



Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust

M. Rafatullah^{a,*}, O. Sulaiman^a, R. Hashim^a, A. Ahmad^b

^a Division of Bio-resource, Paper and Coatings Technology, School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia

^b Division of Environmental Technology, School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia

ARTICLE INFO

Article history:

Received 30 December 2008

Received in revised form 13 May 2009

Accepted 15 May 2009

Available online 21 May 2009

Keywords:

Toxic metal

Adsorption

Isotherm

Kinetic

Intraparticle diffusion

ABSTRACT

The present study proposed the use of meranti sawdust in the removal of Cu(II), Cr(III), Ni(II) and Pb(II) ions from synthetic aqueous solutions. Batch adsorption studies showed that meranti sawdust was able to adsorb Cu(II), Cr(III), Ni(II) and Pb(II) ions from aqueous solutions in the concentration range 1–200 mg/L. The adsorption was favoured with maximum adsorption at pH 6, whereas the adsorption starts at pH 1 for all metal ions. The effects of contact time, initial concentration of metal ions, adsorbent dosage and temperature have been reported. The applicability of Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm was tried for the system to completely understand the adsorption isotherm processes. The adsorption kinetics tested with pseudo-first-order and pseudo-second-order models yielded high R^2 values from 0.850 to 0.932 and from 0.991 to 0.999, respectively. The meranti sawdust was found to be cost effective and has good efficiency to remove these toxic metal ions from aqueous solution.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The presence of toxic heavy metals in industrial effluents has become a matter of environmental concern. Mining, tannery, jewelry, chemical, metallurgical, electrical and electronics large scale industries in industrial nations, and also arts and crafts in developing countries [1] are the main source for metal containing waste pollution. The effect of waste as sludge deposition and wastewater on flora, on marine life and on public health has invited numerous research activities. Increasingly strict discharge limits on heavy metals and their widespread uses, threatening presence at hazardous waste sites have accelerated the search for advanced and economically attractive treatment technologies for their removal. Heavy metals removal from aqueous solution has been commonly carried out by several process, chemical precipitation, solvent extraction, ion exchange, reverse osmosis or adsorption [2,3]. Chemical precipitation, in particular, is the most prevalent method but not suitable for removing low concentration of heavy metal ions. Adsorption processes are promising in this regard as opposed to more conventional chemical precipitation in that, it achieve higher level removal over a wider range of solution conditions. The adsorption, with the selection of suitable

adsorbents, can be an effective technique for the removal of heavy metals from wastewater [4]. Some of the suggested adsorbents are moss peat [5], fly ash [6,7], activated carbon [8–10], zeolite [11], chitosan [12], lignin [13], clay [14], biomass [15,16], xanthate [17] and cactus material [18]. All the adsorbents are not economically suitable enough for wastewater treatment. Though they generally have high metal adsorption capacity but are expensive and difficult to be separated from the wastewater after use. Therefore, a growing research interest has been developed in search of low cost alternatives to these adsorbents. Sawdust has received particular attention as an economical adsorbent for removing heavy metals from wastewater due to its abundance, easily available and low cost. Further it will be a step ahead towards exploring the possibility on the use of waste biomass for industrial wastewater pollution management. The studies on the use of meranti sawdust as adsorbent are limited. It is a common tree present in all tropical countries such as Malaysia and Indonesia. Meranti tree is widely used for furniture making and the waste sawdust produced is generally used for heating in the boiler.

The aim of this paper is to assess the ability of meranti sawdust to adsorb Cu(II), Cr(III), Ni(II) and Pb(II) ions from aqueous solutions. The effect of the solution pH, temperature, contact time and adsorbent dosage on the removal of Cu(II), Cr(III), Ni(II) and Pb(II) ions was studied. The adsorption isotherm and probable mechanism are explained and also tried to find out the kinetics and order of reaction at the surface of the adsorbent.

* Corresponding author. Tel.: +60 4 653 2241; fax: +60 4 657 3678.

E-mail address: mohd.rafatullah@yahoo.co.in (M. Rafatullah).

2. Materials and methods

2.1. Adsorbent

Meranti sawdust was collected from Kedah, Malaysia. The sawdust was washed with distilled water and then dried in a dryer at 70 °C until all the moisture had evaporated. The material was ground to a fine powder in a still mill. The resulting material was sieved in the size range of 100–150 µm particle size. To remove the colour and water soluble substances, the ground powder was washed with 0.5 M HCl at room temperature for 4 h. After that, the sawdust was filtered out, several times washed with distilled water until no chloride was released and dried in a dryer at 70 °C. The material was placed in an airtight container for further use.

2.2. Adsorbate solutions

The stock solution (1000 mg/L) of metal ions was prepared by dissolving their corresponding nitrate salts {Cu(NO₃)₂·2.5H₂O, CrN₃O₉·9H₂O, N₂NiO₆·6H₂O and Pb(NO₃)₂} in distilled water. The solution was further diluted to the required concentrations before use. All the chemicals used were of analytical reagent grade and were obtained from Sigma–Aldrich and Fluka (Germany).

2.3. Scanning electron microscopy, Fourier Transform Infrared study and surface area analysis

Surface morphology was studied with Leo Supra 50 VP Field Emission Scanning Electron Microscope (Carl-Zeiss SMT, Oberkochen, Germany). The scanning electron micrograph (SEM) of the natural meranti sawdust (NMS) and metal ions loaded meranti sawdust at bar length equivalent to 20 µm, working voltage 15 kV with 250× magnification are shown in Fig. 1. For the main functional groups that might be involved in metal adsorption, a Fourier Transform Infrared (Nicolet, AVATAR FTIR-360) analysis was done on the natural meranti sawdust and metals loaded meranti sawdust to determine the surface functional groups, and the spectra were recorded from 4000 to 400 cm⁻¹. The surface area of meranti sawdust was determined using a Micromeritics ASAP 2010 gas adsorption surface analyzer.

2.4. Adsorption experiments

The studies of the kinetics of adsorption were carried out at 30 °C. 100 ml of the solution containing the desired quantity of the metal ion was treated with 0.5 g of sawdust in stoppered conical flasks for the different times using a temperature-controlled shaker. The solution–sawdust mixtures were stirred at 100 rpm and at the end of predetermined time interval the reaction mixtures were filtered out and analyzed for its metal ion concentrations using Atomic Absorption Spectrometer, AAS (Analyst 100 PerkinElmer). The batch equilibrium studies for the determination of the effect of optimum metal ion concentration were conducted for the equilibrium time mixing at a constant speed of 100 rpm to obtain value of maximum adsorption.

The effect of pH of the initial solution on the equilibrium uptake of Cu(II), Cr(III), Ni(II) and Pb(II) ions was analyzed over a pH ranges from 1 to 8. The effect of pH of the solution was adjusted by either 0.1 M NaOH or 0.1 M HCl solutions. The adsorption studies were also conducted in batch experiments as function of adsorbent dosage (2, 4, 6, 8 and 10 g), contact time (1, 5, 10, 20, 30, 60, 120, 150 and 180 min) and metal ions concentration (1, 5, 10, 25, 50, 100 and 200 mg/L) for maximum adsorption. The percentage of metal

adsorption by the adsorbent was computed using the equation:

$$\% \text{ adsorption} = \left\{ \frac{C_i - C_e}{C_i} \right\} 100 \quad (1)$$

where C_i and C_e are the initial and equilibrium concentration of metal ions (mg/L) in the solution. Adsorption capacity was calculated by using the mass balance equation for the adsorbent [19]:

$$q = \frac{(C_i - C_e)V}{W} \quad (2)$$

where q is the adsorption capacity (mg/g), C_i is the initial concentration of metal in solution (mg/L), C_e is the equilibrium concentration of metal in solution (mg/L), V is the volume of metal ion solution (L) and W is the weight of the adsorbent (g).

3. Results and discussion

3.1. Characterization of meranti sawdust

The meranti sawdust mainly consists of lignin, cellulose, hemicellulose and many hydroxyl groups such as tannins. All those components are active ion exchange compounds. Lignin, the third major component of the wood cell wall is built up from the phenylpropane nucleus; an aromatic ring with a three carbon side chain is promptly available to interact with cationic metal ions [20].

The Brunauer–Emmett–Teller (BET) surface area and average pore diameter were determined. The value of BET surface area was under the detection level of the apparatus is 0.62 m² g⁻¹. Pore sizes are classified in accordance with the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC), that is, micropores (diameter (d) < 20 Å), mesopores (20 Å < d < 500 Å), and macropores (d > 500 Å). The average pore diameter determined by Barrett–Joiner–Halenda (BJH) method was 253.4 Å, suggesting that meranti sawdust consists of mesopores.

Fig. 1 shows the surface morphology of the natural meranti sawdust and metal loaded meranti sawdust. Meranti sawdust is a heterogeneous material consisting largely of small spheres, irregular and porous cell wall of plant cells. The surface seems to be rough and protrusions. Pores can be seen however, not extending into the matrix.

FTIR spectra for meranti sawdust in natural form and loaded with metal ions are shown in Fig. 2. In case of NMS, there is a strong peak at 3445 cm⁻¹ representing the –OH stretching of phenol group of cellulose and lignin, and the peak at 2927 cm⁻¹ indicates the presence of –CH₂ stretching of aliphatic compound. The appearance of peaks at 1735 and 1633 cm⁻¹ indicate the presence of C=O stretching of aldehyde group and C=C stretching of phenol group, respectively where as the peaks between 1508 and 1372 cm⁻¹ in the spectrum of NMS may be assigned to C=C of aromatic ring. The peaks at 1243 and 1041 cm⁻¹ might be due to C–O stretching of phenolic group and ether group of cellulose, respectively [21,22]. The FTIR spectrum of metal loaded adsorbent, shown in Fig. 2, indicates that the peaks due to above functional groups are slightly affected in their position and intensity. It indicates that the adsorption of metal ions on the surface of sawdust is either through complexation or through physical which might be through weak electrostatic interaction and Van der Waals forces. However no chemical bonding takes place in this process. Thus the FTIR of the surface moieties remain unchanged. The FTIR spectra of meranti sawdust loaded with Cu(II), Cr(III), Ni(II) and Pb(II) show elongation of these bands after metal adsorption indicating the role of these group in adsorption which might be due to the close proximity of such transition metals in the periodic table.

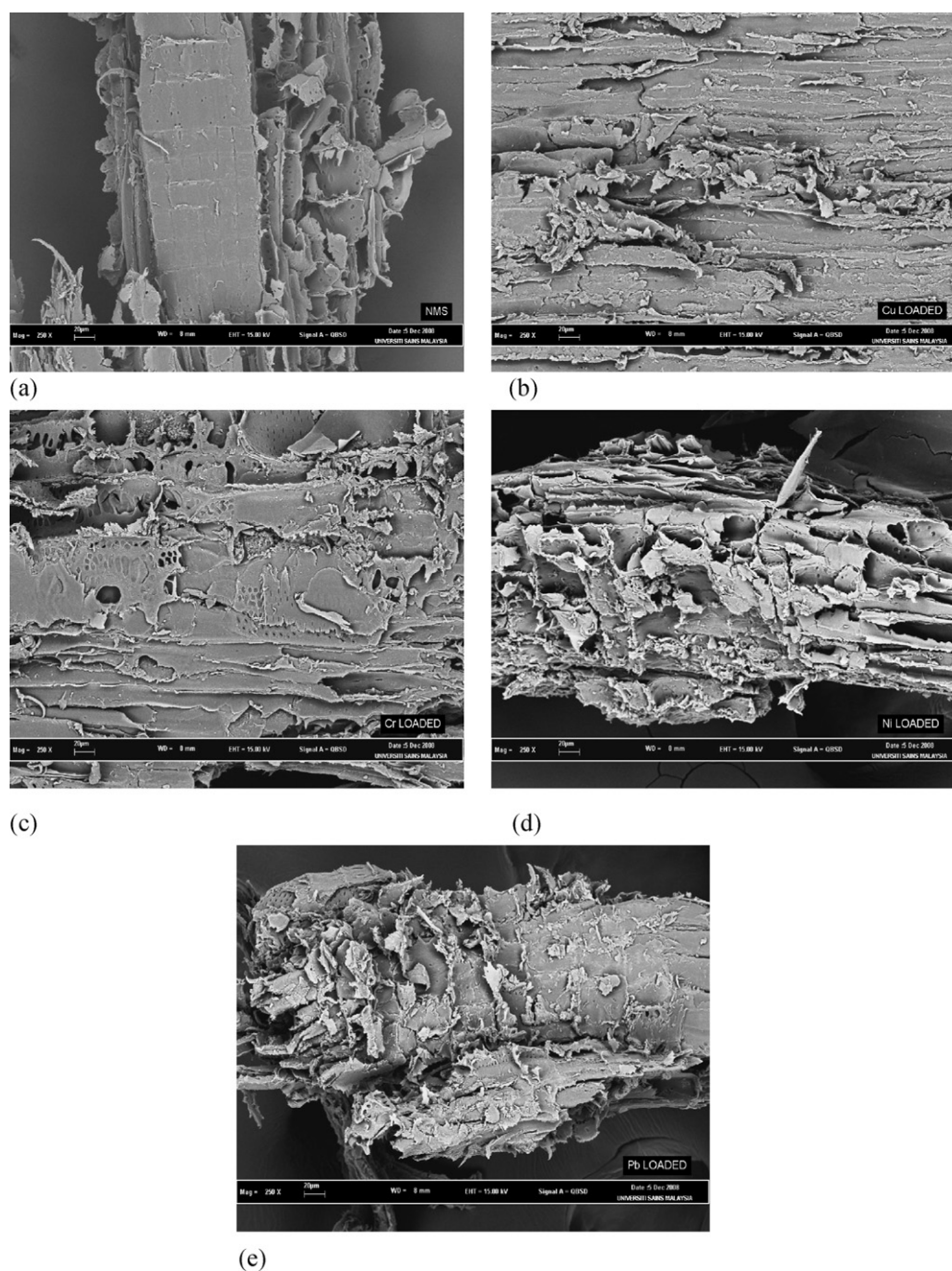


Fig. 1. SEM micrograph of meranti sawdust (magnification, 250): (a) natural meranti sawdust, (b) Cu(II) loaded, (c) Cr(III) loaded, (d) Ni(II) loaded and (e) Pb(II) loaded.

3.2. Effect of contact time

Preliminary kinetic experiments were conducted to assess the time taken for the equilibrium to be obtained and the results are presented in Fig. 3 for Cu(II), Cr(III), Ni(II) and Pb(II) metal ions. It is readily apparent from the figure that significant removal of different metal ions occurred in 20 min and no appreciable changes in terms of removal were noticed after 120 min. The adsorption plot reveals that the rate of percent adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions is initially high which is probably due to the availability of larger surface area of the sawdust for the adsorption of these ions. As the surface adsorption sites become exhausted, the rate of uptake is controlled by the rate of transport from the exterior to the interior sites of the adsorbent particles. In all subsequent experiments the equilibrium time was maintained at 120 min, which was considered sufficient for the removal of different metal ions by meranti

sawdust. A similar result has been found by Unlu and Ersoz [23] in adsorption characteristic of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions.

3.3. Effect of pH

pH of the solution is the most important parameter affecting metal ion adsorption. This is because hydrogen ion competing with the positively charged metal ions on the active sites of the adsorbent. The effect of pH on the adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions on meranti sawdust has been studied by varying it in the ranges of 1–8 as shown in Fig. 4. As shown in Fig. 4, the uptake of Cu(II), Cr(III), Ni(II) and Pb(II) ions depends on pH, it increases with the increase in pH reaching the maximum adsorption at pH 6. On higher pH values a slight decrease of adsorption for Cu(II), Cr(III), Ni(II) and Pb(II) ions was observed. Based on the

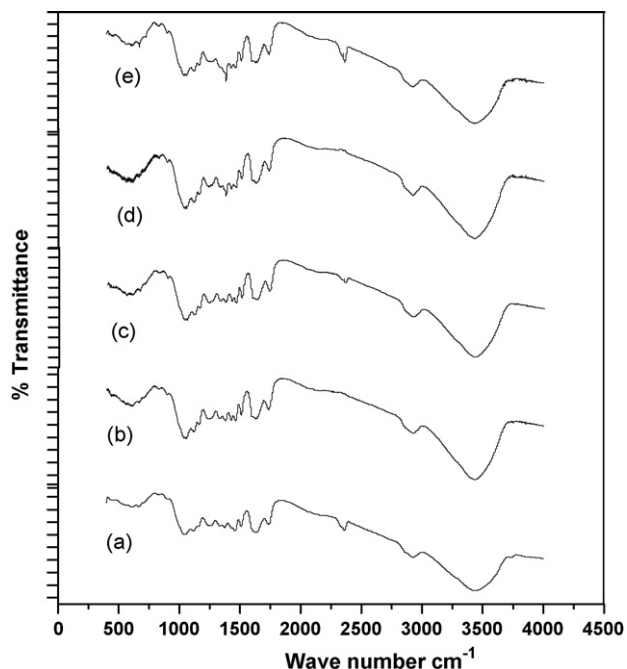


Fig. 2. FTIR spectra of meranti sawdust: (a) natural meranti sawdust, (b) Cu(II) loaded, (c) Cr(III) loaded, (d) Ni(II) loaded and (e) Pb(II) loaded.

behavior of heavy metal adsorption on sawdust, it is speculated that the ion exchange and hydrogen bonding may be the principal mechanism for the removal of heavy metals [24]. There are a number of parameters to support this speculation, including the components and complexing properties of the sawdust, the properties of heavy metals and the adsorption behavior, such as the effect of pH of the aqueous media leading to change in speciation. At pH value lower than 3, the adsorption capacities were found to be low due to the competitive adsorption of HO_3^+ ions and metal ions for the same active adsorption site. As the pH increased, the adsorption surface become less positive and therefore electrostatic attraction between the metal ions and sawdust surface is likely to be increased. The

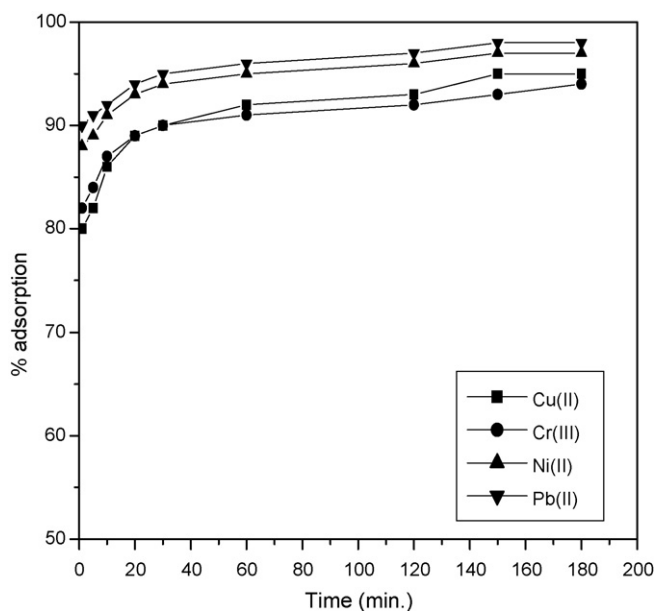


Fig. 3. Effect of contact time on the adsorption of metal ions (initial concentration = 100 mg/L, agitation speed = 100 rpm, temperature = 30 °C and adsorbent dosage = 5.0 g/L).

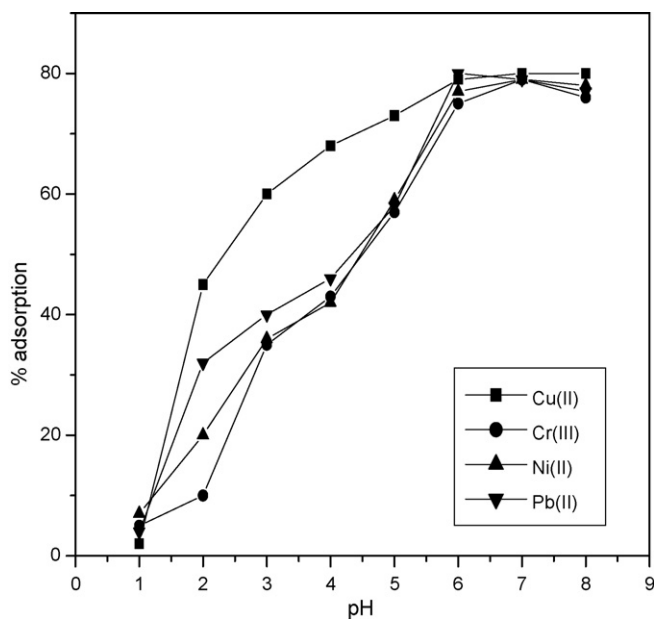
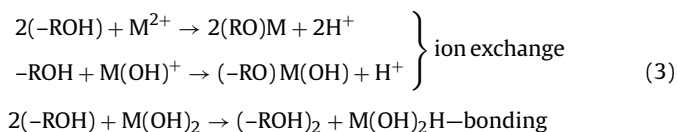


Fig. 4. Effect of pH on the adsorption of metal ions (initial concentration = 100 mg/L, agitation speed = 100 rpm, temperature = 30 °C, contact time = 120 min and adsorbent dosage = 5.0 g/L).

maximum sorption efficiency at pH 6 may be due to the interaction of M^+ , $\text{M}(\text{OH})^+$, $\text{M}(\text{OH})_2$ with surface functional groups present in the sawdust. A slightly decrease in adsorption at high pH is due to the formation of soluble hydroxyl complexes. These species are adsorbed at the surface of sawdust by ion exchange mechanism with the functional groups present in sawdust or by hydrogen bonding as shown below [25]:



where M represents the metal ions and R represents the matrix of sawdust, respectively.

A similar theory was proposed by several earlier workers for metal sorption on different adsorbents. At higher pH values than 6, metal precipitation appeared and the adsorbent was deteriorated with the accumulation of metal ions [26–29]. Therefore, pH 6 was selected to be the optimum pH for further studies.

3.4. Effect of initial metal concentration

In batch adsorption processes, the initial metal ion concentration of metal ions in the solution plays a key role as a driving force to overcome the mass transfer resistance between the solution and solid phases. Therefore, the amount of metal ions adsorbed was expected to be higher with a higher initial concentration of metal ions. The effect of initial concentration of Cu(II), Cr(III), Ni(II) and Pb(II) ions at pH 6 while, keeping the dosage of the sawdust (5 g/L) constant and temperature at 30 °C on the adsorption process is shown in Fig. 5. The percent adsorption increased with the increase of initial metal ion concentration as shown in Fig. 5. The amount of all metal ions adsorbed at equilibrium appeared to follow the same increasing trend with the initial metal ion concentration. As a result of the above observations, it was indicated that the adsorption process of different heavy metal ions on meranti sawdust was to be dependent on concentration of adsorbate up to some extent.

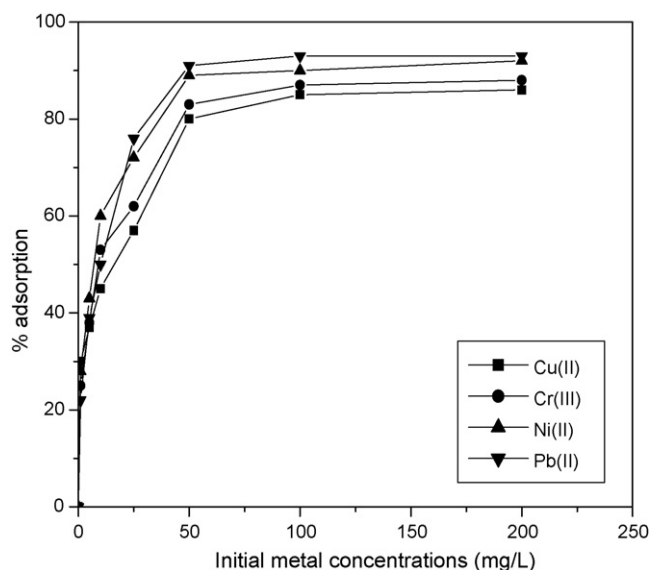


Fig. 5. Effect of initial metal concentration on the adsorption (contact time = 120 min, agitation speed = 100 rpm, temperature = 30 °C, pH 6.00 and adsorbent dosage = 5.0 g/L).

3.5. Effect of adsorbent dosage

The adsorption studies of Cu(II), Cr(III), Ni(II) and Pb(II) ions on meranti sawdust were done at 30 °C temperature by varying the quantity of adsorbent from 2 to 10 g while keeping the volume of the metal solutions constant at pH 6. The influence of adsorbent dosage in percent adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions is shown in Fig. 6. The adsorption of Cu(II) by meranti sawdust increased from 65 to 89%, Cr(III) increased from 68 to 94%, Ni(II) increased from 73 to 97% and Pb(II) increased from 76 to 96%, respectively, by increasing the sawdust dosage from 2 to 10 g/L under equilibrium conditions. The results showed that the adsorption increased with the increase in the dose of sawdust. The increase in the adsorption percentage is due to the increase in active sites on the adsorbent and thus making easier penetration of the metal ions to the sorption sites.

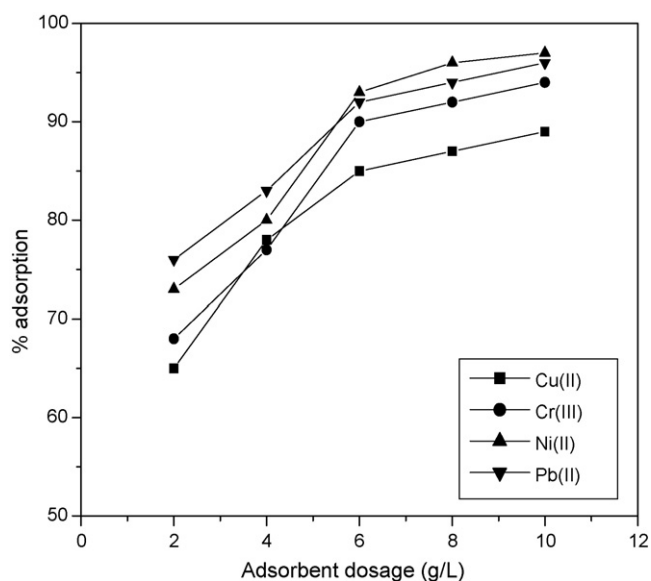


Fig. 6. Effect of adsorbent dosage on the adsorption of metal ions (initial concentration = 100 mg/L, agitation speed = 100 rpm, temperature = 30 °C, contact time = 120 min and pH 6.00).

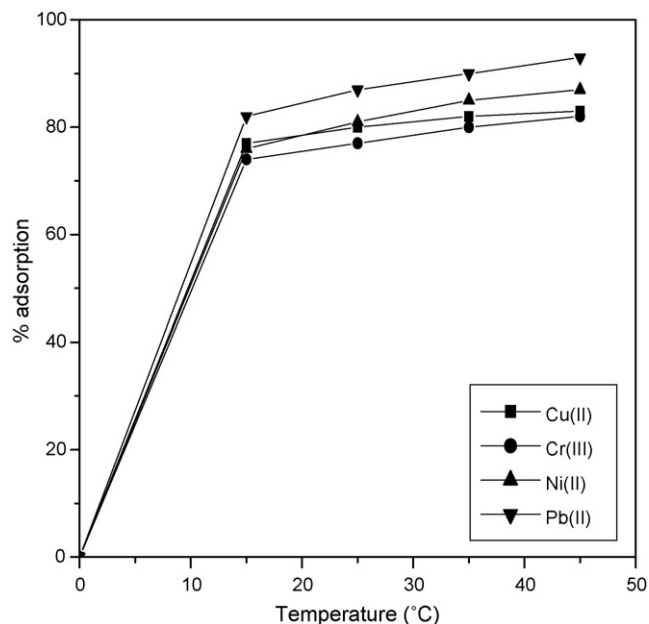


Fig. 7. Effects of temperature on the adsorption of metal ions (initial concentration = 100 mg/L, contact time = 120 min, agitation speed = 100 rpm, pH 6.00 and adsorbent dosage = 5.0 g/L).

3.6. Effects of temperature

Temperature is a highly significant parameter in the adsorption processes. For adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions onto meranti sawdust, adsorption experiments were run to study the effect of temperature variation at 15, 25, 35 and 45 °C at optimum pH value of 6 and adsorbent dose level of 5 g/L. The equilibrium contact time for adsorption was maintained at 120 min. The results were evident from Fig. 7. It was observed that the percentage of adsorption increased along with an increase of temperature.

3.7. Adsorption behavior of sawdust (isotherm studies)

The adsorption isotherms reveal the specific relation between the concentration of the adsorbate and its adsorption degree onto adsorbent surface at a constant temperature. To quantify the adsorption capacity of meranti sawdust for the removal of Cu(II), Cr(III), Ni(II) and Pb(II) ions from aqueous solution, the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were used.

3.7.1. Langmuir model

This model assumes that the adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes. The data of the equilibrium studies for adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions onto meranti sawdust may follow the following form of Langmuir model:

$$\frac{C_e}{A_m} = \left(\frac{1}{K}\right) \left(\frac{1}{b}\right) + \left(\frac{1}{b}\right) (C_e) \quad (4)$$

where C_e is the equilibrium concentration (mg/L) and A_m is the amount adsorbed per specified amount of adsorbent (mg/g), K is the equilibrium constant and b is the amount of adsorbate required to form a monolayer. Hence, a plot of C_e/A_m vs C_e (Fig. 8) should be a straight line with a slope $(1/b)$ and an intercept as $1/Kb$. The values of constants K and b were calculated and reported in Table 1. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L [30], also known as

Table 1
Adsorption isotherm model constants and correlation coefficients for the adsorption of metal ions on meranti sawdust at 30 °C.

Adsorption isotherms	Isotherm constants	Metal ions			
		Cu(II)	Cr(III)	Ni(II)	Pb(II)
Langmuir	K (mg/g)	32.051	37.878	35.971	34.246
	b (L/mg)	0.050	0.019	0.016	0.016
	R^2	0.990	0.993	0.995	0.995
	R_L	0.384	0.581	0.634	0.646
Freundlich	K (mg/g) (L/mg) ^{1/n}	1.460	1.477	1.483	1.504
	n	1.101	1.035	1.119	1.046
	R^2	0.996	0.982	0.992	0.987
Dubinin–Radushkevich	$'Y$ (mol ² /J ²)	1.845	1.877	1.951	2.011
	C_m (mg/g)	0.334	0.354	0.438	0.410
	E (kJ/mol)	5.205	5.161	5.061	4.986
	R^2	0.994	0.995	0.991	0.998

the separation factor, given by

$$R_L = \frac{1}{1 + b(C_0)} \quad (5)$$

The value of R_L lies between 0 and 1 for favourable adsorption, while $R_L > 1$ represents unfavourable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$.

The isotherm data have linearized using Langmuir isotherm as shown in Fig. 8, the high values of correlation coefficient ($R^2 = 0.990$ – 0.995) indicates a good agreement between the parameters and confirms the monolayer adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions on to meranti sawdust surface. The dimensionless parameter R_L remained between 0.384 and 0.646 ($0 < R_L < 1$) consistent with the requirement for a favourable adsorption process.

3.7.2. Freundlich model

The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. According to this model:

$$A_m = (K)(C_e^{1/n})$$

$$\ln A_m = \ln K + (1/n) \ln C_e \quad (6)$$

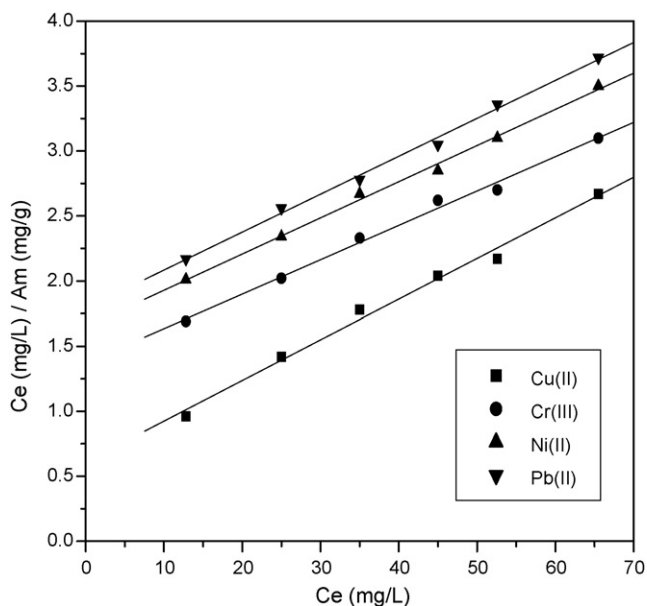


Fig. 8. Langmuir adsorption isotherm plots for the adsorption of metal ions at 30 °C.

where all the terms have the usual significance and n is an empirical constant. Thus, a plot of $\ln A_m$ vs $\ln C_e$ (Fig. 9) should be a straight line with a slope $1/n$ and an intercept of $\ln K$. This model deals with the multilayer adsorption of the substance on the adsorbent. The related parameters were calculated and reported in Table 1. The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent while Langmuir type isotherm hints towards surface homogeneity of the adsorbent. This leads to the conclusion that the surface of sawdust is made up of small heterogeneous adsorption patches which are very much similar to each other in respect of adsorption phenomenon.

3.7.3. Dubinin–Radushkevich (D–R) isotherm model

To determine the adsorption occurred is physical or chemical in nature, the equilibrium data were applied to D–R model [31]. The linearized form of the D–R model is given below:

$$\ln C_{ads} = \ln C_m - 'Y\varepsilon^2 \quad (7)$$

where C_{ads} is the adsorbed metal ions on the surface of adsorbent (mg/L), C_m is the maximum adsorption capacity (mg/g), $'Y$ is the activity coefficient related to mean adsorption energy (mol²/J²) and ε is the Polanyi potential (kJ² mol²).

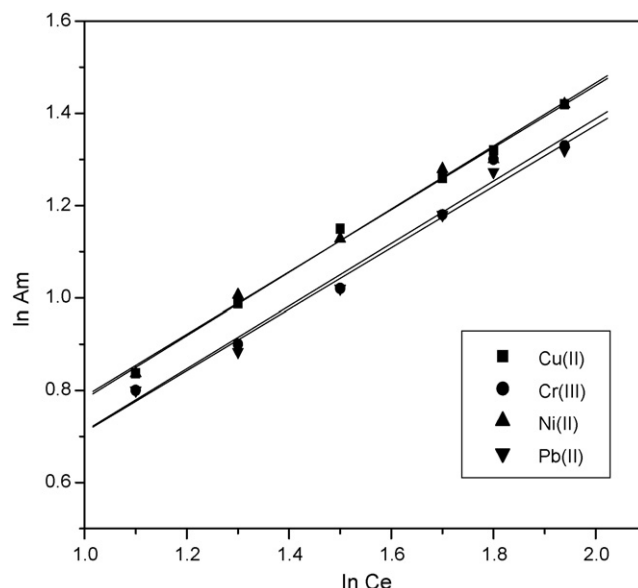


Fig. 9. Freundlich adsorption isotherm plots for the adsorption of metal ions at 30 °C.

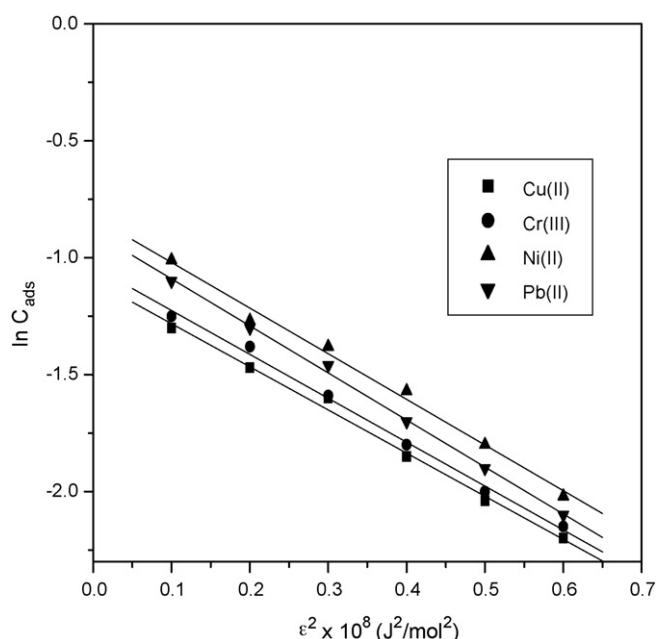


Fig. 10. D–R adsorption isotherm plots for the adsorption of metal ions at 30 °C.

Polanyi potential [32] can be calculated by using the following equation:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

The mean adsorption energy, E (kJ/mol) is calculated with the help of following equation:

$$E = 1/\sqrt{-2Y} \quad (9)$$

Fig. 10 shows the plot of Eq. (7) between $\ln C_{\text{ads}}$ vs ε^2 is a straight line from which values of all parameters for Cu(II), Cr(III), Ni(II) and Pb(II) ions were calculated and listed in Table 1. The adsorption potential is independent of the temperature, but it depends upon the nature of the adsorbent and adsorbate. The mean free energy of the adsorption E , which is the free energy for the transfer of one mole of metal ions from the infinity to the surface of the adsorbent, provide information about the nature of adsorption either chemical ion exchange or physical adsorption. The values of E lie between 8 and 16 kJ/mol depict the adsorption process follows the chemical ion exchange and if $E < 8$ kJ/mol, the adsorption process is of a physical nature [33,34]. The mean adsorption energy $E = 5.205$, 5.161, 5.061 and 4.986 kJ/mol was calculated for Cu(II), Cr(III), Ni(II) and Pb(II) ions, respectively.

From Table 1, the Langmuir adsorption isotherm and D–R adsorption isotherm models yielded best fit as indicated by the highest R^2 values for all metal ions compared to the Freundlich adsorption isotherm model. Table 2 lists a comparison of maximum

monolayer adsorption capacity of different metal ions on various adsorbents. Meranti sawdust is found to have a relatively large adsorption capacity of 32.051, 37.878, 35.971, and 34.246 mg/g for Cu(II), Cr(III), Ni(II), and Pb(II) ions, respectively, and this indicates that it could be considered a promising material for the removal of these metal ions from aqueous solutions.

3.8. Kinetic studies

Kinetics of the adsorption process have been evaluated for this work. This study describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid–liquid interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbents. The results obtained from the experiments were used to study the kinetics of Cu(II), Cr(III), Ni(II) and Pb(II) ions adsorption. The rate of kinetics on meranti sawdust was analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion model. The conformity between experimental data and the model predicted values was expressed by correlation coefficient (R^2).

3.8.1. Pseudo-first-order model

The pseudo-first-order rate model equation given by Lagergren [42] in 1898 is

$$\frac{dq}{dt} = k'_1(q_e - q) \quad (10)$$

where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q the amount of solute adsorbed at any time (mg/g) and k'_1 is the adsorption constant. Eq. (10) is integrated for the boundary conditions $t=0$ to >0 ($q=0$ to >0) and then rearranged to obtain the following linear time dependence function:

$$\log(q_e - q) = \log(q_e) - (k'_1/2.303)t \quad (11)$$

This is the most popular form of pseudo-first-order kinetic model equation. Fig. 11 shows an example for these plots. The correlation coefficient in this model lies between 0.850 and 0.932, it showed that this model have very poor correlation coefficients for best fit data. Therefore, it can be concluded that this model has no satisfactory value to be predicted as a suitable model. Constant k'_1 and correlation coefficients for all possible changes have been calculated and summarized in Table 3.

3.8.2. Pseudo-second-order model

The rate constant for the adsorption of metal ions on sawdust was determined by Lagergren equation. This equation modified by Ho and McKay [43–45] and the differential equation for this reaction is

$$dq/dt = k'_2(q_e - q)^2 \quad (12)$$

Table 2
Comparison of adsorption capacities of various adsorbents for different metal ions.

Adsorbents	Maximum monolayer adsorption capacity (mg/g)				References
	Cu(II)	Cr(III)	Ni(II)	Pb(II)	
Meranti sawdust	32.051	37.878	35.971	34.246	This work
Chitosan	16.80	–	2.40	16.36	[35]
Chabazite	5.10	–	4.50	6.00	[36]
Chabazite-phillipsite	0.37	0.25	0.56	–	[37]
Clinoptilolite	25.4	2.4	0.9	124	[11,38]
Blast furnace sludge	16.1	9.6	–	64.2	[39]
Corncobs	7.62	–	13.5	8.29	[40]
Peanut husk	10.15	7.67	–	29.14	[41]

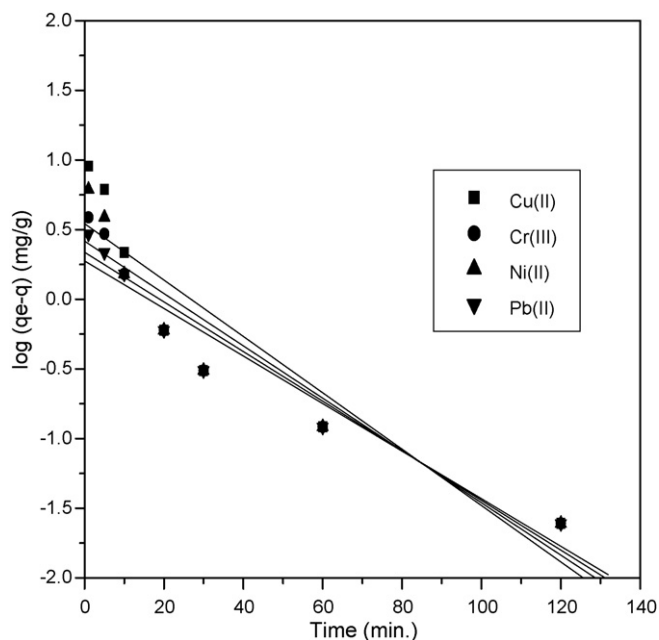


Fig. 11. Pseudo-first-order kinetic plots for the adsorption of metal ions at 30 °C.

Integrating Eq. (12) for the boundary conditions $t = 0$ to > 0 and $q = 0$ to > 0 and rearranging to obtain the linearized form which is shown as follows:

$$\frac{t}{q} = \left(\frac{1}{k'_2 qe^2} \right) + \left(\frac{1}{qe} \right) t \quad (13)$$

$$h = k'_2 qe^2 \quad (14)$$

In these equations, h is the initial sorption rate (mg/(g min)). The plot of t/q vs t of Eq. (13) should give a linear relationship, from which k'_2 and h can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand. The sample plot for meranti sawdust at 30 °C for Cu(II), Cr(III), Ni(II) and Pb(II) ions is given in Fig. 12, and values for k'_2 and h were calculated and reported in Table 3. The correlation coefficient (R^2) values for this model is very high with minimum value found was 0.991 and most of the values reached 0.999 which is very much ideal correlation coefficient value to be a perfect model. Hence it can be established that the adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions onto meranti sawdust perfectly follow the pseudo-second-order kinetic model.

It may be concluded from the values of k'_2 of different metal ions that the reaction-taking place is of the pseudo-second-order. The values of k'_2 also indicated the following preferential adsorp-

Table 3
Pseudo-first-order, pseudo-second-order and intraparticle diffusion models for the adsorption of metal ions on meranti sawdust at 30 °C.

Models	Parameters	Metal ions			
		Cu(II)	Cr(III)	Ni(II)	Pb(II)
Pseudo-first-order kinetic	k'_1 (min ⁻¹)	0.046	0.040	0.043	0.039
	R^2	0.850	0.911	0.879	0.932
Pseudo-second-order kinetic	k'_2 (g mg ⁻¹ min ⁻¹)	0.086	0.097	0.103	0.106
	h (mg/(g min))	29.599	36.289	35.190	42.569
	R^2	0.998	0.999	0.999	0.991
Intraparticle diffusion	k_p (min ^{1/2})	0.937	0.696	0.792	0.635
	R^2	0.803	0.897	0.844	0.929

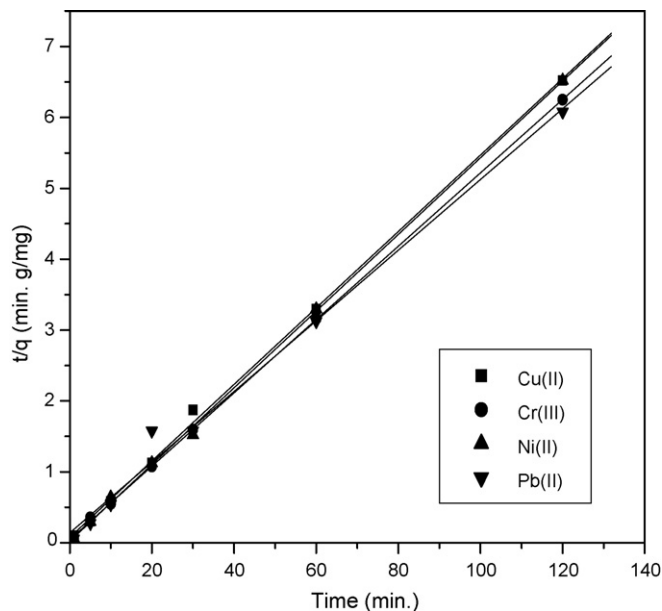


Fig. 12. Pseudo-second-order kinetic plots for the adsorption of metal ions at 30 °C.

tion of different heavy metal ions [Pb(II) > Ni(II) > Cr(III) > Cu(II)] on meranti sawdust. In a batch reactor with rapid stirring, there is also a possibility that the transport of adsorbate ions from the solution into the pores of the adsorbent is the rate-controlling step [46]. This possibility was tested in terms of a graphical relationship between the amount of heavy metals adsorbed (mg/g) and the square root of time (min^{1/2}) and the results are shown in Fig. 13 for different metal ions. It is clear from this figure that these plots gave straight lines of each metal ion but did not pass through the origin showing that the intraparticle diffusion is not the sole rate limiting factor for the adsorption of different metal ions [47]. The rate constant for intraparticle diffusion k_p , of different metal ions was determined from the slopes of the respective plots and the values are listed in Table 3.

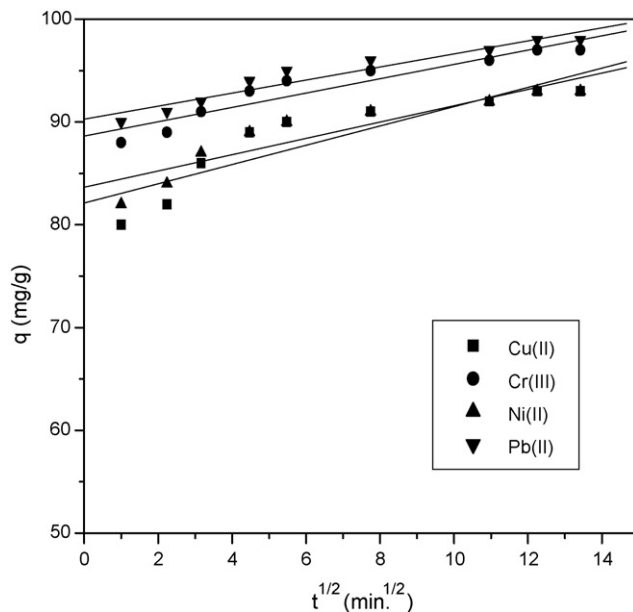


Fig. 13. Plots of amount adsorbed vs square root of time for metal ion adsorption.

4. Conclusions

The results obtained in this study demonstrated the potential use of meranti sawdust for the adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions from aqueous solutions. The amount of Cu(II), Cr(III), Ni(II) and Pb(II) ions adsorbed into the meranti sawdust increased with an increase in concentration and dosage of adsorbent. The reaction rate for the adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions increased with an increase in temperature. The kinetic studies indicated that equilibrium in the adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions on sawdust was reached in 120 min of contact between the sawdust and the solution. It was found that the kinetics of the adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions on sawdust followed pseudo-second-order model. The adsorption dynamic studies indicated that the rate of controlling step was mainly intraparticle diffusion but was not the only rate-limiting step for the metal ions. The adsorption isotherms followed the Langmuir model of isotherms, Dubinin–Radushkevich models predict the physical nature of the adsorption. Taking into consideration of the above results, it can be concluded that the meranti sawdust is a suitable adsorbent for the removal of Cu(II), Cr(III), Ni(II) and Pb(II) ions from aqueous solution in terms of low cost, natural and abundant availability.

Acknowledgement

This work was funded by Universiti Sains Malaysia under the Post Doctoral Fellowship Scheme.

References

- [1] M. McCann, Hazards in cottage industries in developing countries, *Am. J. Ind. Med.* 30 (1996) 125.
- [2] M. Suzuki, Role of adsorption in water environment processes, *Water Sci. Technol.* 35 (7) (1997) 1–11.
- [3] K.C. Sekhar, S. Subramanian, J.M. Modak, K.A. Natarajan, Removal of metal ions using an industrial biomass with references to environmental control, *Int. J. Miner. Process.* 53 (1998) 107–120.
- [4] C.P. Huang, M.O. Corapcioglu, The adsorption of heavy metal on to hydrous activated carbon, *Water Res.* 21 (9) (1987) 1031–1044.
- [5] B.L. Summers, L.B. Gress, W.H. Philipp, S.B. Eastep, Peat-moss pellets for removal of metal-ion contaminants dissolved in dilute wastewater. U.S., 11 pp., Cont-in-part of U.S. Ser. No. 249, 733 (1995).
- [6] F. Franco, G. Prati, M. Pia, Coal fly ash and alginate for the removal of heavy metals from aqueous solutions, *Ann. Chim.* 86 (3–4) (1996) 125–132.
- [7] A. Mathur, S.K. Khare, D.C. Rupainwar, Removal of heavy metals from main sewer-water of Varanasi city by adsorption on fly ash and blast furnace slag, *J. Ind. Pollut. Control* 5 (1989) 52–57.
- [8] C. Faur-Brasquet, K. Kadirvelu, P. Le Cloirec, Proceedings—Annual Conference, American Water Works Association, 2001, pp. 649–656.
- [9] R. Saravanane, T. Sundararajan, R.S. Sivamurthy, Efficiency of chemically modified low cost adsorbents for the removal of heavy metals from waste water: a comparative study, *Ind. J. Environ. Health* 44 (2) (2002) 78–87.
- [10] S.J. Park, Y.M. Kim, J.R. Lee, in: Proceedings of the Pacific Basin Conference, 3rd, Kyongju, Republic of Korea, Adsorpt. Sci. Technol. (2003) 437–441.
- [11] S.K. Ouki, M. Kavannagh, Treatment of metals-contaminated wastewaters by use of natural zeolites, *Water Sci. Technol.* 39 (10–11) (1999) 115–122.
- [12] G.L. Rorrer, T.Y. Hsien, J.D. Way, Synthesis of porous magnetic chitosan beads for removal of Cd ions from waste water, *Ind. Chem. Eng. Res.* 32 (1993) 2170–2178.
- [13] S.K. Srivastava, A.K. Singh, A. Sharma, Studies on the uptake of lead and zinc by lignin obtained from black liquor, a paper industry waste material, *Environ. Technol.* 15 (1994) 353–361.
- [14] B.J.W. Tuin, M. Tels, Removing heavy metals from contaminated clay soils by extraction with hydrochloric acid, EDTA or hypochlorite solutions, *Environ. Technol.* 11 (11) (1990) 1039–1052.
- [15] Y. Hua, R. Gerald, Evaluation of treatment techniques for increasing the uptake of metal ions from solution by nonliving biomass derived from several strains of lichen, *Sphagnum* (peat) moss, and *Eichhornia crassipes* (water hyacinth) root, *J. Microb.* 90 (363) (1997) 97–109.
- [16] Z. Yanfu, H. Yanyan, R. Gerald, Evaluation of treatment techniques for increasing the uptake of metal ions from solution by nonliving seaweed algal biomass, *J. Environ. Monit. Assess.* 33 (1) (1994) 61–70.
- [17] J.E. Hanway, R.G. Mumford, P.N. Mishra, Treatment of industrial effluents for heavy metals removal using the cellulose xanthate process, *AIChE Symp. Ser.* 75 (190) (1979) 306–314.
- [18] M.M. Davila-Jimenez, M.P. Elizalde-Gonzalez, W. Geyer, J. Mattusch, R. Wenrich, Adsorption of metal cations from aqueous solution onto a natural and a model biocomposite, *Colloids Surf. A: Physicochem. Eng. Aspects* 219 (2003) 243–252.
- [19] H.S.F. Vieira Regine, V. Boya, Biosorption: a solution to pollution? *Int. Microbiol.* 3 (1) (2003) 17–24.
- [20] A. Shukla, Y. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, The role of sawdust in the removal of unwanted materials from water, *J. Hazard. Mater.* B95 (2002) 137–152.
- [21] M.P. Cruz, L.C.A. Barbosa, C.R.A. Maltha, J.L. Gomide, A.F. Milanez, Chemical characterization of pitch in *Eucalyptus* pulp and paper industry, *Quim. Nova* 29 (2006) 459–466.
- [22] P.S. Rao, K.V.N.S. Reddy, S. Kalyani, A. Krishnaiah, Comparative sorption of copper and nickel solutions by natural neem (*Azadirachta indica*) sawdust and acid treated sawdust, *Wood Sci. Technol.* 41 (2007) 427–442.
- [23] N. Unlu, M. Ersoz, Adsorption characteristic of heavy metal ions onto low cost biopolymeric sorbent from aqueous solutions, *J. Hazard. Mater.* 136 (2006) 272–280.
- [24] M. Ajmal, A.H. Khan, S. Ahmad, A. Ahmad, Role of sawdust in the removal of copper(II) from industrial wastes, *Water Res.* 32 (1998) 3085–3091.
- [25] H.A. Elliot, C.P. Huang, Adsorption characteristics of some Cu(II) complexes on aluminosilicates, *Water Res.* 15 (1981) 849–855.
- [26] V.C. Srivastava, I.D. Mall, I.M. Mishra, Characterization of mesoporous rice husk ash(RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA, *J. Hazard. Mater.* B134 (2006) 257–267.
- [27] F.N. Acar, Z. Eren, Removal of Cu(II) ions by activated poplar sawdust(Samsun Clone) from aqueous solutions, *J. Hazard. Mater.* 137 (2006) 909–914.
- [28] P. King, P. Srinivas, Y.P. Kumar, V.S.R.K. Prasad, Sorption of copper (II) ion from aqueous solution by *Tectona grandis* L.f. (teak leaves powder), *J. Hazard. Mater.* 136 (2006) 560–566.
- [29] Y. Liu, X. Shen, Q. Xian, H. Chen, H. Zou, S. Gao, Adsorption of copper and lead in aqueous solution onto bentonite modified by 4'-methylbenzo-15-crown-5, *J. Hazard. Mater.* 137 (2006) 1149–1155.
- [30] K.R. Hall, L.C. Egleton, A. Acrivos, T. Vermeulen, Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, *Ind. Eng. Chem. Fundam.* 5 (1966) 212–219.
- [31] M.M. Dubinin, E.D. Zaverina, L.V. Radushkevich, Sorption and structure of activated carbons. I. Adsorption of organic vapours, *Zh. Fiz. Khim.* 21 (1947) 1351–1362.
- [32] M. Polanyi, Theories of the adsorption of gases. A general survey and some additional remarks, *Trans. Faraday Soc.* 28 (1932) 316–332.
- [33] K. Saltali, A. Sari, M. Aydin, Removal of ammonium ions from aqueous solution by natural Turkish (Yildizeli) zeolite for environmental quality, *J. Hazard. Mater.* B 141 (2006) 258–263.
- [34] R. Ahmed, T. Yamin, M.S. Ansari, S.M. Hasany, Sorption behaviour of lead(II) ions from aqueous solution onto Haro river sand, *Adsorpt. Sci. Technol.* 24 (2006) 475–486.
- [35] C. Huang, Y.C. Chung, M.R. Liou, Adsorption of Cu(II) and Ni(II) by pelletized biopolymer, *J. Hazard. Mater.* 45 (1996) 265–277.
- [36] S.K. Ouki, M. Kavannagh, Performance of natural zeolites for the treatment of mixed metal-contaminated effluents, *Waste Manage. Res.* 15 (1997) 383–394.
- [37] K.M. Ibrahim, T. NasserEd-Deen, H. Khoury, Use of natural chabazite-phillipsite tuff in wastewater treatment from electroplating factories in Jordan, *Environ. Geol.* 41 (2002) 547–551.
- [38] J. Peric, M. Trgo, N.V. Medvidovic, Removal of zinc, copper and lead by natural zeolites: a comparison of adsorption isotherms, *Water Res.* 38 (2004) 1893–1899.
- [39] A. Lopez-Delgado, C. Perez, F.A. Lopez, Sorption of heavy metals on blast furnace sludge, *Water Res.* 32 (1998) 989–996.
- [40] R. Zacaria, Adsorption of several metal ions onto low-cost biosorbents: kinetic and equilibrium studies, *Environ. Sci. Technol.* 36 (2002) 2067–2073.
- [41] Q. Li, J. Zhai, W. Zhang, M. Wang, J. Zhou, Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk, *J. Hazard. Mater.* 141 (2007) 163–167.
- [42] S. Lagergren, About the Theory of So Called Adsorption of Soluble Substances, vol. 4, *Kungliga Svenska Vetenskapsakademiens, Handlingar*, 1898, Band 24, pp. 1–39.
- [43] Y.S. Ho, J.C.Y. Ng, G. McKay, kinetics of pollutants sorption by biosorbents: review, *Sep. Purif. Methods* 29 (2000) 189–232.
- [44] Y.S. Ho, G. McKay, A comparison of chemisorptions kinetic models applied to pollutant removal on various sorbents, *Trans. IChemE* 76B (1998) 332–340.
- [45] G. McKay, B. Al-Duri, Study of the mechanism of pore diffusion in batch adsorption systems, *J. Chem. Technol. Biotechnol.* 48 (1990) 269–275.
- [46] V.J.P. Poots, G. McKay, J.J. Healy, Removal of basic dye from effluent using wood as an adsorbent, *Water Pollut. Control Fed.* 50 (1978) 926–935.
- [47] G. McKay, M.S. Otterburn, A.G. Sweeney, The removal of colour from effluent using various adsorbents. III. Silica: rate processes, *Water Res.* 14 (1980) 15–20.