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Batch and fixed-bed column techniques for removal of Cu(II) and Fe(III) using carbohydrate natural polymer modified complexing agents

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ABSTRACT

Wood sawdust, a by-product of the world industry, is a low cost and promising industrial waste with cellulose–lignin polymeric structure. Its sorption properties after physical loading with Alizarin Red S (phase I) and Eriochrome Black T (phase II) for the removal of Fe(III) and Cu(II) under variable conditions of solution pH, contact times, weight of phase and concentration of the metal ion were investigated. Scanning electron microscope and Fourier transfer infrared spectra of phases before and after uptake of Fe(III) and Cu(II) were recorded to characterize the nature of the functional groups responsible for binding of these metal ions onto the studied modified polymers. Their equilibrium data were fitted with a Langmuir model. The adsorption kinetics data were best fitted with the pseudo-second-order. As a view to find a suitable application of phase I it was found that, Fe(III) in natural water samples were quantitatively recovered using column experiments.

1. Introduction

The release of heavy metals into our environment is still large. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. It is well known that some metals can have poisonous or otherwise harmful effects on many forms of life (Yu, Zhang, Shukla, & Doris, 2000). Heavy metals do not degrade into harmless end products in the metabolism and they are accumulated in the food chain water–plants–animals–humans (Gupta, Gupta, & Sharma, 2001; Shukla & Pai, 2005a) thereby posing the greatest threat to the living organisms. The numerous metals, which are significantly toxic to human beings and ecological environments, including, copper, iron, nickel, lead, etc. (Shukla & Pai, 2005a, 2005b). Copper is present in the wastewater of several industries such as metal cleaning and platting paths, refiners, paper and pulp, fertilizer, and wood preservatives (Gundogan, Acemioglu, & Alma, 2004; Kamaria & Ngah, 2009). The extensive intake of the copper by mans leads to severe mucosal irritation, hepatic and renal damage, muscle ache, hemolytic and heart failure (Kamaria & Ngah, 2009). On the other hand, taking into consideration the important role played by iron(III) in biological systems, it was found that, cells use iron catalytically in many important and diverse reactions, e.g., electron transport, nitrogen fixation, detoxification, etc. Its bioavailability depends on its redox state and the pH, some microorganisms are able to use ferric ion as an electron acceptor in anaerobic respiration (Malki et al., 2006). However, if it is in excess, it can also play an important role in the progression of several types of damage to the human body, so maintaining a balance of Fe(III) in the body is essential to human health. There are many treatment processes that can be used for the removal of metal ions from aqueous, and, certainly, the cost plays an important, if not crucial, role for determining which one is to be applied. These include chemical precipitation (Esalah, Weber, & Vera, 2000), floatation (Zouboulis, Matis, Lanara, & Neskovic, 1997), biosorption (Sag, Akcael, & Kutsal, 2002), electrolytic recovery, membrane separation (Canet, Ilpide, & Seta, 2002), activated carbon adsorption (Toles & Marshall, 2002), liquid–liquid extraction (LLE) and solid phase extraction (SPE) techniques (Farajzadeh, Bahram, Zorita, & Mehr, 2009; Soliman & Ahmed, 2009; Soliman & Ahmed, 2010), etc. In fact SPE has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes. It has several advantages over other techniques, including stability and reusability of the solid phase, reach of high preconcentration factors, easiness of separation and enrichment under dynamic conditions, no need for organic solvents and minimal costs due to low consumption of reagents. In this context, adsorption with activated carbon, for example, could be highly efficient for the removal of numerous trace elements from water, but the high cost of activated carbon inhibits its large-scale use as adsorbent. Then, the need for effective and economical removal of unwanted materials resulted in a research for unconventional methods and materials that might be useful in this field. Scien-

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tists have, therefore, centred their interest on cheaper materials like natural products/biological wastes for metal ion adsorption (Argun, Dursun, Ozdemir, & Karatas, 2007; Gerente, Mensil, Andres, Thibault, & Cloiree, 2000; Zhu, Fan & Zhang, 2008). The most popular adsorbents among them are biopolymers, such as agricultural wastes (Shukla & Pai, 2005b). They are available in large quantities and have a low price and has a good mechanical stability like sugar cane bagasse (Garg, Kaur, Jawa, Sud, & Garg, 2008), sugar beat pulp (Reddad et al., 2002), and different low cost adsorbents (Ngah & Hanafiah, 2008). Moreover, the utility of popular wood-sawdust in removing heavy metal ions from wastewater was examined. Wood sawdust, a solid waste product obtained from mechanical wood processing, can be used as a low cost adsorbent of heavy metals (Wahab, Jellali, & Jedidi, 2010), largely due to its lignocellulosic composition. It is mainly composed of cellulose (45–50%) and lignin (23–30%), both with a capacity for binding metal cations due to hydroxyl, carboxylic and phenolic groups present in their structure (Sciban, Radetic, Kevresan, & Klasnja, 2007). The cellulosic biomaterials when loaded covalently by specific dyestuffs give an enhancement in their adsorptive capacity for metal ions (Shukla & Pai, 2005a, 2005b). So, there are different applications in different research aspects using modified wood-sawdust for removal or recovery of different metal ions from aqueous solutions (Godea, Atalay, & Pehlivan, 2008; Pereira, Gurgel, & Gil, 2010).

The main objective of this paper is to employ, a simple and direct extraction method, SPE and low cost adsorbent, wood sawdust after its modification with Alizarin Red S and Eriochrome Black T for the removal of Fe(III) and Cu(II) ions from aqueous solutions using both batch and fixed bed column techniques.

2. Experimental

2.1. Materials

The origin of the wood used is scots pine. It is a typical and well-known softwood type. The scots pine (*Pinus sylvestris*) tree is a species of pine. Alizarin Red S dye and Eriochrome Black T were purchased from Aldrich Chemical Company, USA. Organic solvents used were of spectroscopic grade. ACS reagent grade concentrated HCl and sodium hydroxide were obtained from Aldrich and used for justifying the pH values. Samples of Nile River water, drinking tap-water, natural drinking-water and doubly distilled waters were collected from El-Minia City, Egypt. All experimental work used distilled water from running distilled water at lab.

2.2. Apparatus

The FT-IR-spectra of the phases before and after metal-ion sorption were obtained from KBr pellets by using FT/IR (model 410) JASCO (Japan). SEM analysis obtained using JSM-5400 LV JEOL (Japan). A Fisher Scientific Accumet pH-meter (Model 825) calibrated against two standard buffer solutions at pH 4.0 and 9.2 were used for all pH measurements. Atomic absorption measurements were performed with Aquanova-Genway spectrometry.

2.3. Synthesis of wood sawdust physically loaded Alizarin Red S (WS-A, phase I) and wood sawdust physically loaded Eriochrome Black T (WS-E, phases II)

WS-A, phase I was prepared by reflux of 5.0 g wood sawdust (WS) with 1 mmole of Alizarin Red S monohydrate dye with mixture of ethanol and water (20/80, v/v) refluxed for at least 4 h, cooled, filtered, washed with doubly distilled water and dried in oven at 50 °C. On the other hand, WS-E, phase II can be prepared as follows: 1.0 g wood sawdust was impregnated in 0.5 mmole of Eriochrome Black T in mixture of ethanol and triethanolamine for 12 h. After repeating decantation and filtration, the modified wood sawdust washed with deionized water until pH value of the solutions reached 7.0 then dried in oven 40–50 °C.

2.4. Sorption measurements using batch method

The metal uptake capacities of wood sawdust and its new modified phases (I and II) towards: Fe(III) and Cu(II) ions were determined in triplicate under static conditions by the batch equilibrium technique. Metal chloride solutions were prepared in 0.1 M hydrochloric acid to avoid hydrolysis. Then, 300.0 and 200.0 mg of each of phases I and II, respectively was added to a mixture of 1.0 ml of 0.1 M of the metal ion; the total volume was completed to 50 ml by doubly distilled water in a 100 ml measuring flask with justifying the pH values using 0.1 N HCl and NaOH to cover the pH range 1.0–4.0 for Fe(III) and 1.0–8.0 for Cu(II). This mixture was mechanically shaken for different time intervals at room temperature to attain equilibrium. Then, the solid phase was separated by filtration, and washed with doubly distilled water; the unretained metal ion in the filtrate was determined by complexometric ethylenediaminetetraacetic acid titration (Soliman & Ahmed, 2010).

2.5. Sorption measurements using column method

A glass column of 30 cm length and 2 cm internal diameter was used. A small piece of glass wool was placed at the bottom of the column and above the known quantity of the phase. Fe(III) and Cu(II) solutions with initial concentration of 0.001 M were allowed to flow downward through the column at a specific flow rate. Samples were collected from the outlet of the column at different time intervals and analyzed for metal ion concentration. The experiment was terminated when the concentration of the metal ion at the outlet of the column equals the initial concentration of Fe(III) and Cu(II).

2.6. Stability studies

2.6.1. Effect of buffer treatment on the stability of wood sawdust phases

The effect of medium on the stability of WS-A, phases I and WS-E, phase II was investigated in pH 1.0–10.0 under static conditions (Soliman, Saleh, & Ahmed, 2004). In this study, 500 mg of each of the phase was impregnated with 25 ml of the selected buffer in 50 ml measuring flask for 10 h, then mechanically shaken for another 60 min. The phase was separated by filtration, washed and dried. To show the extent of decomposition or hydrolysis of the modified chelate on a wood sawdust surface (i.e. stability of the phase), 300.0 and 200.0 mg of each of phases I and II, respectively of medium treated phases along with an untreated one taken as the standard, were used to evaluate the Fe(III) and Cu(II) ions sorption capacity under the same conditions as previously described for batch experiments and the pH of the highest uptake and then comparing the Fe(III) and Cu(II) uptake values obtained with that of the standard untreated one.

3. Results and discussion

3.1. Characterization of wood sawdust phases

The surface morphology of phase I and phase II were analyzed using a scanning electron microscope before and after Fe(III) and copper (II) ions sorption (Fig. 1). The microphotographs before metal ions sorption revealed clearly smooth and even surface has wide thickness between fibres (Fig. 1(a) and (b)). After Fe(III) and Cu(II) sorption the micrographs revealed the presence of more dense and rough surface with narrow thickness (Fig. 1(c) and (d)).

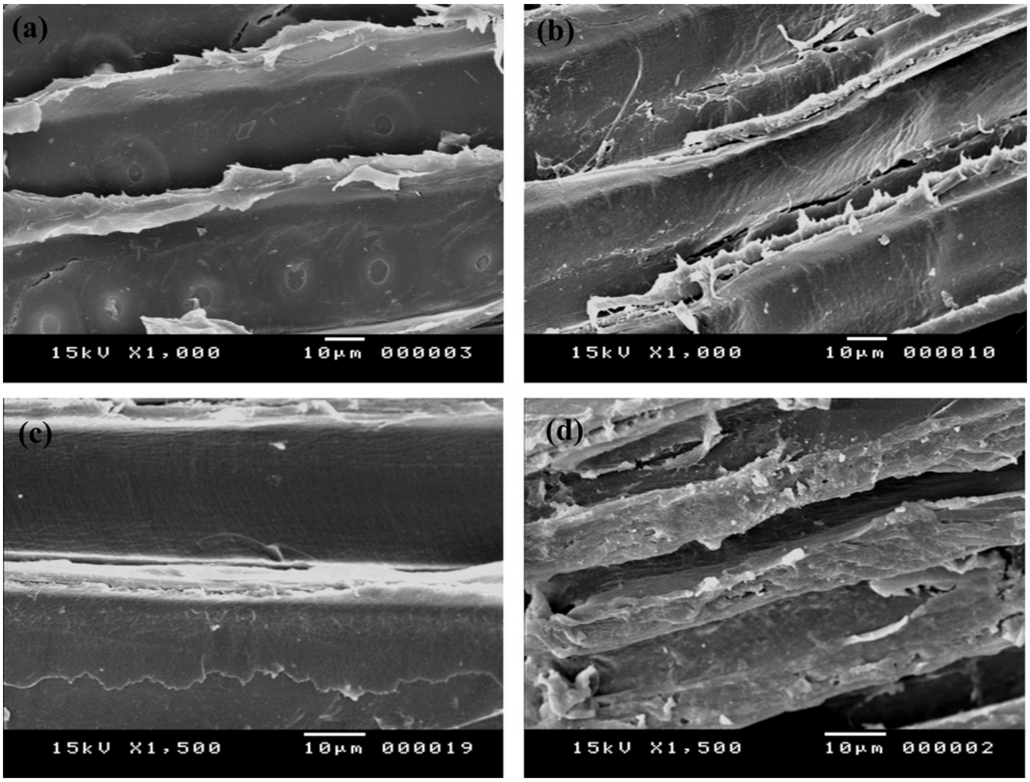

Fig. 1. SEM images of (a) WS-A, (b) WS-A after sorption of Fe(III), (c) WS-E, and (d) WS-E after sorption of Cu(II).

These changes of the structure of phases confirm the presence of the selected metal ions on the surface of these phases.

Functional groups in wood sawdust were determined using FT-IR spectroscopy. The wood sawdust FT-IR spectrum showed number of major intense bands, around 3381.57 cm^{-1}, 2920.06 cm^{-1}, 1725.98 cm^{-1}, 1659.45 cm^{-1}, 1381.75 cm^{-1} and 1030.77 cm^{-1}. The broad band around 3381.57 cm^{-1} is attributed to the surface of hydroxyl groups of cellulose, absorbed water, hemicellulose and lignin. The peaks around 2920.06 cm^{-1} represented C–H stretching vibrations. The presence of the peak at 1725.98 cm^{-1} might be assigned to the carbonyl (C=O) stretching vibration. The peaks at 1659.45 cm^{-1} and 1509.99 cm^{-1} in wood sawdust spectrum were caused by the stretching band of carboxyl (–COO) groups. The vibrations in 1426.1 cm^{-1} can be due to aliphatic and aromatic C–H groups in the plane deformation vibrations of methyl, methylene and methoxy groups. A narrow band spectrum was observed at around 1381.75 cm^{-1}. This can be attributed to the aromatic CH and carboxyl–carbonate structures. In addition, the peaks at 1267.97–1030.77 cm^{-1} represented C–OH stretching vibration. After physical modification of wood sawdust with Alizarin Red-S dye and Eriochrome Black T, it was noticed differences in FT-IR spectra. Some peaks have little shifts like C–H stretching vibrations, however, peaks belong to –OH, –C–OH and –COO stretching vibrations have significant shifts to 3429.78, 1078.98 and 1600.63 cm^{-1}, respectively, for WS-A, phase I and to 3428.81, 1098.26 and 1628.59 cm^{-1}, respectively, for WS-E, phase II. The participation of $–C–NO_2$ and –N=N of Eriochrome Black T for binding to Cu(II) should not be neglected, although they could not easily be detected due to different overlapping in the –CH aromatic and –COO stretching vibrations. Moreover, there are disappearance of some peaks due to –C=O stretching vibrations and $–CH_3$, $–CH_2$ and $–OCH_3$ groups. These results supported the physical modification of wood sawdust phases. The two new physically modified sawdust phases (I and II) were brown and dark blue, respectively. An obvious color change occurred after metal ion sorption by the phases due to complex formation. The color of phase I changed to dark brown after sorption of Fe(III) and of phase II changed to dark violet color after sorption of Cu(II) ions. On the other hand, the intensities of the previous bands after sorption of Fe(III) on phase I and Cu(II) on phase II were markedly decreased with some shifts especially for –CO and –COO and –OH groups. Thus, FT-IR studies reveal that several functional groups, which are able to bind with heavy metal ions, in particular Fe(III) and Cu(II) ions were are present in the wood sawdust phases (Ning-chuan, Xue-yi, & Sha, 2009; Rahman & Islam, 2009).

3.2. Equilibration studies of phases I and II for uptake of Fe(III) and Cu(II) as a function of pH and the shaking time

From Fig. 2(a) and (b), it is noteworthy that a strong dependence of the metal ion percentage of extraction values on the pH of the tested metal ion solution is observed, which can be summarized by the significant increase in the percentage extraction value ongoing from 1.0 to 4.0 for Fe(III) using phase I and from pH 1.0–6.0 for Cu(II) using phase II. The optimum pH value was chosen to be 4.0 for Fe(III) and 6.0 for Cu(II) because precipitation of iron and copper hydroxide were observed at pH greater than 4.0 and 6.0, respectively (Kamaria & Ngah, 2009). However, the two phases showed low efficiency towards the extraction of these two metal ions from aqueous solutions at low pH values. At lower pH value, the H^+ ions compete with metal cation for the exchange sites in the system, thereby partially releasing the latter (Kamaria & Ngah, 2009). With increase in pH of the solution the extent of extraction was found to range from 30.8 to 100% for Fe(III) from pH 1.0 to 4.0 with phase I and from 37.1 to 100% for Cu(II) from pH 1.0 to 6.0 with phase II. For adsorption of Cu(II) ions it was clearly indicated that, at pH 6.0 there are three species present in solution, Cu^{2+} (in very small quantity), $CuOH^+$ and $Cu(OH)_2$ (in large quantity). These species are adsorbed at the surface of the WS phases either by ion exchange mechanism or by hydrogen bonding as shown below (Ajmal, Khan,

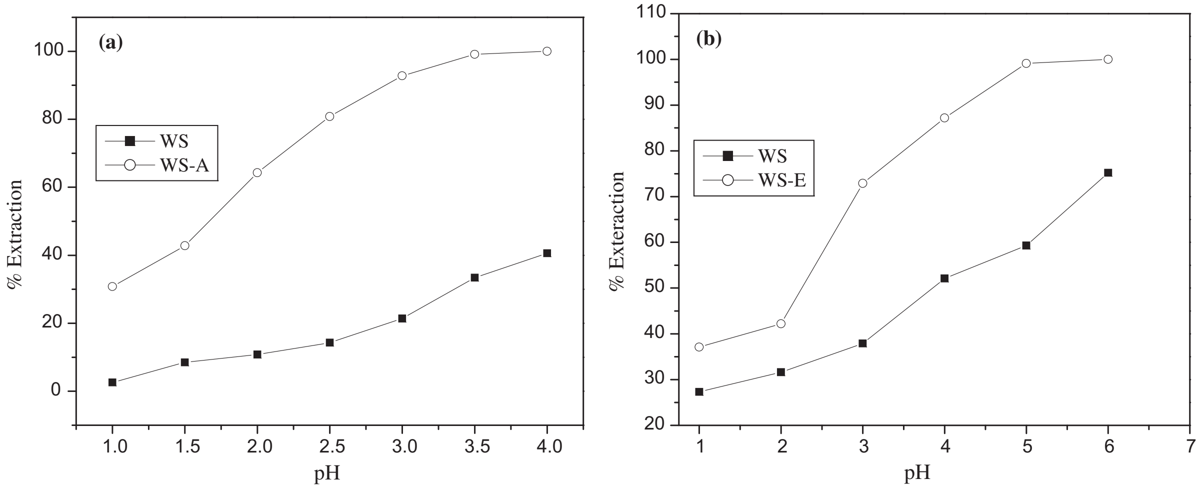

Fig. 2. Effect of pH on percentage extraction of: (a) Fe(III) using WS and WS-A and (b) Cu(II) using WS and WS-E.

Ahmad, & Ahmad, 1998):

$$\left.\begin{array}{l} 2(-\mathrm{ROH}) + \mathrm{Cu}^{2+} \rightarrow 2(\mathrm{RO})\mathrm{Cu} + 2\mathrm{H}^{+} \\ -\mathrm{ROH} + \mathrm{CuOH}^{+} \rightarrow (-\mathrm{RO})\mathrm{CuOH} + \mathrm{H}^{+} \end{array}\right\} \text{Ion exchange}$$

$$2(-\mathrm{ROH}) + \mathrm{Cu(OH)}_2 \rightarrow (-\mathrm{ROH})_2\mathrm{Cu(OH)}_2 \quad \text{H-bonding}$$

(where ±R represents the matrix of wood sawdust phase). By comparing the values of the percentage of extraction of phases I and II with the native wood sawdust it was found that, Fe(III) ions showed a maximum adsorption 40.5% at pH 4.0 and Cu(II) ions showed 75.2% adsorption at pH 6.0 for natural wood sawdust. The respective values for modified wood sawdust phases were 100% for both Fe(III) with phase I and Cu(II) with phase II at the same optimum pH values (Fig. 2(a) and (b)). Thus, it is clear from these results that the modification of adsorbents by the use of the specific reactive dye is justifiable in terms of the enhanced metal ion adsorption. Although the original materials are cheap and easily available, the cost incurred in loading them with dyestuff has to be taken into account while making the adsorption process economically viable. It is also assured that as compared to any chemical modification or conversion to activated carbon adsorbent from a variety of cheap biomass available, the dye loading process will be much cheaper (Shukla & Pai, 2005a).

The effect of the shaking time on the percentage of extraction was also investigated for Fe(III) and Cu(II) ions by the static technique. In this, 300.0 and 200.0 mg of each of phases I and II, respectively, was added to 1 ml of 0.1 M of the metal ion at the previous conditions and automatically shaken for the selected period time 2, 5, 10, 20, 30, 45 and 60 min. The mixture was filtered, washed with doubly distilled water several times and the free metal ions were determined as described above at the selected optimum pH of the maximum uptake. The equilibrium is reached within 45 min of contact and reached a saturation level. In the beginning, the ions adsorbed, occupied selectively the active sites on wood sawdust phases. As the contact time increased the active sites on the sorbent were filled. The results were clearly indicated that the equilibrium for Fe(III) and Cu(II) are attained in 45 min of contact (100.0%) using phases I and II, respectively.

3.3. *Effect of initial Fe(III) and Cu(II) concentrations*

The effect of initial concentration of Fe(III) and Cu(II) using wood sawdust-A, phase I and wood sawdust-E, phase II on their percentage of extraction was studied at concentrations of 10.0–100.0 μmole at fixed sorbent weight of 300.0 and 200.0 mg of each of phases I and II, respectively, pH 4.0 for Fe(III) and 6.0 for Cu(II) and contact time 45 min. The results showed that the percentage extraction of Fe(III) and Cu(II) ions initially increased with concentration of 10.0 μmole. As the concentration was increased from 40.0 to 100.0 μmole, the percentage extraction decreased indicating that the metal uptake is highly dependent on the initial concentration of Fe(III) and Cu(II) in solution. At lower metal concentration, the ratio of number of moles of Fe(III) and Cu(II) in solution to the available surface area is low and hence binding is independent of initial concentration. At higher concentrations the available sites for binding is less and hence metal removal is dependent on the initial concentration.

3.4. *Effect of weight of phases*

The weights of phases I and II were varied from 50.0 to 500.0 mg keeping all the other experimental variables, viz., pH 4.0 for Fe(III) and 6.0 for Cu(II), initial concentration (100.0 μmole), and contact time 45 min. Fig. 3(a) and (b) presents the adsorbent weight profile versus Fe(III) and Cu(II) adsorbed per unit mass. It may be observed that on increasing the adsorbent weight, the percentage extraction of Fe(III) at pH 4.0 was increased up to a weight of 300.0 mg and of Cu(II) at pH 6.0 increased to 200.0 mg to be 100.0% with WS-A, phase I and WS-E, phase II, respectively. On the other hand, the percentage extraction of these metals reaches to 100.0% at 500 mg and 400 mg of native WS with Fe(III) and Cu(II), respectively.

3.5. *Freundlich and Langmuir isotherms of the new physically loaded wood-sawdust phases*

The simplest adsorption isotherm is based on the assumptions that every adsorption site is equivalent and the ability of a particle to bind is independent of whether or not adjacent sites are occupied (Shukla, Yu, Dorris, & Shukla, 2005). To find out the mechanistic parameters associated with Fe(III) and Cu(II) sorption, the results obtained by the adsorption experiments were analyzed by the well known models given by Freundlich and Langmuir models. The sorption isotherms for binding of Fe(III) and Cu(II) with WS-A, phase I and WS-E, phase II were determined by the batch technique at pH 4.0 and 6.0, respectively. Thus, solutions of Fe(III) and Cu(II) in the concentration range: (4.0×10^{-4} to 2.0×10^{-3} M) were shaken for 45 min with a constant weight 300.0 and 200.0 mg of WS-A and WS-E, respectively.

The basic assumption of Freundlich isotherm is that if the concentration of the solute in the solution at equilibrium, C_e was raised

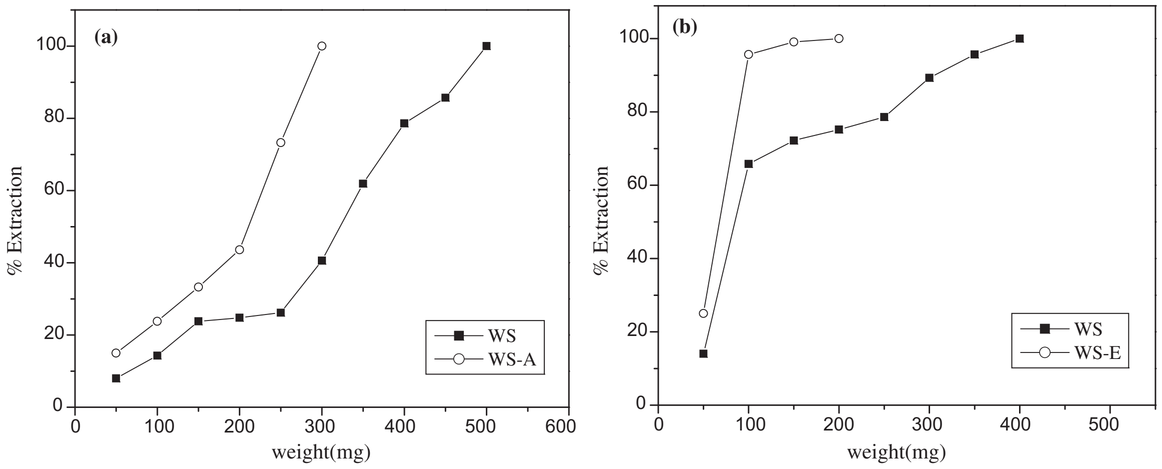

Fig. 3. Effect of weight on percentage extraction of: (a) Fe(III) using WS and WS-A and (b) Cu(II) using WS and WS-E.

to the power $1/n$, the amount of solute sorbed being q_e, then $C_e^{1/n}q_e$ was a constant at a given temperature. This model is more widely used but provides no information on the monolayer biosorption capacity and it assumes neither homogeneous site energies nor limited levels of sorption. The non-linear form of Freundlich equation expressed as follows:

$$q_e = K_f C_e^{1/n} \quad \text{(non-linear form)} \tag{1}$$

Here, K_f and $1/n$ are Freundlich constants (indicators of the sorption capacity and intensity, respectively). Taking logs and rearranging of Eq. (1), it can given the linear form of Freundlich model which expressed as

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad \text{(linear form)} \tag{2}$$

The constants K_f and $1/n$ can be calculated from the intercept and slope of this linear equation, respectively (Table 1). From this table, it is clearly showed that the data is not fitting well to the Freundlich model (Li, Zhai, Zhang, Wang, & Zhou, 2007).

The Langmuir equation, which is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with a negligible interaction between the adsorbed molecules is given by the following equation:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_o}\right) C_e + \left(\frac{1}{Q_o b}\right) \quad \text{(linear form)} \tag{3}$$

where C_e and q_e are the equilibrium concentrations of adsorbate in the liquid and adsorbed phases in mmol ml^{-1} and mmol g^{-1}, respectively (Rao, Reddy, Venkateswarlu, & Seshaiah, 2009). Q_o and b are Langmuir constants, which are related to the maximum Fe(III) and Cu(II) sorption capacity (mmol g^{-1}) and affinity parameter (ml mmol^{-1}), respectively, and can be calculated from the intercept ($1/Q_o b$) and slope ($1/Q_o$) of the linear plot, C_e/q_e vs. C_e given in Fig. 4(a) and (b). The correlation coefficient ($r^2 = 0.97$ for the sorption of Fe(III) on WS-A and 0.99 for the sorption of Cu(II) on WS-E showed that the Langmuir model fitted the results better than Freundlich model. Moreover, the essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as $R_L = 1/(1 + bC_o)$, where, b is the Langmuir constant (indicates the nature of sorption and the shape of the isotherm accordingly); C_o is the initial concentration of the analyte. The R_L value indicates the type of the isotherm as follows:

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The R_L for Fe(III) and Cu(II) sorption supports a highly favourable sorption process based on the Langmuir model. The different parameters of the Freundlich and Langmuir isotherm constants are collected in Table 1. Data were fitted with non-linear regressions using a least-square fitting program (origin 6.0) to obtain the best estimate of all constants for the Freundlich and Langmuir isotherms.

3.6. Kinetic studies

The sorption kinetic data of Fe(III) and Cu(II) measured on phases I and II, respectively, was analyzed in terms of pseudo-first-order and pseudo-second-order sorption equations (Kamaria & Ngah, 2009). The pseudo-first-order equation is shown below:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first-order sorption, q_t (mmol g^{-1}) denotes the amount of sorption at time t (min), and q_e (mmol g^{-1}) is the amount of sorption at equilibrium. After definite integration by application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (4) becomes:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \tag{5}$$

Table 1
Parameters of Freundlich and Langmuir isotherm constants for binding of Fe(III) and Cu(II) using phases I and II, respectively, at room temperature.

Sorbent	Freundlich constants			Langmuir constants			
	K_f	$1/n$	r^2	Q_o[a]	b[b] $\times 10^3$	r^2	R_L
Wood sawdust-A (phase I)	25.06	1.418	0.89	0.361	0.996	0.97	0.32
Wood sawdust-E (phase II)	41.11	1.484	0.94	0.621	1.646	0.99	0.21

[a] mmol g^{-1}.
[b] ml/mmol.

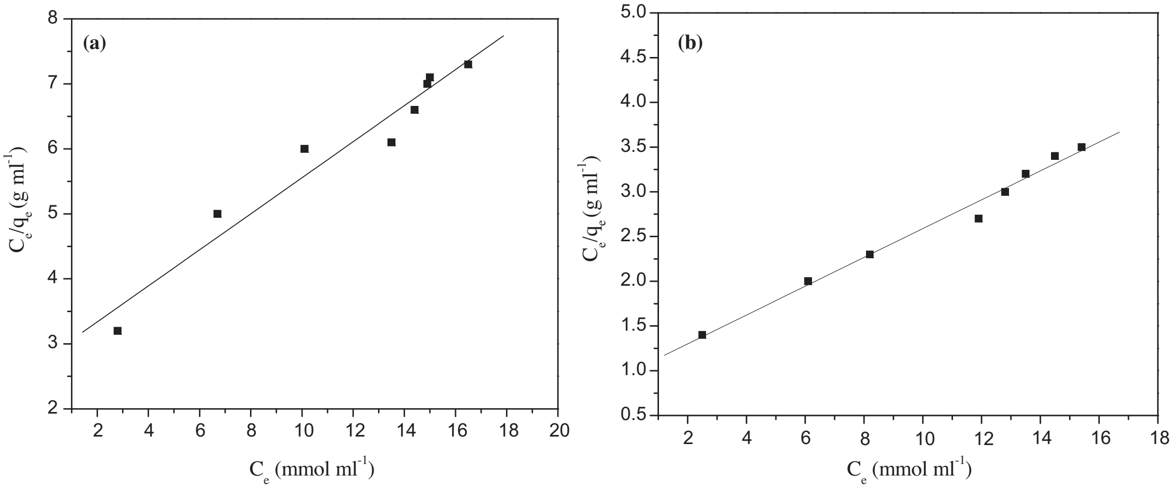

Fig. 4. Langmuir plot for the sorption of: (a) Fe(III) using WS-A and (b) Cu(II) using WS-E at constant temperature.

The kinetic plots were drawn for the two phases and the adsorption rate constant ($k_1 = 0.099$ and 0.108) and adsorption capacity ($q_e = 0.1$ and 0.05 mmol g^{-1}) for phases I and II, respectively were calculated from the slope and intercepts of plots of $\log(q_e - q_t)$ against 't'. The calculated q_e values not agree with the experimental values, although the regression coefficient of above 0.96 for both two phases which shows that the model can be applied but is not appropriate to describe the entire process.

The sorption kinetic data of Fe(III) and Cu(II) measured on phases I and II were analyzed in terms of a pseudo-second-order sorption equation (Reddad et al., 2002). This equation can be written as

$$\frac{dq_e}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

Here, k_2 (g/mmol/min) is the rate constant. Integration of Eq. (6) and application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, give:

$$\frac{1}{q_e} - q_t = \frac{1}{q_e} + k_2 t \tag{7}$$

The following equation can be obtained on rearranging Eq. (7) into a linear form as follows:

$$\frac{t}{q_t} = \frac{1}{\upsilon_o} + \left(\frac{1}{q_e}\right) t \tag{8}$$

$\upsilon_o = kq_e^2$ is the initial sorption rate (mmol g^{-1} min^{-1}), where, k (gm mmol^{-1} min^{-1}) is the rate constant of sorption, q_e (mmol g^{-1}) is the amount of metal ion sorbed at equilibrium, and q_t (mmol g^{-1}) the amount of meal ion on the surface of the sorbent at any time t (min). υ_o and q_e can be obtained from the intercept and slope of a plot of t/q_t vs. t (Fig. 5(a) and (b)), respectively. They were calculated to be $\upsilon_o = 0.480$, $q_e = 0.353$ mmol g^{-1}, $K_2 = 3.84$ min^{-1} for phase I and = 2.105, $q_e = 0.587$ mmol g^{-1} and $k_2 = 6.12$ min^{-1} for phase II. The calculated q_e values (0.353, 0.587 mmol g^{-1}) agree very well with the experimental values (0.350, 0.585 mmol g^{-1}) and a correlation coefficient of above 0.99, for phases I and II, respectively, shows that the model can be applied for the entire adsorption process and confirms the sorption of Fe(III) and Cu(II) onto the wood sawdust phases.

3.7. Uptake of Fe(III) and Cu(II) with phases I and II using column method

3.7.1. Effect of bed height

To investigate the effect of bed height on the breakthrough curve of Fe(III) and Cu(II) ions adsorption onto the wood phases, other parameters such as the inlet concentration, flow rate and pH were kept constant. For $T = 298$ K, flow rate = 1.0 ml/min, $C_{in} = 0.001$ M and pH 4.0 for Fe(III) and 6.0 for Cu(II), it was observed that an increase in column height from 0.7 to 3.0 cm leads to an increase of the volume treated due to high contact time and an increase in breakpoint time. The steepness of the breakthrough curves is a strong function of the bed height (Fig. 6(a) and (b)).

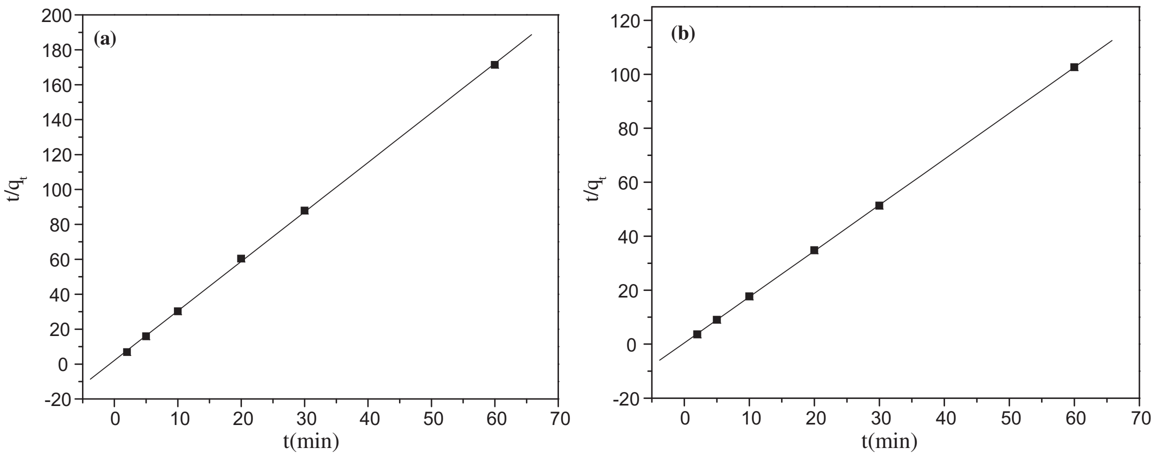

Fig. 5. Pseudo-second-order kinetic plot for the sorption of: (a) Fe(III) using WS-A and (b) Cu(II) using WS-E.

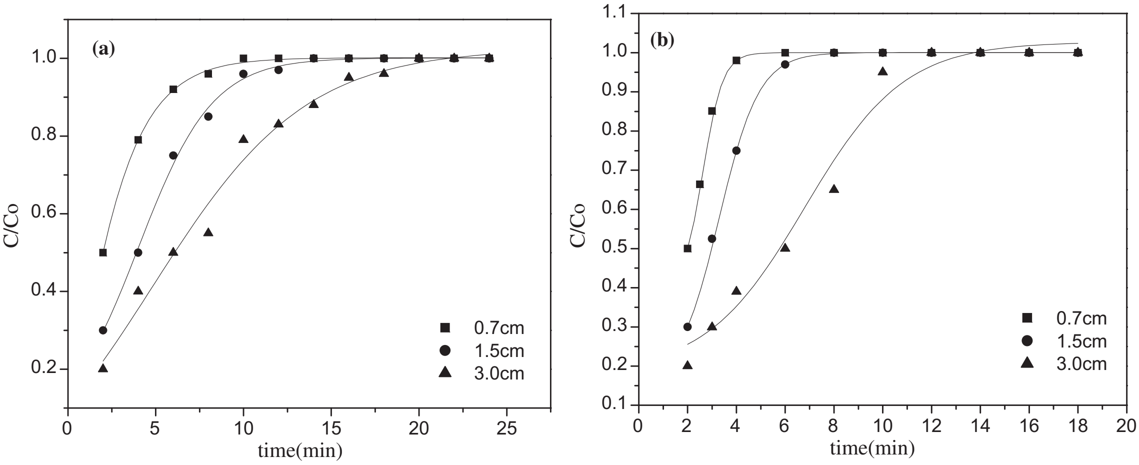

Fig. 6. Effect of bed height on the uptake of: (a) Fe(III) using WS-A, and (b) Cu(II) using WS-E at flow rate 1 ml/min.

3.7.2. Effect of flow rate

In this case, temperature, inlet concentration, bed height and pH were 298 K, 0.001 M, 0.7 cm and 4.0 for Fe(III) and 6.0 for Cu(II), respectively. The results for different solution flow rates are shown for fixed bed height and inlet adsorbate concentration in Fig. 7(a) and (b). When the flow rate increased from 1 to 5 ml/min, the breakthrough curve became steeper and the breakpoint time decreased. This is because in the high flow rate of the solution, the residence time of the solute in the column is not enough to progress mass transfer and removing of Fe(III) and Cu(II) ions from the solution. This causes increasing the anionic content in the outlet stream of the column (Haghsheno, Mohebbi, Hashemipour, & Sarrafi, 2009).

3.8. Buffer treatment on the stability of the Phases I and II

The study of prolonged medium (pH 1.0–10.0) effect on the stability of the new phases is important from practical application point of view. The results of medium effect showed that for WS-A, phase I there is no hydrolysis (0.0%) at pH 1.0–4.0 and the low hydrolysis as experienced by this phase at the pH range which calculated to be 2.9%. On the other hand, there is no hydrolysis (0.0%) at pH 5.0–10.0 and low hydrolysis as experienced and calculated to be 5.6% by WS-E, phase II at the range pH 1.0–4.0.

3.9. Wood sawdust phases regeneration

The application of phases I and II for further extraction of metal ions after first use requires an efficient method for their reuse. In fact, regeneration using acid or base treatment as in ion-exchangers is not adequate for wood sawdust modified organic complexing agents, due to the great possibility of protonation of active donor centres in the ligand, also because acid or base treatment may increase the chance of hydrolysis of the bound complexing agent. Therefore, it was selected to use another strong complexing agent such as ethylenediaminetetraacetic acid (EDTA) to back-extract the metal ion from metal chelate formed modified wood-sawdust phase in the regeneration process. Thus Fe(III)-phase I (dark brown) and Cu(II)-phase II (dark violet) complexes were mixed with excess (0.1M-EDTA) solution and shaken for 60 min, filtered off, washed with double distilled water and dried. 300.0 and 200.0 mg of treated wood sawdust phases I and II, respectively, along with untreated one taken as standard were used to evaluate the metal ion percentage extraction for Fe(III) and Cu(II), respectively, under the same batch conditions which described previously at the optimum pH value. It was firstly observed that original color of the phases, brown for phase I and dark blue for phase II, were restored and the results of percentage extraction determined after the second extraction were very close to percentage extraction found in the first one with percentage decrease in efficiency not exceed 1.2% for both phases. The efficiency of phase regeneration was obtained using the

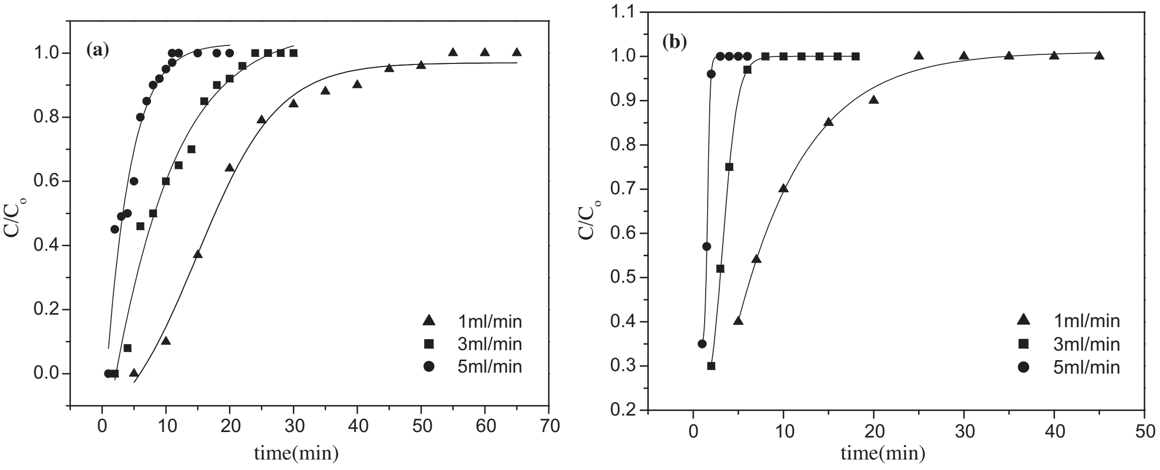

Fig. 7. Effect of flow rate on the uptake of: (a) Fe(III) using WS-A, and (b) Cu(II) using WS-E with bed height 0.7 cm.

Table 2
Recovery of Fe(III) spiked natural water samples with wood sawdust and (wood sawdust-A, phase I) using column technique.

Sample	Added (ppm)	% Recovery wood sawdust	% Recovery wood sawdust-A (phase I)
Nile River water	2.5	86.0 ± 0.10	96.0 ± 0.10
	5.0	88.0 ± 0.20	95.0 ± 0.02
Drinking tap-water	2.5	90.0 ± 0.05	96.0 ± 0.10
	5.0	90.0 ± 0.10	95.0 ± 0.10
Natural drinking-water	2.5	89.0 ± 0.05	95.0 ± 0.15
	5.0	93.0 ± 0.10	95.4 ± 0.10
Doubly distilled water	2.5	90.0 ± 0.20	95.0 ± 0.20
	5.0	92.0 ± 0.15	96.5 ± 0.10

$N = 3$, R.S.D.% = 0.056–0.210. *Experimental conditions*: 2.5 and 5.0 ppm are spiked Nile River water, drinking tap-water, natural drinking-water, and doubly distilled water samples, weight of phase 300 mg and the sample volume 50 ml at pH 4.0 with flow rate 1 ml/min.

Table 3
Comparison of wood sawdust physically loaded Eriochrome Black T (wood sawdust-E, phase II) with some recent sorbents used for determination of Cu(II).

Sorbent	Metal uptake (mmol g^{-1})	Equilibrating time (min)	pH range of Cu(II) uptake	Weight of sorbent (mg)	Simplicity of sorbent synthesis	
					Synthesis steps	Time needed for synthesis (h)
H_2SO_4 modified chitosan (Kamaria & Ngah, 2009)	3.5	120	5.33	500	Multisteps	24
Chemically modified orange peel (Ning-chuan et al., 2009)	1.14	120	4.5–6.0	100	Multisteps	24
Modified oak sawdust (Argun et al., 2007)	0.051	240	4.0	2000	Multisteps	8
Citric acid modified soybean straw (Zhu et al., 2008)	0.450	60	5.0	500	Multisteps	24
Modified jute fibers (Shukla & Pai, 2005b)	0.122	120	5.5	1000	Multisteps	>24
Modified peanut husk (Li et al., 2007)	0.059	60	4.0	200	Two steps	3
Wood sawdust-E, phases II [this work]	0.585	45	6.0	200	One step	12

following equation:

$$\text{Efficiency of regeneration}\,(\%) = \frac{\text{total adsorption capacity in the second run}}{\text{total adsorption capacity in the first run}} \times 100$$

Generally, the efficiency of regeneration using 0.01 M EDTA reached up to 95.5 ± 2 and 96 ± 1% for WS-A and WS-E, respectively. It has already been shown that the dye does not leach out from the dyed wood-sawdust phase under the conditions of regeneration (Shukla & Pai, 2005a).

4. Applications

4.1. Determination of Fe(III) in natural water samples with WS-A, phase I using column studies

Column experiments were performed in a mini-column (length 3.6 cm, diameter 1 cm). 300.0 mg of phase I was put between two layers of glass wool, the first at the bottom to avoid loss of sorbent when the sample solution passes through the column and the second at the top to retain it. Then, 50 ml solution of each of the natural water sample (Nile River water, drinking tap-water, natural drinking-water, and doubly distilled water) containing 2.5 and 5.0 ppm of Fe(III) (adjusted at pH 4.0 by fine addition of concentrated HCl) passed through the column with flow rate of 1.0 ml/min. The quantitative recovery values of Fe(III) as shown in Table 2 indicate the suitability and validity of using phase I for selective extraction of Fe(III) from natural water samples by column technique prior to determination by AAS.

5. Comparison of determination of Cu(II) using (WS-E, phases II) with alternative natural sorbents

The proposed method was compared to a variety of recent sorbents reported in literature for the determination of Cu(II). The distinct features are summarized in Table 3. The modified wood sawdust phase (WS-E, phase II) described in this work showed high affinity and selectivity of Cu(II) (values of equilibrating time, 45 min and weight of sorbent, 200 mg). This is in addition to the direct mode of separation and the simplicity of sorbent synthesis (refluxed one step for 12 h).

6. Conclusion

Wood-sawdust phases I and II as a natural carbohydrate polymers and solid phase extractors have the following advantages: (i) benign lignocellulosic material, inexpensive and rich in oxygen containing functional groups. (ii) They have pronounced capability for extraction of Fe(III) in aqueous solution in the pH 1.0–4.0 and Cu(II) at pH 1.0–8.0. (iii) Their sorption performance were fitted well with Langmuir model with correlation factor $r^2 = 0.97$ for phase I, 0.99 for phase II along with fast kinetics obeying pseudo-second-order type $r^2 = 0.99$ for both phases I and II. (iv) The WS-A, phase I was applied for the removal of trace amounts of Fe(III) spiked natural water samples by AAS with no matrix interference using column technique. (iv) The WS-E, phase II showed high affinity and selectivity of Cu(II) in compared to the other recent sorbents reported in the literature.

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