A novel agricultural waste adsorbent for the removal of lead (II) ions from aqueous solutions

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ABSTRACT

The present study explores the ability of modified soda lignin (MSL) extracted from oil palm empty fruit bunches (EFB) in removing lead (II) ions from aqueous solutions. The effect of contact time, point zero charge (pH_{pzc}) and pH of the solution, initial metal ion concentration and adsorbent dosage on the removal process were investigated. Furthermore, the MSL is characterized by SEM, XRF, FT-IR and surface area analysis. Equilibrium adsorption isotherms and kinetics were investigated. The experimental data were analyzed by the Langmuir, Freundlich and Temkin models of adsorption. The kinetic data obtained at different initial concentrations were analyzed using pseudo-first-order and pseudo-second-order models. The results provide strong evidence to support the hypothesis of adsorption mechanism.

1. Introduction

Heavy metals in water have been a major preoccupation for researchers for many years due to their toxicity towards aquatic life, human beings and the environment. As they do not degrade biologically like organic pollutants, their presence in industrial effluents and drinking water is a public health problem. Lead is recognized as multifunctional metal, which is an essential element to produce pipes, paints, bullets and also one of the metals used in the pewter industry. The purpose of lead in industrial sector brings to a leaded-waste production. Lead is a poisonous metal that can damage human nervous system and cause brain disorder. A long term exposure to lead may cause nephropathy, abdominal pains and particularly harmful to woman's ability to reproduce [1,2].

Many studies have been conducted to determine the best methods for the removal of metal ions from water namely: chemical precipitation, ion-exchange, electrochemical deposition, solvent extraction and adsorption. Among these methods, adsorption has been shown as the most appealing in terms of economic and an environmental friendly procedure to remove heavy metals in wastewater [3]. For heavy metal ions of low concentrations ($<100\,mg\,L^{-1}$), adsorption is a much preferable technique to remove heavy metals in wastewater. Activated carbon is the most popular material used as an adsorbent. However, it is quite expensive. The discovery of alternative adsorbent to replace the costly activated carbon is highly encouraged. Nowadays, researchers are focusing more on various adsorbent which have metal-binding capacities and able to remove unwanted heavy metals from contaminated water at lower cost. Production of lignin obtained from industrial waste fulfills the requirement of low-cost adsorbent.

The use of agricultural wastes for the treatment of polluted water is also an attractive and promising option for the environment. A wide variety of agricultural waste materials such as *Moringa oleifera* bark [4], sawdust [5], by-product of steelmaking industry [6,7], bagasse fly ash [8], rubber tree leaf powder [9], *Saraca indica* leaf powder [10], tree fern [11], *Melocanna baccifera* (bamboo) [12], rice husk [13], lalang (*Imperata cylindrica*) leaf powder [14] are being used as low-cost alternatives to expensive adsorbents.

Lignin is polyphenolic polymer extracted from black liquor [15], which is a waste from pulping process in the production of paper from EFB of oil palm. Black liquor produced is considered toxic and an unusable waste from the pulping and paper industry. Black liquor was found to consist of high amount of lignin. Colloidal lignin extracted into black liquor by alkali digestion of plant tissue can be precipitated when pH of liquor is made acidic. Lignin is a compound rich with functional groups, such as carbonyl, ether and hydroxyl [16]. Lignin has been used for metals adsorption by some researchers [17–20], however the potential of MSL extracted from EFB of oil palm for heavy metals adsorption has not been explored

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yet. This is a double edged enterprise that aims to overcome the problem related to the disposal of EFB in the palm oil refinery factory as well as to recycle the unwanted materials into a valuable product.

The aim of this paper is to assess the ability of MSL to adsorb lead (II) ions from aqueous solutions. The effect of contact time, pH of the solution, initial concentration and dosage of the adsorbents on the removal of lead (II) ions were studied. The adsorption isotherm and probable mechanism are explained and also try to find out the kinetics and order of reaction at the surface of the adsorbent.

2. Experimental materials and methods

2.1. Materials

The raw material used in this study consisted of oil palm empty fruit bunch long fiber supplied by Sabutek (M) Sdn. Bhd., Teluk Intan, Malaysia, a local company specializing in recycling oil palm lignocellulosic wastes. The EFB fiber was pulped in a 20 L stainless steel rotary digester unit together with 20% (w/v) NaOH (cooking liquor) for 3 h at a maximum cooking temperature of 170 °C. The mixture of cooking liquor to EFB fiber was in the ratio of 2:8 (v/w). Prior to the pulping process, the fiber was soaked in water for 2 days to remove dirt.

2.2. Preparation of soda lignin

The pH of black liquor was measured as 12.45 and its density was determined to be 0.987 g/mL. The soda lignin was precipitated from concentration black liquor by acidifying it to pH 2.0 using calculated amount of 20% (v/v) sulfuric acid. The precipitate was filtered and washed with distilled water at pH 2.0, which was prepared using the same acid as in the earlier step. The soda lignin was dried in an oven at 55 °C for 24 h.

2.3. Preparation of MSL

The modification of soda lignin was performed by mixing 10.0 g of soda lignin extracted from black liquor of oil palm EFB with 1.0 M of NaOH (500 mL). The mixture was stirred for 2 h at 80 °C. Then the mixture was cool at room temperature and continued stirred for 2 h. Then the MSL was precipitated from the mixture by acidifying it to pH 7.0 using 0.5 M of acetic acid. The precipitate was filtered and washed with distilled water at pH 7.0, which was prepared using the same acid as in the earlier step. The MSL was dried in an oven at 55 °C for 24 h. The MSL was then ground and sieved to a constant size (100–125 μm) before use.

2.4. Adsorbate solution

Stock solution (1000 mg/L) of lead (II) was prepared by dissolving lead 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).

2.5. SEM, FT-IR, XRF study and surface area analysis

Surface morphology was studied with Leo Supra 50 VP Field Emission Scanning Electron Microscope (Carl-Ziess SMT, Oberkochen, Germany). The various elements present in MSL were determined by energy dispersive X-ray analyzer (INCA-400 of Oxford Instruments Analytical, Bucks, UK). Fourier Transform Infrared (PerkinElmer FT-IR System 1600 Model) analysis was done on the MSL and lead (II) ions adsorbed MSL to determine the surface functional groups that might be involved in lead (II) ions adsorption

and the spectra were recorded from 4000 to 400 cm^{-1}. The chemical composition of MSL was determined by wavelength dispersion X-ray fluorescence analysis using Rigaku RIX 3000. The surface area of the MSL was measured by using a Micrometrics ASAP-2010 BET surface area analyzer.

2.6. Batch adsorption studies

Batch adsorption studies were carried out by shaking 0.5 g of MSL with 50 mL of the aqueous solutions of lead (II) ions in different conical flask using a temperature-controlled shaker. The solution–adsorbents mixtures were stirred at 250 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 (Analyst 200 AA, PerkinElmer, USA). The adsorption experiments were also conducted to determine the equilibrium time (5–360 min.), initial concentrations (5–100 ppm) and dosage of the adsorbent (0.02–1.0 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. The percentage of metal adsorption by the adsorbents was computed using the equation:

$$\% \text{ adsorption} = \left\{ \frac{C_i - C_e}{C_i} \right\} \times 100 \tag{1}$$

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

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

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

2.7. Point of zero charge (pH$_{PZC}$) and pH measurements

The pH of the aqueous slurry was determined by adding 1 g of MSL in 50 mL distilled water, stirred and the final pH was measured after 24 h. The pH was found 4.91. The determination of pH$_{PZC}$ of MSL was performed according to the solid addition method [21]: 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 6 by adding 0.1 M HCl or NaOH solutions. Then, 1 g of MSL was added to each flask, stirred and the final pH of the solutions was measured after 24 h. The value of pH$_{PZC}$ can be determined from the curve that cuts the pH$_0$ line of the plot ΔpH versus pH$_0$. The pH$_{PZC}$ of MSL was found 4.70.

2.8. Batch kinetic studies

The procedures of kinetic experiments were basically to those of equilibrium experiments. The aqueous solutions were taken at preset time intervals, and the concentration of lead (II) ions was similarly measured. The amount of adsorption at time t, was calculated by:

$$q_t = \frac{(C_i - C_t)V}{W} \tag{3}$$

where C_t (mg/L) is the concentration of lead (II) ions at any time.

2.9. Desorption experiments

For the desorption study, 0.08 g of MSL was in contacted with 100 mg L^{-1} of Pb (II) ions solution for 3 h. After adsorption experiment, MSL was collected by filtration and washed with distilled

water for three times to remove excess lead (II) ions. Then it was contacted with 50 mL of different concentrations (1×10^{-3}, 2×10^{-3}, 1×10^{-2}, 2×10^{-2}, 1×10^{-1}, 2×10^{-1} mol L^{-1}) of different desorbing solutions (HCl, HNO$_3$ and EDTA). The mixture was stirred at 400 rpm for 1 h, filtered and analyzed. A blank was also carried out in which distilled water was used for desorbing lead (II) ions. The experiment was carried out in triplicate to avoid any discrepancy in experimental results. The percentage of desorption (D_p) of lead (II) ions was calculated from the following expression:

$$D_p = \left(\frac{m_r}{m_0} \right) \times 100 \tag{4}$$

where m_r is the amount of lead (II) ions desorbed (mg) and m_0 is the amount of lead (II) ions adsorbed (mg).

3. Results and discussion

3.1. Characterization of MSL

Characteristics of MSL such as surface area, pore diameter, moisture content and ash content were determined. The BET surface area and Langmuir surface area were found to be 0.26 and 0.40 m^2 g^{-1}, respectively by using the nitrogen adsorption method. The influence of other properties on the extent of adsorption was evaluated by measuring the moisture content (1.92%) and ash content (16.5%). 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 157.23 Å, suggesting that MSL consists of mesopores.

The SEM micrographs of MSL before and after lead (II) ions adsorption are shown in Fig. 1(a) and (b). It is clear from the micrographs that MSL possesses a rough surface morphology, where there is a good possibility for lead (II) ions to be adsorbed. The surface of lead (II) ions treated adsorbent is different from the surface of natural adsorbent. The EDX study showed the elemental composition of MSL (Fig. 1(c)), which showed that MSL has a high percentage of carbon (60.20%) and oxygen (32.08%). Based on the particle morphology, the MSL seems to be suitable to be used as adsorbent. MSL is composed mainly of oxides such as Na$_2$O (1.4%), SiO$_2$ (0.19%), P$_2$O$_5$ (0.012%), K$_2$O (0.21%), Fe$_2$O$_3$ (0.013%), SO$_3$ (2.8%) and trace amount of MgO, Al$_2$O$_3$, CaO, CuO, ZnO, etc.

The FT-IR spectrum of MSL (Fig. 2) displays a number of absorption peaks indicating the presence of different types of functional groups. A wide absorption peak at 3408 cm^{-1} is assigned to aromatic and aliphatic OH groups while peaks at 2929 and 2850 cm^{-1} are related to the C–H vibration of CH$_3$ and CH$_2$ groups of side chains and aromatic methoxyl groups. The absorption peak at 1708 cm^{-1} assigned as unconjugated carbonyl vibration. Three strong absorption peaks at 1602, 1515 and 1462 cm^{-1} correspond to typical aromatic ring vibrations of the phenylpropane skeleton. The absorption peak at 1424 cm^{-1} shows aromatic methyl group vibrations. The absorption peaks at 1328 and 1217 cm^{-1} assigned to syringyl ring C–O stretching. The peaks observed at 1116 and 831 cm^{-1} corresponding to the presence of syringyl units [22,23]. The FT-IR spectrum for lead (II) ions loaded MSL shows intensity of the peaks were shifted slightly substantially lower than those in the MSL, suggesting the participation of these functional groups in the binding of lead (II) ions by MSL. The wave numbers of MSL shifted from 3408 to 3422 cm^{-1}, from 2929 to 2934 cm^{-1} after lead (II) ions adsorption (Fig. 2), these decreases were attributed to aromatic and aliphatic OH groups participating in lead (II) ions adsorption onto MSL.
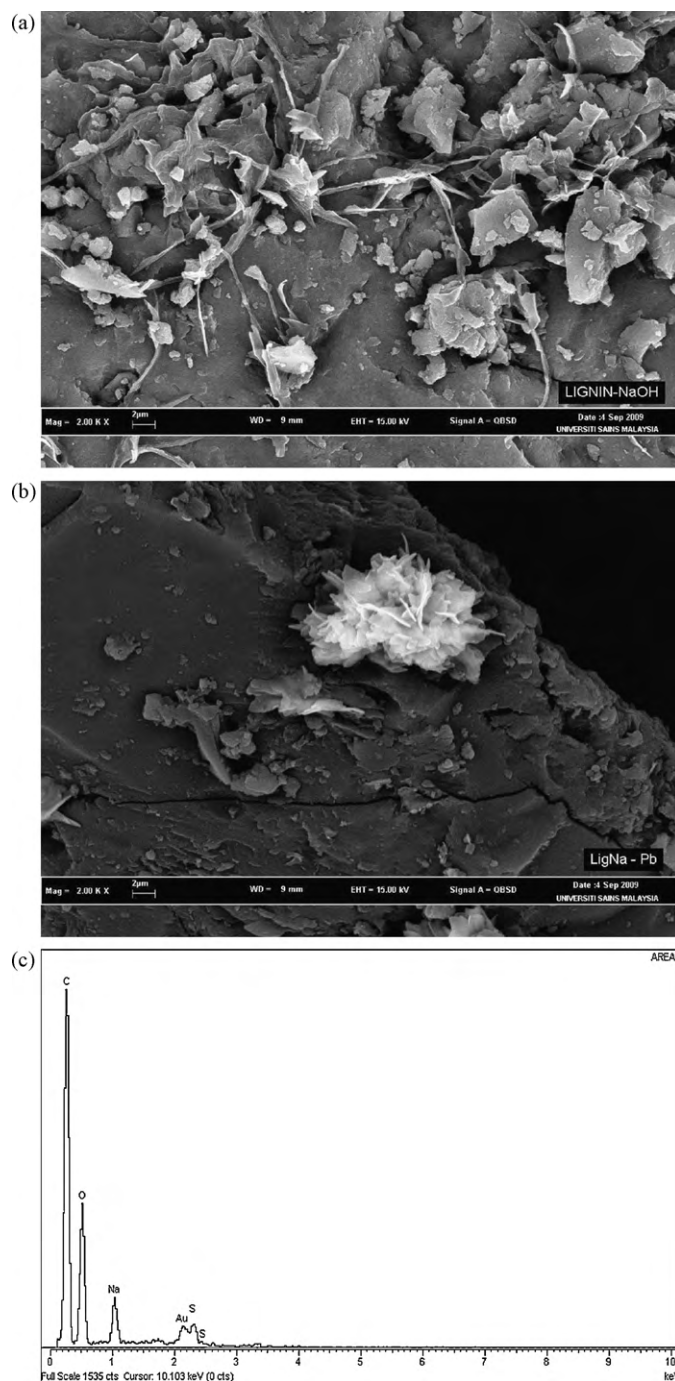

Fig. 1. SEM micrograph of MSL (magnification, 2000×): (a) before adsorption, (b) after adsorption and (c) EDX spectra of MSL.

3.2. Effect of contact time and initial metal concentration

The effect of contact time on the adsorption capacity of lead (II) ions at different initial concentrations is shown in Fig. 3. It shows that the adsorption of lead (II) ions 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. Based on the results, the contact time was fixed at 60 min for the rest of batch experiments to ensure that the equilibrium was reached. A similar result was also observed for the removal of cadmium (II) and
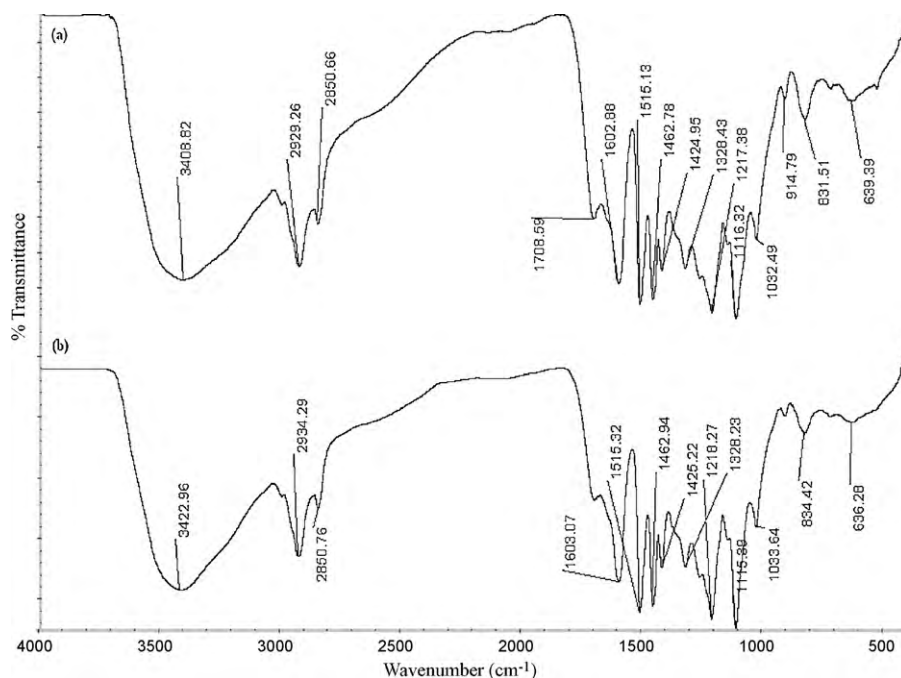
Fig. 2. FT-IR of MSL: (a) before adsorption and (b) after adsorption.

lead (II) ions from aqueous solutions by adsorption onto sawdust of *Pinus sylvestris* [7]. Fig. 3 also shows the amount of lead (II) ions adsorbed per unit mass of adsorbent increased with the increase in initial concentration. The amount of lead (II) ions adsorbed at equilibrium increased from 2.47 to 21.54 mg/g as the initial concentration was increased from 5 to 100 ppm. The initial heavy metals concentration provides an important driving force to overcome the mass transfer resistance of heavy metals ions between the aqueous and solid phases, and therefore, a higher initial metal concentration will enhance the rate of adsorption.

3.3. Point of zero charge (pH_{PZC}) measurements and effect of pH

The 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. The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. The effect of pH on the adsorption of lead (II) ions on MSL has been studied by varying it in the ranges of 2.0–6.0 as shown in Fig. 4. As shown in Fig. 4, the uptake of lead (II) ions depends on pH, at low pH value of 2.0, MSL adsorbed low amount of lead (II) ions. When the initial pH of the lead (II) ions solution was increased, the adsorption capacity was increased as well. Sharp increment in adsorption capacity was observed from pH 2.0 to 3.0, indicating that more Pb (II) ions were adsorbed on MSL at higher pH values. The adsorption capacity then continued with a small increment at pH 3.0–5.0 and reached a plateau at pH 5.0–6.0. The optimum pH for adsorption of Pb (II) was recorded at pH 5.0. Above this pH a slow decrease in the sorption of metal ion was observed. The lead (II) ions in aqueous solution may
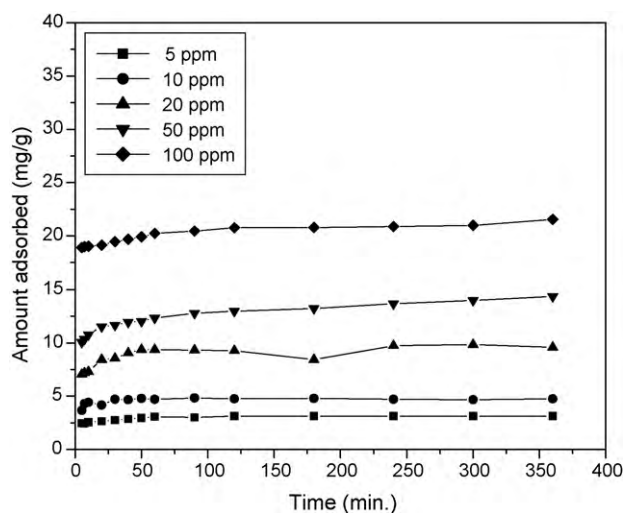

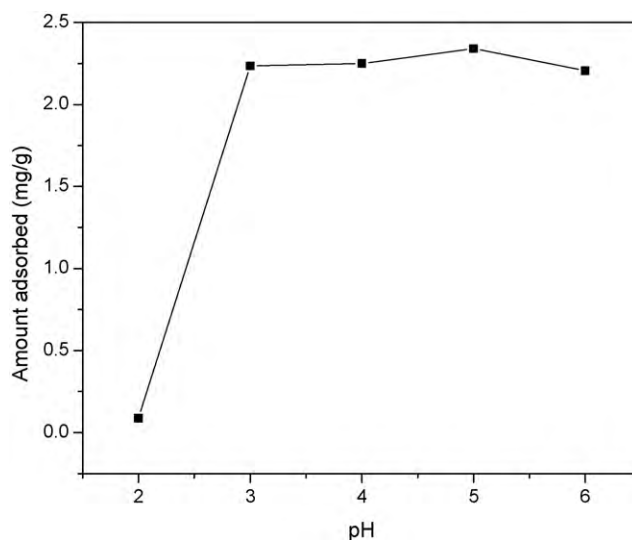**Fig. 3.** Effect of contact time and initial concentration of lead (II) ions adsorption.

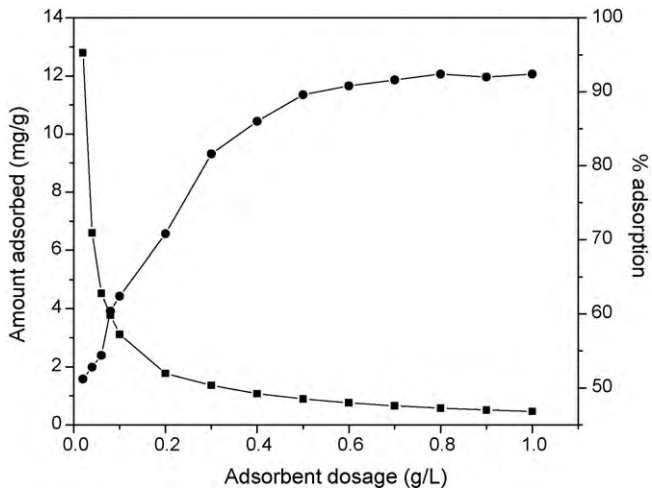**Fig. 4.** Effect of the solution pH on lead (II) ions adsorption.

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

Fig. 6. Effect of particle size on lead (II) adsorption.

undergo solvation, hydrolysis and polymerization. Lead (II) ions can form several hydrolysis products, which exist under different conditions [24,25]. In dilute aqueous solutions of pH less than 6, lead ions exist as Pb^{2+} or $Pb(OH)^+$ or both, whereas the formation of Pb^{2+} hydrolysis products occur at pH greater than 6.0 which might lead to its polymerization. Due to this reason all the experiments were carried out at pH 5. A similar phenomenon was observed for the biosorption of lead from aqueous solutions by *M. oleifera* bark [4].

3.4. Effect of adsorbent dosage

Fig. 5 shows the adsorption of lead (II) ions by MSL at different dosage of adsorbent (0.02–1.0 g) at initial concentration of 100 ppm metal solution at 27 °C. When the adsorbent dosage was increased from 0.02 to 1.0 g, 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 0.3 g, the decrease in lead (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. Adsorption increased from 51.2 to 92.4% with increase in adsorbent dose. Maximum removal of lead (II) ions was observed with an adsorbent dose of 0.8 g and there after a slow increase in the percentage removal was seen reaching a constant value with respect to the adsorbent dosage.

3.5. Effect of particle size

The batch adsorption experiments were carried out using five different particle sizes, 53–75, 75–100, 100–125, 125–150 and 150–200 μm at pH 5 with an adsorbent dose of 0.5 g/50 mL, shaking time 60 min at 27 °C. Fig. 6 shows the amount of lead (II) ions adsorbed per unit mass of MSL increased with the decrease in particle size. Increases the particle sizes are contributed to less availability of surface area to form binding and then decrease the uptake of lead (II) ions adsorption onto MSL. The MSL of particle size 100–125 μm was selected for adsorption studies due to the sufficient adsorption capacity and easiness of its preparation. Moreover, the lower particle size 53–100 μm has good adsorption capacity but it is very difficult to prepare the MSL of this particle size and require a lot of labor.
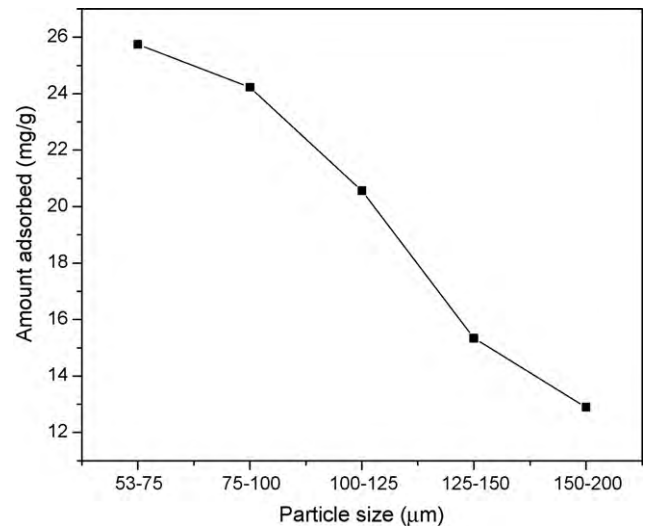
3.6. Adsorption isotherm studies

To quantify the adsorption capacity of MSL for the removal of lead (II) ions from aqueous solutions, the Langmuir, Freundlich and Temkin isotherm models were used at different temperatures.

3.6.1. 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 [26]. The data of the equilibrium studies for adsorption of lead (II) ions onto MSL may follow the following form of Langmuir model:

$$\frac{C_e}{q_e} = \left(\frac{1}{b}\right)\left(\frac{1}{K_L}\right) + \left(\frac{1}{b}\right)(C_e) \tag{5}$$

where C_e is the equilibrium concentration (mg/L) and q_e 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 C_e/q_e versus C_e should be a straight line with a slope $(1/b)$ and an intercept as $(1/bK_L)$ as shown in Fig. 7. The Langmuir type adsorption isotherm indicates surface homogeneity of the adsorbent and hint towards
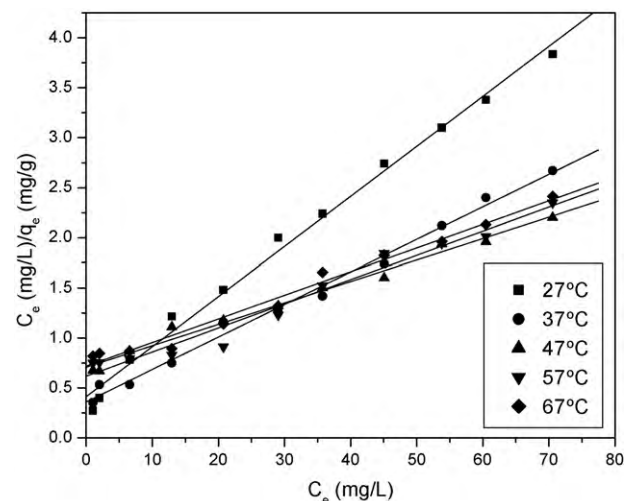

Fig. 7. Langmuir isotherm plots for lead (II) ions adsorption at different temperatures.

Table 1
The related parameters for the adsorption of lead (II) ions on MSL at different temperatures.

Adsorption isotherms and its constants	Temperatures (°C)				
	27	37	47	57	67
Langmuir adsorption isotherm constants					
b (mg/g)	20.00	30.76	46.72	41.49	42.37
K_L (L/mg)	0.120	0.090	0.030	0.038	0.032
R^2	0.992	0.991	0.985	0.969	0.984
Freundlich adsorption isotherm constants					
K_F (mg/g) (L/mg)$^{1/n}$	1.804	1.628	1.597	1.567	1.483
n	2.766	1.640	1.890	2.712	2.975
R^2	0.962	0.984	0.987	0.896	0.935
Temkin adsorption isotherm constants					
K_T (L/mg)	0.605	0.366	0.238	0.197	0.186
B	1.070	1.172	1.055	1.007	1.050
R^2	0.979	0.928	0.987	0.988	0.948

the conclusion that the surface of adsorbent is made up of small adsorption patches which are energetically equivalent to each other in respect to adsorption phenomenon. The correlation coefficient (R^2) values of 0.969–0.992 indicated that the adsorption data of lead (II) ions onto MSL was well fitted to the Langmuir isotherm. The values of constants K_L and b were calculated and reported in Table 1.

3.6.2. Freundlich model

The Freundlich model can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer adsorption [27]. According to this model:

$$q_e = (K_F)(C_e^{1/n}) \tag{6}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

where K_F is Freundlich equilibrium constant, n is an empirical constant and rest of the terms have the usual significance. Thus, a plot of $\ln q_e$ versus $\ln C_e$ should be a straight line with a slope $1/n$ and an intercept of $\ln K_F$ as shown in Fig. 8. The related parameters were calculated and reported in Table 1.

3.6.3. Temkin model

Temkin and Pyzhev [28], considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The Temkin isotherm has been used in the form as follows:

$$q_e = \left(\frac{RT}{b}\right) \ln(K_T C_e) \tag{8}$$

This equation can be expressed in its linear form as

$$q_e = B \ln K_T + B \ln C_e \tag{9}$$

where $B = (RT/b)$, a plot of q_e versus $\ln C_e$ yielded a linear line, as shown in Fig. 9, enables 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. 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 1.

From Table 1, the Langmuir adsorption isotherm model yielded best fit as indicated by the highest R^2 values at all temperatures compared to the Freundlich and Temkin adsorption isotherm models. Table 2 lists a comparison of maximum monolayer adsorption capacity of lead (II) ions on various waste adsorbents. MSL from EFB is found to have a relatively large adsorption capacity of 46.72 mg/g at 47 °C and this indicates that it could be considered a promising material for the removal of lead (II) ions from aqueous solutions.
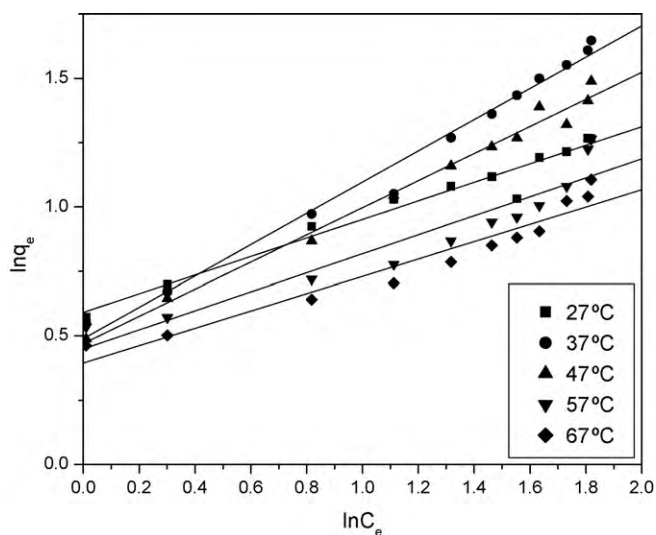

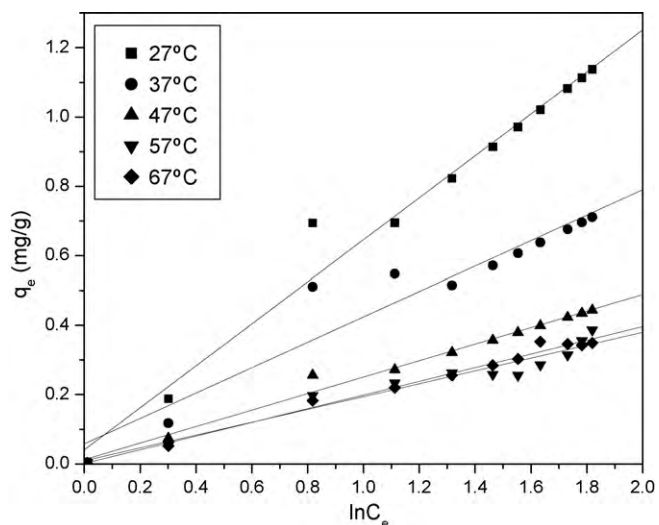**Fig. 8.** Freundlich isotherm plots for lead (II) ions adsorption at different temperatures.

Fig. 9. Temkin isotherm plots for lead (II) ions adsorption at different temperatures.

Table 2
Comparison of adsorption capacities of various adsorbents for lead (II) ions.

Adsorbents	Maximum monolayer adsorption capacity (mg/g)	References
MSL from EFB	46.72	This study
Meranti sawdust	34.24	[5]
Rolling mill scale	02.74	[6]
Blast furnace sludge	79.87	[6]
Bagasse flyash	02.50	[8]
Rubber leaf powder	46.73	[9]
Saraca indica leaf powder	01.19	[10]
Tree fern	40.00	[11]
Lignin from woods	08.20–09.00	[17]
Corncobs	08.29	[29]
Bentonite	07.56	[30]
Activated carbon	06.68	[30]
Blast Furnace slag	05.52	[30]
Fly ash	04.98	[30]
Kaolin	04.50	[30]

3.7. Kinetic studies

The modeling of the kinetics of adsorption of lead (II) ions on MSL was investigated by two common models, namely, pseudo-first-order model and pseudo-second-order model. The conformity between experimental data and the model predicted values was expressed by correlation coefficient (R^2).

3.7.1. Pseudo-first-order model

The pseudo-first order rate model of Lagergren [31] is based on solid capacity and generally expressed as follows:

$$\log(q_e - q) = \log(q_e) - \left(\frac{k_1}{2.303}\right) t \tag{10}$$

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. This is the most popular form of pseudo-first-order kinetic model. Values of k_1 at different temperature were calculated from the plots of $\log(q_e - q)$ versus t (Fig. 10) for lead (II) ions. Constant k_1 and correlation coefficients (R^2) have been calculated and summarized in Table 3. The correlation coefficients (R^2) values obtained were relatively low, it showed that this model have very poor correlation coefficients (R^2) for best fits data.
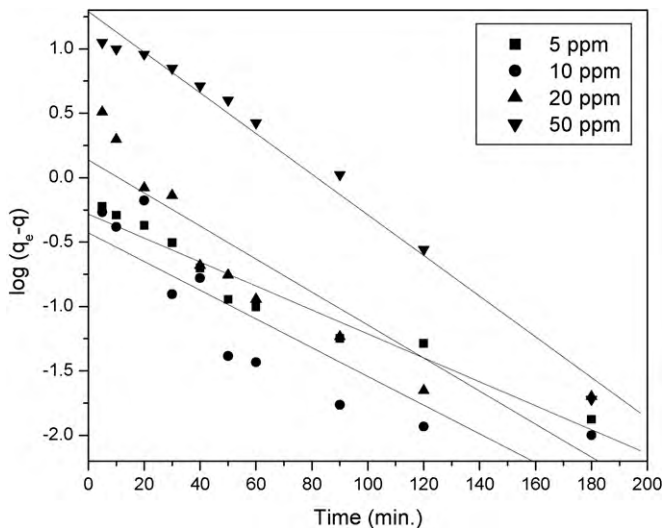
Table 3
Pseudo-first-order and pseudo-second-order models for the adsorption of lead (II) ions onto MSL.

Kinetic models and its parameters	Initial concentrations (ppm)			
	5	10	20	50
$q_{e,exp}$ (mg/g)	3.070	4.083	5.231	6.034
Pseudo-first-order kinetic model				
q_e (mg/g)	0.521	0.374	1.373	19.52
k_1 (min^{-1})	0.021	0.025	0.029	0.036
R^2	0.946	0.786	0.837	0.982
Pseudo-second-order kinetic model				
q_e (mg/g)	3.178	4.826	5.411	6.238
k_2 (g mg^{-1} min^{-1})	0.304	0.849	2.659	1.157
h (mg g^{-1} min^{-1})	3.070	19.77	77.85	45.02
R^2	0.999	0.999	0.981	0.989

3.7.2. Pseudo-second-order model

The kinetic data were analyzed using the pseudo-second-order model [32] which, can be expressed as:

$$\frac{t}{q} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t \tag{11}$$

$$h = k_2 q_e^2 \tag{12}$$

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. 11). The k_2 and q_e determined from the model are presented in Table 3 along with the corresponding correlation coefficient (R^2) values. The values of the calculated and experimental q_e are presented in Table 3. It can be seen from this table that the adsorption of lead (II) ions perfectly follow the pseudo-second-order kinetic model.

3.8. Ion-exchange mechanism

The existence of ion-exchange mechanism during the lead (II) ions sorption by MSL from EFB was investigated in this work by following the release of Ca^{2+}, Mg^{2+}, K$^+$, H$^+$ and Na$^+$ from this material after the sorption of lead (II) ions. For this study, 0.10 g MSL was mixed with 50 mL, 100 ppm of lead (II) ions solution at pH 5.0. The mixture were stirred for 1 h and the final pH of the solution found to be lower than the initial pH, which indicates that H$^+$ ions were also exchanged with lead ions. The net release of Ca^{2+}, Mg^{2+}, K$^+$, H$^+$
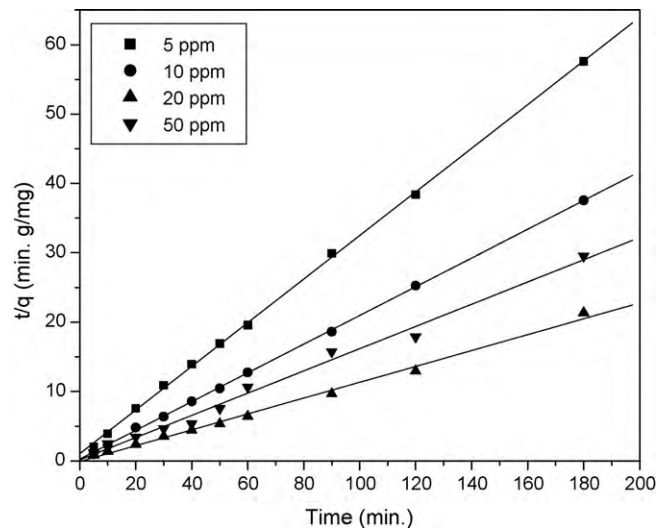

Fig. 10. Pseudo-first-order kinetic plots for lead (II) ions adsorption onto MSL.

Fig. 11. Pseudo-second-order kinetic plots for lead (II) ions adsorption onto MSL.

Table 4
Amount of Ca^{2+}, Mg^{2+}, Na^+, K^+ and H^+ release due to adsorption of lead (II) ions.

System	Total Pb^{2+} (mmol/L)	$[Ca^{2+}]$ (mmol/L)	$[Mg^{2+}]$ (mmol/L)	$[K^+]$ (mmol/L)	$[Na^+]$ (mmol/L)	$[H^+]$ (mmol/L)	$R_{b/r}$
Blank	0.000	0.022	0.007	0.135	3.915	0.148	
MSL with Pb^{2+}	0.038	0.039	0.012	0.148	4.024	0.066	0.904

Table 5
Desorption of MSL by HNO_3, HCl and EDTA as desorbing solution at various concentrations.

Desorbing solution	Concentration (mol/L)	Desorption (%) MSL
HNO_3	1×10^{-3}	46.00
	2×10^{-3}	57.00
	1×10^{-2}	81.00
	2×10^{-2}	72.50
	1×10^{-1}	86.50
	2×10^{-1}	95.00
HCl	1×10^{-3}	26.00
	2×10^{-3}	40.50
	1×10^{-2}	66.50
	2×10^{-2}	69.00
	1×10^{-1}	83.50
	2×10^{-1}	79.50
EDTA	1×10^{-3}	32.50
	2×10^{-3}	21.50
	1×10^{-2}	37.50
	2×10^{-2}	34.50
	1×10^{-1}	90.00
	2×10^{-1}	90.50

and Na^+ due to the adsorption process was calculated by subtracting the amount of cations released from blanks from the amount of cations measured in the effluent after lead (II) adsorption.

The ion-exchange mechanism is given by the $R_{b/r}$ ratio [17]:

$$R_{b/r} = \frac{[Pb^{2+}]}{[Ca^{2+}]} + [Mg^{2+}] + \left[\frac{K^+}{2}\right] + \left[\frac{Na^+}{2}\right] + [H^+] \tag{13}$$

The concentration of cations is expressed in m mol/L. If the $R_{b/r}$ ratio is equal to 1, this is an indication that ion-exchange is a predominant mechanism [33]. Based on Table 4, the calculated value of $R_{b/r}$ is 0.904 which is close to 1. It suggests that the ion-exchange is another mechanism involved in the removal of lead (II) ions on MSL as well as complexation reaction.

3.9. Desorption study

The desorption studies help to elucidate the behaviour of adsorption, the recovery of lead (II) ions from aqueous solutions, recycling of the adsorbent and practical applications of treatment of industrial effluent. As the concentration of desorbing solutions (HCl, HNO_3 and EDTA) increases, more lead (II) ions were able to be desorbed. As shown in Table 5, more than 80% of lead (II) ions were able to be desorbed from MSL using 0.02 mol/L HCl, HNO_3 and EDTA solutions. This result showed that the test adsorbent could be reused without significant losses in its initial adsorption capacity.

4. Conclusion

The results obtained show that the modified soda lignin from oil palm empty fruit bunches, an abundantly available agricultural waste, can be used for the removal of lead (II) ions from aqueous solution. The amount of lead (II) ions uptake (mg/g) was found to increase with increase in contact time, pH and initial metal ion concentration. Equilibrium data fitted very well in the Langmuir isotherm equation, confirming the monolayer adsorption capacity of lead (II) ions onto MSL with a monolayer adsorption capacity of

46.72 mg/g at 47 °C. The rate of adsorption was found to conform to pseudo-second-order kinetics with a good correlation. These results demonstrate the MSL from oil palm empty fruit bunches is expected to be economically feasible for the removal of lead (II) ions from aqueous solutions.

References

[1] B.L. Carson, H. Vellis, J.L. McCann, Toxicology and Biological Monitoring of Metals in Humans, Lewis Publisher, Michigan, 1986.
[2] B.M. Richard, Heavy Metals, Introduction to Environmental Toxicology, Elsevier, New York, 1980.
[3] A. Ahmad, M. Rafatullah, O. Sulaiman, M.H. Ibrahim, Y.Y. Chii, B.M. Siddique, Removal of Cu(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of meranti wood, Desalination 247 (2009) 636–646.
[4] D.H.K. Reddy, K. Seshaiah, A.V.R. Reddy, M.M. Rao, M.C. Wang, Biosorption of Pb^{2+} from aqueous solutions by *Moringa oleifera* bark: equilibrium and kinetic studies, J. Hazard. Mater. 174 (2010) 831–838.
[5] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust, J. Hazard. Mater. 170 (2009) 969–977.
[6] M.I. Martín, F.A. López, C. Pérez, A. López-Delgado, F.J. Alguacil, Adsorption of heavy metals from aqueous solutions with by-products of the steelmaking industry, J. Chem. Technol. Biotechnol. 80 (2005) 1223–1229.
[7] M.I. Martiĭn, F.A. Loĭpez, F.J. Alguacil, Possibility of using by-products of the steelmaking industry for removing lead from aqueous solutions, Revista de Metalurgia 44 (2008) 258–264.
[8] V.K. Gupta, I. Ali, Removal of lead and chromium from wastewater using bagasse fly ash-a sugar industry waste, J. Colloid Interface Sci. 271 (2004) 321–328.
[9] M.A.K.M. Hanafiah, W.S.W. Ngah, S.C. Ibrahim, H. Zakaria, W.A.H.W. Ilias, Kinetics and thermodynamic study of lead adsorption onto rubber (*Hevea brasiliensis*) leaf powder, J. Appl. Sci. 6 (2006) 2762–2767.
[10] P. Goyal, P. Sharma, S. Srivastava, M.M. Srivastava, *Saraca indica* leaf powder for decontamination of lead: removal, recovery, adsorbent characterization and equilibrium modeling, Int. J. Environ. Sci. Technol. 5 (2008) 27–34.
[11] Y.S. Ho, W.T. Chiu, C.S. Hsu, C.T. Huang, Sorption of lead ions from aqueous solution using tree fern as a sorbent, Hydrometallurgy 73 (2004) 55–61.
[12] H. Lalhruaitluanga, K. Jayaram, M.N.V. Prasad, K.K. Kumar, Lead(II) adsorption from aqueous solutions by raw and activated charcoals of *Melocanna baccifera* Roxburgh (bamboo)—a comparative study, J. Hazard. Mater. 175 (2010) 311–318.
[13] M. Akhtar, S. Iqbal, A. Kausar, M.I. Bhanger, M.A. Shaheen, An economically viable method for the removal of selected divalent metal ions from aqueous solutions using activated rice husk, Colloids Surf. B: Biointerfaces 75 (2010) 149–155.
[14] M.A.K.M. Hanafiah, W.S.W. Ngah, H. Zakaria, S.C. Ibrahim, Batch study of liquid-phase adsorption of lead ions using lalang (*Imperata cylindrica*) leaf powder, J. Biol. Sci. 7 (2007) 222–230.
[15] R. Sun, J. Tomkinson, G.L. Jones, Fractional characterization of ash-AQ lignin by successive extraction with organic solvents from oil palm EFB fibre, Polym. Degrad. Stabil. 68 (2000) 111–119.
[16] K.V. Sarkanen, C.H. Ludwig, Lignins: Occurrence, Formation, Structure and Reactions, Wiley-Interscience, New York, 1971.
[17] A. Demirbas, Adsorption of lead and cadmium ions in aqueous solutions onto modified lignin from alkali glycerol delignication, J. Hazard. Mater. 109 (2004) 221–226.
[18] X. Guo, S. Zhangand, X. Shan, Adsorption of metal ions on lignin, J. Hazard. Mater. 151 (2008) 134–142.
[19] H. Harmita, K.G. Karthikeyan, X.J. Pan, Copper and cadmium sorption onto kraft and organosolv lignins, Bioresour. Technol. 100 (2008) 6183–6191.
[20] Y. Wu, S. Zhang, X. Guo, H. Huang, Adsorption of chromium(III) on lignin, Bioresour. Technol. 99 (2008) 7709–7715.

[21] L.S. Balistrieri, J.W. Murray, The surface chemistry of goethite (α-FeOOH) in major ion seawater, Am. J. Sci. 281 (1981) 788–806.

[22] D. Ibarra, J.C. del Río, A. Gutiérre, I.M. Rodríguez, J. Romero, M.J. Martínez, A.J. Martínez, Chemical characterization of residual lignins from eucalypt paper pulps, J. Anal. Appl. Pyrol. 74 (2005) 116–122.

[23] A. Tejado, C. Pena, J. Labidi, J.M. Echeverria, I. Mondragon, Chemical characterization of lignins from different sources for use in phenol–formaldehyde resin synthesis, Bioresour. Technol. 98 (2007) 1655–1663.

[24] V. Gomez-Serrano, A. Macias-Garcia, A. Espinosa-Mansilla, C. Valenzuella-Calahorro, Adsorption of mercury, cadmium and lead from aqueous solution on heat-treated and sulphurized activated carbon, Water Res. 32 (1998) 1–4.

[25] J. Burgess, Metal Ions in Solution, Ellis Horwood, Chichester, 1978.

[26] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (9) (1918) 1361–1403.

[27] H. Freundlich, Ueber die adsorption in Loesungen, Z. Phys. Chem. 57 (1907) 385–470.

[28] M.J. Temkin, V. Pyzhev, Recent modifications to Langmuir isotherms, Acta Physiochim. USSR 12 (1940) 217–222.

[29] R. Zacaria, Adsorption of several metal ions onto low-cost biosorbents: kinetic and equilibrium studies, Environ. Sci. Technol. 36 (2002) 2067–2073.

[30] P.C. Mishra, R.K. Patel, Removal of lead and zinc ions from water by low cost adsorbents, J. Hazard. Mater. 168 (2009) 319–325.

[31] S. Lagergren, About the theory of so called adsorption of soluble substances, kungliga Svenska Vetenskapsakademiens, Handlingar, Band 24, No. 04 (1898) 1–39.

[32] Y.S. Ho, J.C.Y. Ng, G. Mckay, Kinetics of pollutants sorption by biosorbents: review, Sep. Purif. Methods 29 (2000) 189–232.

[33] N. Fiol, I. Villaescusa, M. Martinez, N. Miralles, J. Poch, J. Serarols, Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste, Sep. Purif. Technol. 50 (2006) 132–140.