)	R^2	$q_{e, cal}$ (mmol/g)	R^2
Cu(II)	0.941	0.9094	0.110	0.9979
Cd(II)	1.175	0.9878	0.126	0.9969
Pb(II)	0.929	0.9283	0.114	0.9997

CONCLUSION

1. Fir bark modified with sodium hypochlorite was successfully synthesized and characterized by FTIR, SEM, and BET measurements. The higher concentration of COO groups and C=O groups were observed during the modification process in relation to non-modified fir bark.
2. In this study, fir bark modified with sodium hypochlorite was shown to be an efficient adsorbent for the removal of Cu(II), Cd(II), and Pb(II) from aqueous solutions. The adsorbance of metal ions was a function of the contact time, pH, and the initial metal ion concentration. The optimum amount of NaClO was 9.6%, pH was 9, and oxidation time was 120 min.
3. The optimum adsorption conditions were pH 5 for Cu(II), Cd(II), and Pb(II), with 30 min contact time. The maximum adsorption capacities reached were 0.983, 1.223, and 0.966 mmol/g, respectively.
4. The isothermal adsorption of heavy metal ions in aqueous solution can be approximated most appropriately by the Langmuir equation and the pseudo-second order adsorption kinetics model, which indicates that the adsorption of metal ions by fir bark belong a form of monomolecular adsorption and is controlled by a chemical adsorption mechanism.

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