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Removal of cadmium (II) from aqueous solutions by adsorption using meranti wood

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Abstract Meranti wood, an inexpensive material, has been utilized as an adsorbent for the removal of cadmium (II) from aqueous solutions. Various physicochemical parameters such as equilibrium contact time, solution pH, initial metal ion concentration, and adsorbent dosage level were studied. Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherms were used to analyze the equilibrium data at different temperatures. The experimental data fitted well with the Langmuir adsorption isotherm, indicating the monolayer adsorption of the cadmium (II). The monolayer adsorption capacity of meranti wood for cadmium (II) was found to be 175.43, 163.93 and 153.84 mg/g at 30, 40, and 50°C, respectively. The thermodynamics of cadmium (II) adsorption on meranti wood indicates its spontaneous and exothermic nature. Kinetic studies showed that the adsorption followed a pseudo-second-order kinetic model. The results indicated that the meranti wood could be an alternative for more costly adsorbents used for cadmium (II) removal.

Introduction

The contamination of water by toxic heavy metals through the discharge of industrial wastewater is a worldwide environmental problem (Ajmal et al. 2003). Their presence in streams and lakes has been responsible for several health problems with animals, plants and human beings. Numerous metals such as Sb, Cr,

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Cd, Zn, Ni, Cu, Pb, Hg, etc. have toxic effects on human and environment (Taty-Costodes et al. 2003).

Cadmium is a natural, usually minor constituent of surface and groundwater. It may exist in water as the hydrated ion, as inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids (OECD 1994). Cadmium may enter aquatic systems through weathering and erosion of soils and bedrock, atmospheric deposition, direct discharge from industrial operations, leakage from landfalls and contaminated sites, and the dispersive use of sludge and fertilizers in agriculture. Particulate matter may rapidly adsorb much of the cadmium entering fresh waters from industrial sources, and thus, sediment may be a significant sink for cadmium emitted to the aquatic environment (WHO 1992).

In advanced countries, removal of heavy metals in wastewater is normally achieved by advanced technologies such as ion exchange, chemical precipitation, electrochemical deposition (Kaewsarn and Yu 1999; Low et al. 2000; Sekhar et al. 1998; Suzuki 1997), but these technologies do not seem to be economically feasible because of their relatively high costs and developing countries may not be able to afford such technologies. Therefore, there is a need to look into alternatives to investigate a low-cost method, which is effective and economical. To overcome this difficulty there is a strong need to develop economical adsorbents which can be used in developing countries.

Adsorption is an alternative technology for metal separation from aqueous solutions. With the selection of a proper adsorbent, the adsorption process can be a promising technique for the removal of certain types of contaminants (Weng 2002; Ahmad et al. 2009). At present, there is growing interest in using low-cost, commercially available materials for the adsorption of heavy metals. A wide variety of materials such as fruit wastes (Inbaraj and Sulochana 2004; Martinez et al. 2006; Iqbal et al. 2009), cellulosic materials (Yalcinkaya et al. 2002), fly ash (Gupta et al. 2003), clays (Ulmanu et al. 2003; Gupta and Bhattacharyya 2006; Wang et al. 2007), bark (Naiya et al. 2009a), sawdust (Shukla et al. 2002; Taty-Costodes et al. 2003; Ahmad et al. 2007; Naiya et al. 2009a), biomass (Junior et al. 2003; Pandey et al. 2008; Sari and Tuzen 2009), husks (Ajmal et al. 2003; Saeed et al. 2005), alumina (Naiya et al. 2009b), red mud (Lopez et al. 1998) and agricultural wastes (Sun and Shi 1998; Leyva-Ramos et al. 2005; Tan and Xiao 2009) are being used as low-cost alternatives to expensive adsorbents.

Sawdust is a cheap, widely available and abundant natural material. It has been reported to exhibit ion exchange and complexation properties for the heavy metals. Meranti wood has received particular attention as an economical adsorbent for removing cadmium (II) from aqueous solutions due to its abundance, easily available and low cost. Further it will be a step ahead toward exploring the possibility of the use of waste biomass for industrial wastewater pollution management. The studies on the use of meranti wood 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 wood to adsorb cadmium (II) from aqueous solutions. The effect of contact time, pH, initial concentration and dosage of the adsorbents on the removal of cadmium (II) was studied. The adsorption isotherm and probable mechanism are explained and and it was attempted to find out the kinetics and order of reaction at the surface of the adsorbent.

Experimental materials and methods

Adsorbent

Meranti wood 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 procedure used to prepare the adsorbent referred to a previous work (Rafatullah et al. 2009). The resulting material was sieved in the size range of 100–200 μm particle size. The material was placed in an airtight container for further use.

Adsorbate solution

Stock solution (1,000 mg/L) of cadmium (II) was prepared by dissolving cadmium nitrate salt 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).

Scanning electron microscopy, Fourier transform infra red study and surface area analysis

Scanning electron microscopy (Carl-Ziess SMT, Oberkochen, Germany) analysis was carried out on meranti wood to study its surface morphology before and after cadmium (II) adsorption. The various elements present in sawdust were determined by Energy dispersive X-ray analyzer (INCA-400 from Oxford Instruments Analytical, Bucks, UK). For the main functional groups that might be involved in cadmium (II) adsorption, a Fourier Transform Infrared (Nicolet, AVATAR FTIR-360) analysis was done on the plain and cadmium (II) adsorbed meranti wood to determine the surface functional groups, and the spectra were recorded from 4,000 to 400 cm^{-1}. The surface area of meranti wood was determined using a Micromeritics ASAP 2010 gas adsorption surface analyzer.

Adsorption experiments

Batch adsorption studies were carried out by shaking 0.5 g of the adsorbents with 50 ml of the aqueous solutions of cadmium (II) for the different times using a temperature-controlled shaker. The solution-adsorbents mixtures were stirred at 200 rpm and at the end of pre-determined time interval the reaction mixtures were filtered out and analyzed for its metal ion concentrations using Atomic Absorption Spectrometer, AAS (Analyst 100 Perkin Elmer). The adsorption experiments were also conducted to determine the equilibrium time (5, 10, 20, 30, 60, 90, 120, 150, 180 and 210 min), initial concentrations (100, 200, 300, 400 and 500 mg/L) and dosage of the adsorbent (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 g) for maximum adsorption. All the investigations were carried out in triplicate to avoid any discrepancy in experimental results and metal solution controls were kept throughout the experiment to maintain quality control. Adsorption capacity was calculated by using the mass balance equation for the adsorbent:

$$q = (\mathrm{Ci} - \mathrm{Ce})V/W \tag{1}$$

where q is the adsorption capacity (mg/g), Ci is the initial concentration of metal in solution (mg/L), Ce 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).

Effect of solution pH and $\mathrm{pH}_{\mathrm{PZC}}$

The effect of pH of the initial solution on the equilibrium uptake of cadmium (II) was analyzed over a pH range from 2 to 8. The pH of the aqueous slurry was determined by adding 1 g of meranti wood in 50 mL distilled water, stirring and measuring the final pH after 24 h. The pH was found to be 5.8. The determination of $\mathrm{pH}_{\mathrm{PZC}}$ of meranti wood was performed according to the solid addition method (Balistrieri and Murray 1981): 50 mL of 0.01 M KNO_3 solution was placed in conical flasks. The initial pH of the solutions was adjusted to a value between 2 and 8 by adding 0.1 M HCl or NaOH solutions. Then, 1 g of meranti wood was added to each flask, stirred and the final pH of the solutions was measured after 24 h. The value of $\mathrm{pH}_{\mathrm{PZC}}$ can be determined from the curve that cuts the pH_0 line of the plot ΔpH versus pH_0.

Adsorption model

To quantify the adsorption capacity of meranti wood for the removal of cadmium (II) from aqueous solution, the Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherm models were used.

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 (Langmuir 1918). The data of the equilibrium studies for adsorption of cadmium (II) onto meranti wood may follow the following form of Langmuir model:

$$\mathrm{Ce}/A_m = (1/b)(1/K_{\mathrm{L}}) + (1/K_{\mathrm{L}})(\mathrm{Ce}) \tag{2}$$

where Ce is the equilibrium concentration (mg/L) and A_m is the amount adsorbed per specified amount of adsorbent (mg/g), K_{L} is the Langmuir equilibrium constant and b is the amount of adsorbate required to form a monolayer. Hence, a plot of Ce/A_m vs Ce should be a straight line with a slope $(1/K_{\mathrm{L}})$ and an intercept as $(1/bK_{\mathrm{L}})$.

Freundlich model

The Freundlich model can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer adsorption (Freundlich 1907). According to this model:

$$A_m = (K_\mathrm{F})\left(\mathrm{Ce}^{1/n}\right) \tag{3}$$

$$\ln A_m = \ln K_\mathrm{F} + 1/n \ln \mathrm{Ce} \tag{4}$$

where K_F is Freundlich equilibrium constant, n is an empirical constant and the rest of the terms have the usual significance. Thus, a plot of ln A_m versus ln Ce should be a straight line with a slope $1/n$ and an intercept of ln K_F.

Dubinin-Radushkevich (D-R) isotherm model

To determine the adsorption being physical or chemical in nature, the equilibrium data were applied to D-R model (Dubinin et al. 1947). The linearized form of the D-R model is given below:

$$\ln C_\mathrm{ads} = \ln C_\mathrm{m} - {}'\mathrm{Y}\varepsilon^2 \tag{5}$$

where C_ads is the adsorbed metal ions on the surface of adsorbent (mg/L), C_m is the maximum adsorption capacity (mg/g), $'\mathrm{Y}$ is the activity coefficient related to mean adsorption energy (mole^2/J^2) and ε is the Polanyi potential (kJ^2 mol^2).

Polanyi potential (Polanyi 1932) can be calculated by using the following equation:

$$\varepsilon = RT \ln(1 + 1/\mathrm{Ce}) \tag{6}$$

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

$$E = 1/\sqrt{-2'\mathrm{Y}} \tag{7}$$

Temkin model

Temkin and Pyzhev (1940) considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The Temkin isotherm has been used in the form as follows:

$$A_m = (RT/b)\ln(K_\mathrm{T}\mathrm{Ce}) \tag{8}$$

This equation can be expressed in its linear form as

$$A_m = B \ln K_\mathrm{T} + B \ln \mathrm{Ce} \tag{9}$$

where $B = (RT/b)$

A plot of A_m versus ln Ce yielded a linear line, enabling the determination of the isotherm constants K_T and B. K_T is the Temkin equilibrium binding constants (L/mg) corresponding to the maximum binding energy and constant B is related to heat of adsorption.

Thermodynamic study of adsorption

The standard free energy change (ΔG°) is the fundamental criterion of spontaneity of a process and can be determined using equilibrium constant as shown below:

$$\Delta G^\circ = -RT \ln K \tag{10}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K) and K is the equilibrium constant.

Similarly, the standard enthalpy change ΔH° from 30 to 50°C was computed from the following equation,

$$\ln K = \Delta S^\circ / R - \Delta H^\circ / RT \tag{11}$$

Results and discussion

Characterization of meranti wood

Characteristics of the adsorbent such as surface area, pore volume, pore diameter, bulk density, moisture content and ash content were determined. The BET surface area and Langmuir surface area were found to be 0.62 m^2g^{-1} and 0.43 m^2g^{-1}, respectively by using the nitrogen adsorption method. The influence of other properties on the extent of adsorption was evaluated by measuring the bulk density (0.29 g/cm^3), pore volume (0.023 (cm^3/g), moisture content (4.50%) and ash content (3.20%). 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 109.70 Å, BJH average adsorption pore diameter = 253.4 Å and BJH average desorption pore diameter = 363.4 Å. suggesting that meranti wood consists of mesopores.

Figure 1a, b show the SEM micrograph of meranti wood before and after cadmium (II) adsorption. It is clear that meranti wood has considerable layers of pores where there is a good possibility for cadmium (II) to be adsorbed. The surface of cadmium (II) treated adsorbent is different from the surface of natural adsorbent. The EDX study of the meranti wood showed the elemental composition of the adsorbent (Fig. 1c), which showed that meranti wood has a high percentage of carbon (52%) and oxygen (43%). Based on the particle morphology, the meranti wood seems to be suitable to be used as adsorbent.

The FTIR spectrum of meranti wood before adsorption and after adsorption shows that some peaks were shifted (Fig. 2; Table 1). There is a strong peak at 3,445 cm^{-1} representing the −OH stretching of phenol group of cellulose and lignin, and the peak at 2,927 cm^{-1} indicates the presence of $-\text{CH}_2$ stretching of aliphatic compound. The appearance of peaks at 1,735 cm^{-1} and 1,633 cm^{-1} indicates the presence of C=O stretching of aldehyde group and C=C stretching of

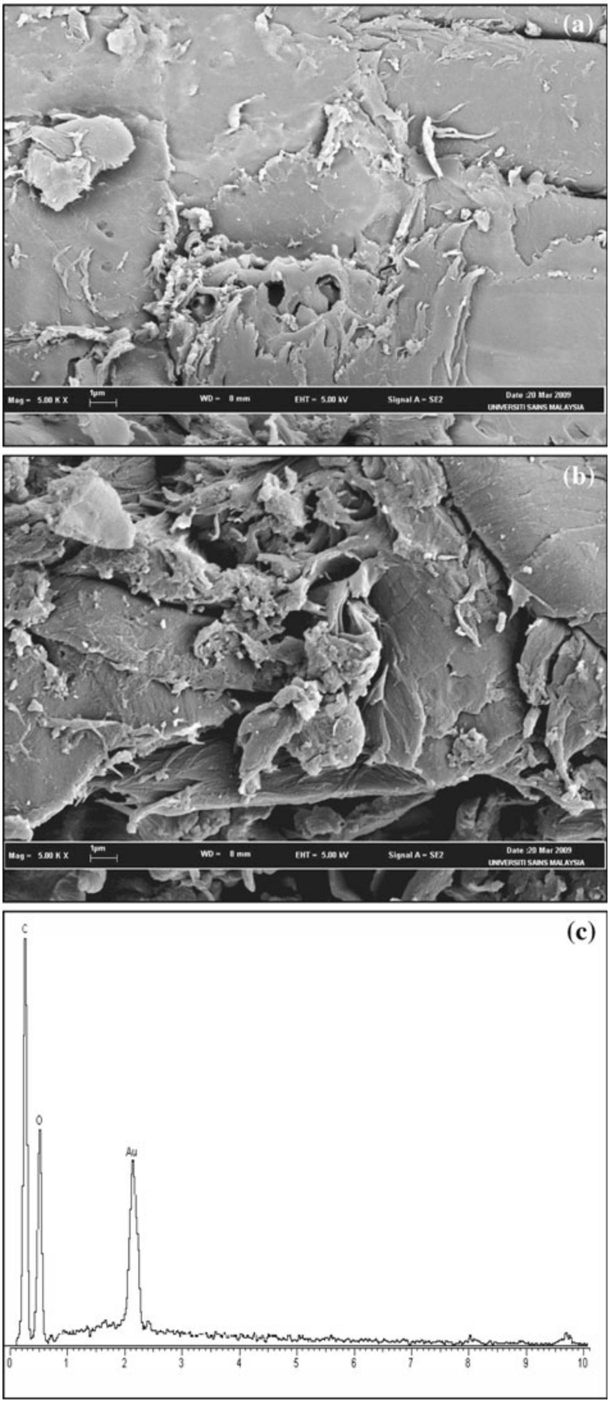

Fig. 1 SEM micrograph of meranti wood (magnification 5,000): **a** before adsorption, **b** after adsorption, **c** EDX graphical representation of meranti wood

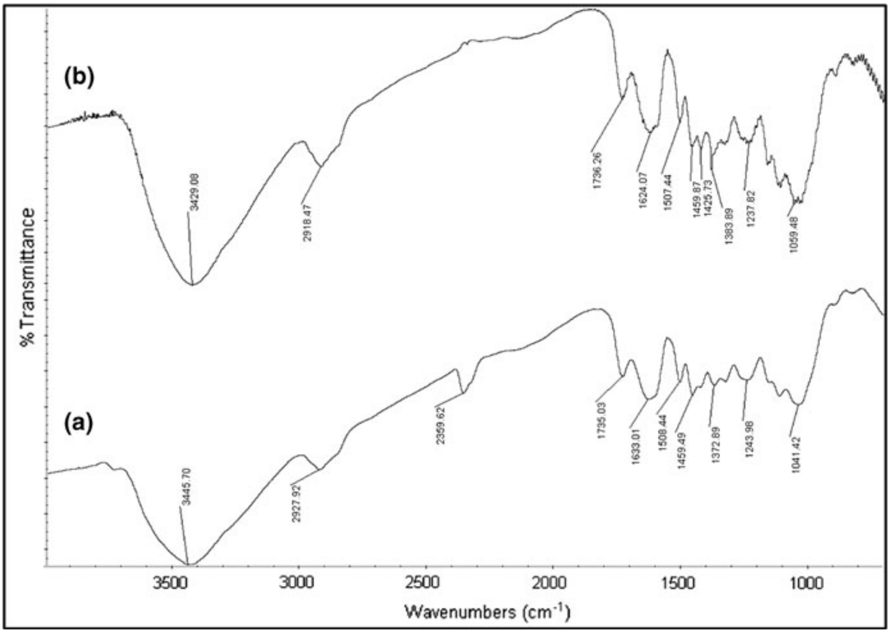

Fig. 2 FTIR spectra of meranti wood: **a** before adsorption, **b** after adsorption

Table 1 FTIR of meranti wood

S. No.	Frequency (cm^{-1})		Differences	Assignment
	Before adsorption	After adsorption		
1	3,445	3,429	16	OH stretching
2	2,927	2,918	9	CH_2 stretching
3	2,359	–	–	NH stretching
4	1,735	1,736	−1	C=O stretching
5	1,633	1,624	9	C=C stretching
6	1,508	1,507	1	C=C of aromatic ring
7	1,459	1,459	–	CH_2 deformation
8	–	1,425	–	OH bending
9	1,372	1,383	−11	C–O–H bending
10	1,243	1,237	6	C–O stretching
11	1,041	1,059	−18	Six member cyclic ether

phenol group, respectively where as the peaks between 1,508 and 1,372 cm^{-1} in the spectrum of meranti wood before adsorption may be assigned to C=C of aromatic ring. The peaks at 1,243 and 1,041 cm^{-1} might be due to C–O stretching of phenolic group and ether group of cellulose, respectively (Rafatullah et al. 2009). The FTIR spectrum, after adsorption shown in Fig. 2b indicates that the peaks due to above functional groups are slightly affected in their position and intensity.

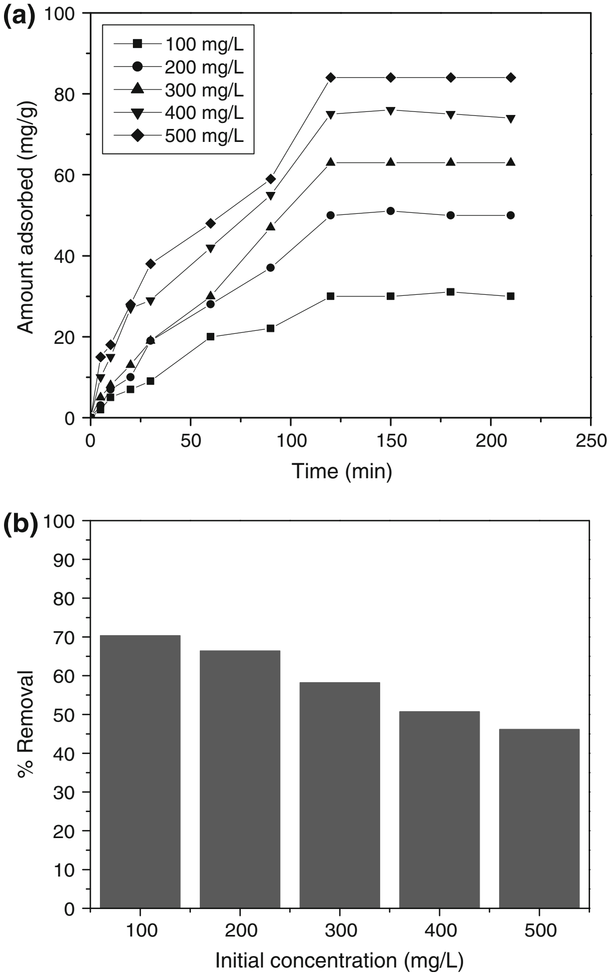

Fig. 3 **a** Effect of contact time and initial metal concentration on cadmium (II) adsorption. **b** Percentage removal versus initial concentration

It indicates that the adsorption of cadmium (II) on the surface of meranti wood is either through complexation or physical which might be through week electrostatic interaction and Van der Waals forces. These changes observed in the spectrum indicate the possible involvement of those functional groups on the surface of meranti wood in the adsorption process.

Effect of contact time and initial metal concentration

The effect of contact time on the removal of cadmium (II) by meranti wood at initial concentrations 100–500 mg/L and 30°C is shown in Fig. 3a. The time curve shows that the removal of adsorbate is rapid but it gradually slows down until it reaches the equilibrium. This is due to the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. The equilibrium was attained after shaking for 120 min. Once equilibrium was attained, the percentage sorption of cadmium (II) did not change with further increases of time. So, it was assumed that longer treatment may have no further effect to change the properties of adsorbents. In batch type of adsorption systems, the rate of removal of adsorbate species from aqueous solution is controlled primarily by the rate of transport of the adsorbate species from the exterior/outer sites to the interior sites of the adsorbent particles. A similar phenomenon was observed for the adsorption of cadmium (II) onto clarified sludge (Naiya et al. 2008) and food waste (Zheng et al. 2008).

It is also evident from Fig. 3a that the amount of cadmium (II) adsorbed (mg/g) increased with increasing cadmium (II) concentration and remained constant after equilibrium time, but the percentage of adsorption decreased (Fig. 3b). The concentration provides an important driving force to overcome all mass transfer resistance of the cadmium (II) between the aqueous and solid phases. Hence, higher initial concentration of cadmium (II) will enhance the adsorption process. The equilibrium adsorption capacity of meranti wood increased with an increase in initial metal concentration. When the initial metal concentration increased from 100 to 500 mg/L, the loading capacity of meranti wood increased from 30 to 84 mg/g. It can be seen that the initial concentration of cadmium (II) had only a small influence on the time of contact necessary to reach equilibrium. However, for low concentrations the initial uptake of cadmium (II) is rapid, indicating a rapid surface reaction. Consequently, the concentration of cadmium (II) will greatly affect the extent and rate of metal uptake on sawdust. A similar result has been found by Tajar et al. (2009) in adsorption of cadmium (II) from aqueous solutions on sulfurized activated carbon prepared from nut shells. The percentage removal of cadmium (II) adsorbed decreased from 70.36 to 46.20% as the initial concentration was increased from 100 to 500 mg/L (Fig 3b).

$\mathrm{pH_{PZC}}$ and effect of pH

The pH of the solutions has an important variable governing metal adsorption. In general, adsorption of cations is favored at $\mathrm{pH} > \mathrm{pH_{PZC}}$. The effect of pH on the adsorption of cadmium (II) on meranti wood was studied by varying it in the pH range 2–8 using different concentrations as shown in Fig. 4. The calculation from the solubility product equilibrium constant (Ksp) demonstrated that the best pH range was 2–8 for cadmium (II) adsorption (Sawyer et al. 2002).

The $\mathrm{pH_{PZC}}$ of an adsorbent is a very important characteristic that determines the pH at which the adsorbent surface has net electrical neutrality. At this value, the acidic or basic functional groups no longer contribute to the pH of the solution. Cations adsorption will be more favorable at pH value higher than $\mathrm{pH_{PZC}}$. The value of $\mathrm{pH_{PZC}}$ is close to the value of pH of aqueous slurry which is 5.5.

The effect of pH on the adsorption of cadmium (II) on meranti wood has been studied by varying it in the range of 2–8 as shown in Fig. 4. As shown in Fig. 4, the

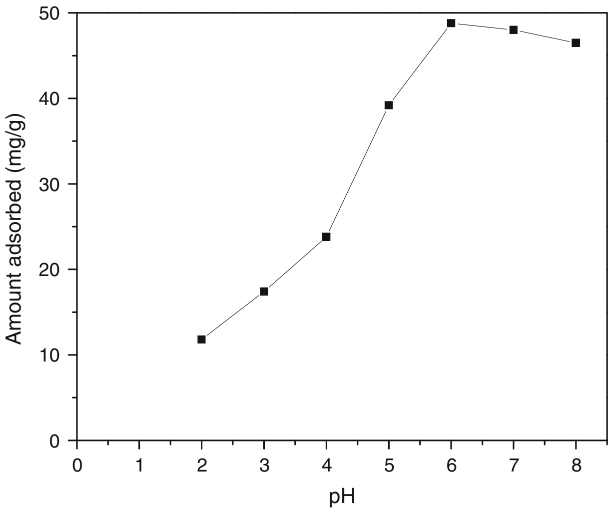

Fig. 4 Effect of the solution pH on cadmium (II) adsorption

uptake of cadmium (II) depends on pH, it increases with the increase in pH reaching the maximum adsorption at pH 6. At higher pH values a slight decrease was observed. Based on the 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 (Shukla et al. 2002). A similar theory was proposed by several earlier workers for cadmium (II) adsorption on different adsorbents. At higher pH values than 6, metal precipitation appeared and the adsorbent was deteriorated with the accumulation of metal ions (Srivastava et al. 2006; Naiya et al. 2008, 2009a, b). Therefore, pH 6 was selected to be the optimum pH for further studies.

Effect of adsorbent dosage

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given concentration of the adsorbate. Figure 5 shows the adsorption of cadmium (II) by meranti wood at different dosage of adsorbent (0.5–5.0 g) at initial concentration of 100 mg/L metal solution and 30°C. When the adsorbent dosage was increased from 0.5 to 5.0 g/L, the percentage adsorption generally increases, but the amount adsorbed per unit mass of adsorbent decreases considerably. The increase in the adsorption percentage or decrease in unit adsorption with increase in the dose of adsorbent is due to the increase in active sites on the adsorbent and thus making easier penetration of the metal ions to the adsorption sites. Especially, when the adsorbent added is beyond 3.0 g, the decrease in cadmium (II) adsorption is not very prominent which is perhaps due to the formation of adsorbent agglomerates reducing available surface area and blocking some of the adsorption sites. Wang et al. (2007) and Gupta and Bhattacharyya (2006) reported of a similar finding for cadmium (II) adsorption onto different clays.

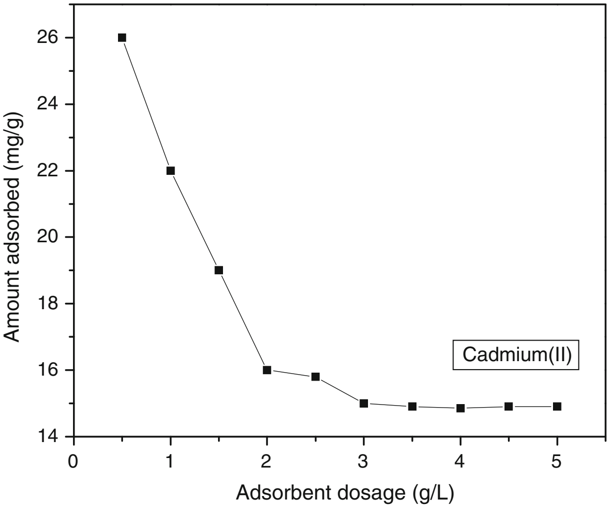

Fig. 5 Effect of adsorbent dosage on cadmium (II) adsorption

Adsorption behavior of sawdust (isotherm studies)

The adsorption isotherms revealed the specific relation between the concentration of the adsorbate and its adsorption degree onto adsorbent surface at a constant temperature. The analysis of the adsorption isotherm data by fitting them to different adsorption isotherm models is an important step to find the suitable adsorption isotherm model that can be used for design purposes. Adsorption isotherm study was carried out on four isotherm models: the Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherm models. The applicability of the isotherm was judged by the correlation coefficient (R^2) values. The Langmuir type adsorption isotherm indicates surface homogeneity of the adsorbent and hints towards the conclusion that the surface of adsorbent is made up of small adsorption patches which are energetically equivalent to each other in respect of adsorption phenomenon. When Ce/A_m is plotted against Ce, a straight line with a slope ($1/K_{\mathrm{L}}$) and an intercept ($1/bK_{\mathrm{L}}$) is obtained, as shown in Fig. 6a. The correlation coefficient (R^2) values of 0.993–0.997 indicate that the adsorption data of cadmium (II) onto meranti wood was well fitted to the Langmuir isotherm. The values of constants K_{L} and b were calculated and are reported in Table 2.

For the Freundlich isotherm, the plot of $\ln A_m$ vs $\ln \mathrm{Ce}$ gives a straight line with a slope $1/n$ and an intercept of $\ln K_{\mathrm{F}}$ as shown in Fig. 6b. This model deals with the multilayer adsorption of the substance on the adsorbent. The related parameters were calculated and are reported in Table 2. The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent and thus is responsible for multilayer adsorption due to the presence of energetically heterogeneous adsorption sites. 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. Figure 6c shows that the

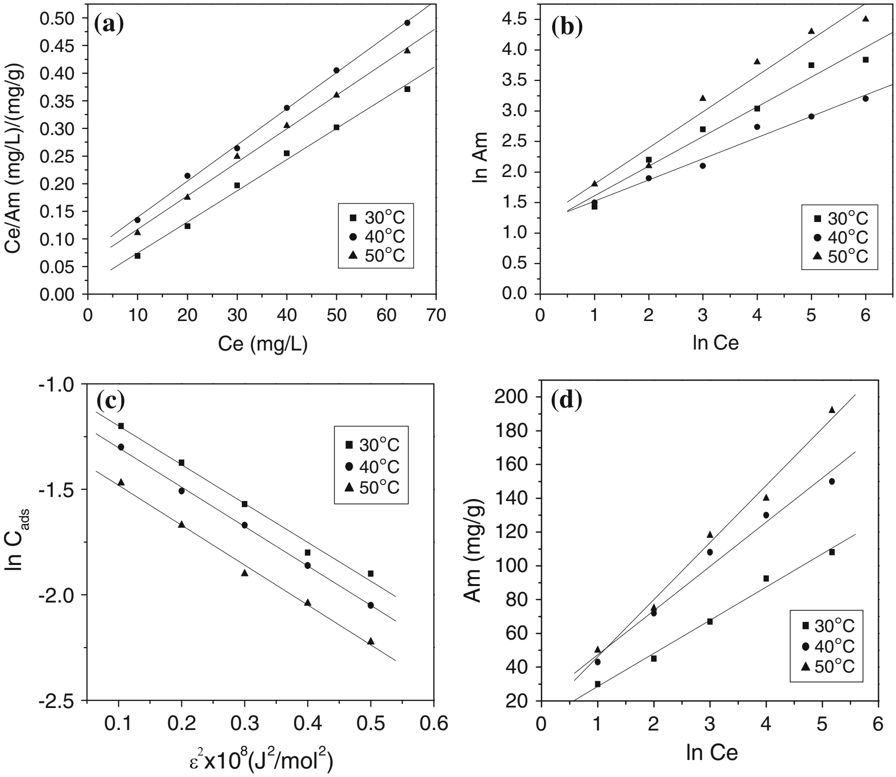

Fig. 6 Isotherm plots for cadmium (II) adsorption at different temperatures: **a** Langmuir adsorption isotherm, **b** Freundlich adsorption isotherm, **c** D-R adsorption isotherm and **d** Temkin adsorption isotherm

plot of Eq. (5) between ln C_{ads} versus ε^2 is a straight line from which values of all parameters for cadmium (II) were calculated and are listed in Table 2. The adsorption potential is independent of the temperature, but dependent om 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, provides information about the nature of adsorption either chemical ion exchange or physical adsorption. The values of E lie between 8–16 kJ/mol and depict the adsorption process follows the chemical ion-exchange and if $E < 8$ kJ/mol, the adsorption process is of a physical nature (Helfferich 1962). The mean adsorption energy $E = 5.212$, 5.175 and 5.143 kJ/mol was calculated for cadmium (II) at 30, 40, and 50°C, respectively. A plot of A_m versus ln Ce yielded a linear line, as shown in Fig. 6d enabling the determination of the isotherm constants K_T and B. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions. The constants K_T and B together with the R^2 values are shown in Table 2.

From Table 2, the Langmuir adsorption isotherm and D-R adsorption isotherm models yielded best fit as indicated by the highest R^2 values at all temperatures

Table 2 Related parameters for the adsorption of cadmium (II) on meranti wood at different temperatures

Adsorption isotherms and their constants	Temperatures (°C)		
	30	40	50
Langmuir adsorption isotherm constants			
K_L (mg/g)	175.43	163.93	153.84
b (L/mg)	0.320	0.107	0.088
R^2	0.993	0.996	0.997
Freundlich adsorption isotherm constants			
K_F (mg/g) (L/mg)$^{1/n}$	3.410	3.237	3.364
n	2.053	2.876	1.690
R^2	0.968	0.977	0.958
Dubinin-Radushkevich isotherm constants			
'Y (mole^2/J^2)	1.840	1.867	1.890
C_m (mg/g)	0.362	0.327	0.274
E (kJ/mol)	5.212	5.175	5.143
R^2	0.988	0.998	0.993
Temkin adsorption isotherm constants			
K_T (L/mg)	19.64	26.19	33.83
B	1.574	2.238	1.440
R^2	0.989	0.980	0.988

compared to the Freundlich and Temkin adsorption isotherm model. Table 3 lists a comparison of maximum monolayer adsorption capacity of cadmium (II) on various adsorbents. Meranti wood is found to have a relatively large adsorption capacity of 175.43 mg/g and this indicates that it could be considered a promising material for the removal of cadmium (II) from aqueous solutions.

Thermodynamic study of adsorption

In order to evaluate the thermodynamic parameters for the adsorption of cadmium (II) onto meranti wood, the adsorption studies were carried out at different temperatures (30, 40, and 50°C). Since Langmuir adsorption isotherm is the best fit value of b was used in places of K in the calculations of all thermodynamic parameters.

A plot of ln K versus $1/T$ should be a straight line as shown in Fig. 7. $\Delta H°$ and $\Delta S°$ values were obtained from the slope and intercept of this plot, respectively. The standard free energy change ($\Delta G°$), standard enthalpy change ($\Delta H°$), and standard entropy change ($\Delta S°$) were obtained from Eqs. (10, 11) and the values associated with the adsorption of cadmium (II) onto meranti wood are listed in Table 4. Negative values of $\Delta G°$ indicate the feasibility of the process and spontaneous nature of the adsorption with a high performance of cadmium (II) for meranti wood. Negative value of $\Delta H°$ indicates the exothermic nature of the process, while negative value of $\Delta S°$ reflects the decrease in the randomness at the solid/liquid interface during the adsorption process (Naiya et al. 2008; Sari and Tuzen 2009).

Table 3 Comparison of adsorption capacities of various adsorbents for cadmium (II)

Adsorbents	Maximum monolayer adsorption capacity (mg/g)	References
Meranti sawdust	175.43	This study
Aerobic granules	172.70	Liu et al. (2003)
Sulfurized nut shells activated carbon	142.86	Tazar et al. (2009)
Exopolysaccharide (SM-A87-EPS)	116.28	Zhou et al. (2009)
Rice husk	103.09	Ajmal et al. (2003)
Dithiocarbamate-anchored polymer/organosmectite	82.20	Say et al. (2006)
Mango peel waste	68.92	Iqbal et al. (2009)
Bone char	61.72	Ko et al. (2003)
Corncob	55.70	Leyva-Ramos et al. (2005)
Jackfruit peel	52.08	Inbaraj and Sulochana (2004)
Activated palygorskite	51.07	Wang et al. (2007)
Calotropis procera	50.50	Pandey et al. (2008)
Streptomyces sp. HL-12	49.02	Yuan et al. (2009)
Sugar beet pulp	46.10	Pehlivan et al. (2008)
Sunflower stalks	42.18	Sun and Shi (1998)
Black gram husk	39.99	Saeed et al. (2005)
Sludge	36.23	Naiya et al. (2008)
Activated alumina	35.06	Naiya et al. (2009b)
Montmorillonite	32.70	Gupta and Bhattacharyya (2006)
Carboxy methyl cellulose	28.70	Yalcinkaya et al. (2002)
Grape stalk waste	27.90	Martinez et al. (2006)
Macrofungus (*Amanita rubescens*)	27.30	Sari and Tuzen (2009)
Teak wood sawdust	26.73	Naiya et al. (2009a)
Aspergillus niger	26.72	Junior et al. (2003)
Chitin	14.70	Benguella and Benaissa (2002)
Red mud	10.60	Lopez et al. (1998)
Bentonite	9.30	Ulmanu et al. (2003)
Low grade Phosphate	7.50	Kandah (2004)
Sporopollenin	7.09	Unlu and Ersoz (2007)
Baggase fly ash	2.00	Gupta et al. (2003)

Kinetic studies

This study describes the solute uptake rate and evidently this 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. In order to determine the adsorption kinetics of cadmium (II), the pseudo-first order, pseudo-second order and Weber–Morris diffusion models were checked. The conformity between experimental data and the model predicted values is expressed by correlation coefficient (R^2).

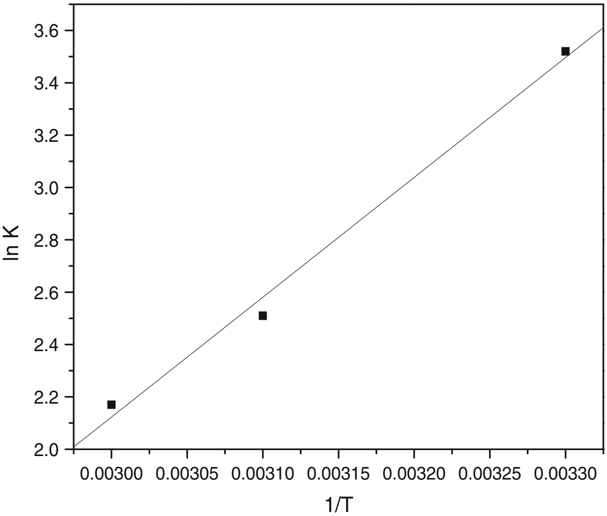

Fig. 7 Plot of ln *K* versus 1/*T* for cadmium (II) adsorption onto meranti wood

Table 4 Values of thermodynamic parameters for the adsorption of cadmium (II) onto meranti wood

Temp. (°C)	ΔG (kJ mole^{-1})	ΔH (kJmole^{-1})	ΔS (kJ mole^{-1}K^{-1})	R^2
30	−9.018			
40	−6.453	−37.17	−0.093	0.961
50	−6.149			

Pseudo-first-order model

The pseudo-first order rate model of Lagergren (1898) is based on solid capacity and generally expressed as follows:

$$\mathrm{d}q/\mathrm{d}t = k_1(q_e - q) \tag{12}$$

where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q is the amount of solute adsorbed at any time (mg/g) and k_1 is the adsorption constant. Equation (12) is integrated for the boundary conditions $t = 0$ to $t > 0$ ($q = 0$ to $q > 0$) and then rearranged to obtain the following linear time dependent function:

$$\log(q_e - q) = \log(q_e) - (k_1/2.303)t \tag{13}$$

This is the most popular form of pseudo-first-order kinetic model. Values of k_1 at different temperatures were calculated from the plots of log ($q_e - q$) versus t (figure not shown) for cadmium (II). Constant k_1 and correlation coefficients (R^2) were calculated and are summarized in Table 5. The correlation coefficient (R^2) values obtained were relatively low, it showed that this model has very poor correlation coefficients (R^2) for best fits data.

Table 5 Pseudo-first-order, pseudo-second-order and intraparticle diffusion models for the adsorption of cadmium (II) onto meranti wood at different temperatures

Kinetic models and their parameters	Temperatures (°C)		
	30	40	50
$q_{e,\ exp.}$ (mg/g)	18.34	19.56	21.10
Pseudo-first-order kinetic model			
$q_{e,\ cal.}$ (mg/g)	12.13	16.75	14.90
k_1 (min^{-1})	0.047	0.062	0.067
R^2	0.941	0.932	0.984
Pseudo-second-order kinetic model			
$q_{e,\ cal.}$ (mg/g)	18.69	20.87	22.42
k_2 (g $mg^{-1}min^{-1}$)	0.067	0.084	0.151
h (mg $g^{-1}min^{-1}$)	23.40	36.58	75.90
R^2	0.996	0.992	0.993
Intraparticle diffusion			
kp ($min^{1/2}$)	1.439	1.841	1.658
C	6.197	6.819	9.956
R^2	0.988	0.985	0.946

Pseudo-second-order model

The kinetic data were analyzed using the pseudo-second-order model (Ho et al. 2000) which, can be expressed as:

$$dq/dt = k_2(q_e - q)^2 \tag{14}$$

Integrating above equation for the boundary conditions $t = 0$ to $t > 0$ and $q = 0$ to $q > 0$ and rearranging to obtain the linearized form which is shown as follows:

$$t/q = (1/k_2q_e^2) + (1/q_e)t \tag{15}$$

$$h = k_2q_e^2 \tag{16}$$

where h is the initial sorption rate (mg/g min). The plot of t/q versus t should give a linear relationship, from which, q_e and k_2 can be determined from the slope and intercept of the plot (Fig. 8). The correlation coefficient (R^2) values for this model are given in Table 5. Hence it can be assumed that the adsorption of cadmium (II) perfectly follows the pseudo second order kinetic model.

Weber–Morris diffusion model

The possibility of intra particle diffusion was examined using the intraparticle diffusion Weber–Morris model (Weber and Morris 1963), taking into account that during the course of adsorption the adsorbed amount is proportional to the square root of contact time,

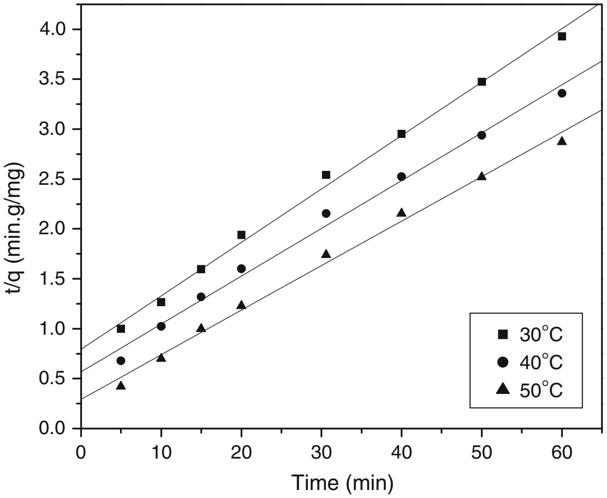

Fig. 8 Pseudo-second-order kinetic plots for cadmium (II) adsorption onto meranti wood

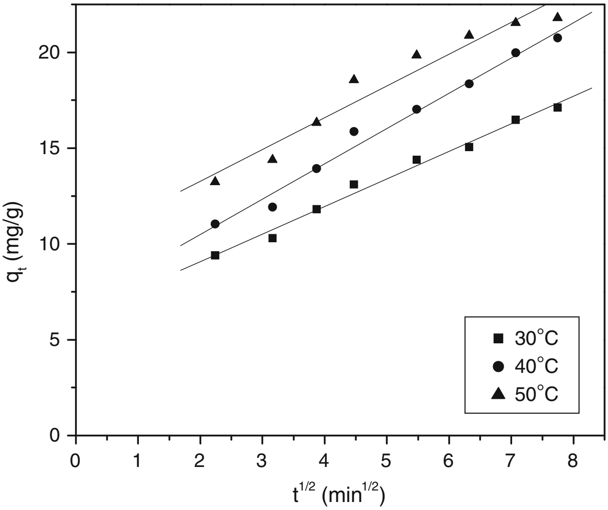

Fig. 9 Intraparticle diffusion constants for cadmium (II) at different temperatures

$$q_t = \mathrm{kp}t^{1/2} + C \tag{17}$$

where q_t is the amount adsorbed (mg/g) at time t (min). In a batch reactor with rapid stirring, there is also a possibility that the transport of cadmium (II) from the solution into the pores of the adsorbent is the rate-controlling step. This possibility was tested in terms of a graphical relationship between the amount of cadmium (II) adsorbed (mg g^{-1}) and the square root of time (min) and the results are shown in Fig. 9 for different temperatures onto meranti wood. It is clear from this figure that these plots gave straight lines but did not pass through the origin showing that the intraparticle diffusion is not the sole rate limiting factor for the adsorption of cadmium (II). The rate constant for intraparticle diffusion kp, of cadmium (II) was determined from the slopes of the respective plots and the values are listed in Table 5.

Conclusion

The present study shows that meranti wood, an agro-based waste biomass, can be used as an adsorbent for the removal of cadmium (II) from aqueous solutions. The amount of cadmium (II) uptake (mg/g) was found to increase with increasing contact time, pH and initial metal ion concentration. Equilibrium data fitted very well in the Langmuir isotherm equation, confirming the monolayer adsorption capacity of cadmium (II) onto meranti wood with a monolayer adsorption capacity of 175.43 mg/g at 30°C. The thermodynamic calculations point towards the feasibility of the adsorption process with spontaneous and exothermic nature. The rate of adsorption was found to conform to pseudo-second-order kinetics with a good correlation. Taking into consideration the above results, it can be concluded that the meranti wood can be an alternative material for more costly adsorbents used for cadmium (II) in wastewater treatment processes.

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