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Effects of pH on isotherms modeling for Cu(II) ions adsorption using maple wood sawdust

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ABSTRACT

The biosorption of copper (II) ions from aqueous solution by an unconventional adsorbent maple wood sawdust was studied as a function of different environmental parameters such as pH, contact time, adsorbent concentration, initial Cu(II) ions concentration and others. Adsorption was carried out in a batch process and it was observed that an increase in the adsorbent concentration with constant copper ions concentration resulted in greater metal removal from solution. Higher metal loading per unit of weight of sorbent was observed with increasing initial copper ions concentrations for a constant sorbent dose. The Langmuir and the Freundlich adsorptions models were applied to describe isotherms and isotherm constants considering the most important parameter, pH. The variation of adsorption isotherm constants showed pH dependence. The isotherms studies revealed that the maximum copper (II) ions adsorption (q_m) 9.51 mg/g maple wood sawdust was obtained at pH value of 6.0.

1. Introduction

The intensification of industrial activities during the last decades contributed greatly to the level of current environmental pollution. The pollution of water with toxic heavy metals is considered dangerous due to their great toxicity and their non-biodegradability. These heavy metal ions can be accumulated through the food chain even at low concentrations, leading to serious problems on aquatic life as well as to animal, plant life and human health. Once copper is absorbed into the gastrointestinal tract, it enters the blood and muscle, liver and brain. Copper acts as an irritant to the skin causing itching and dermatitis, and may cause keratinization of the hands and soles of the feet [1]. Copper causes serious problems to human such as stomach intestinal distress, kidney damage, anemia and even coma and eventual death [2]. One major mechanism of copper toxicity towards microorganisms is disruption of plasma membrane integrity. Copper can cause “pink disease” among infants when 0.8 mg/L in water is consumed and is considered to be carcinogenic to animals [3]. Cu(II) ions from industrial and mining effluents can eliminate all fishes and marine plants for miles downstream from the source [4].

Copper bearing mining wastes and acid mine drainage discharge significant quantities of dissolved copper into wastewater. Copper has many industrial applications. For example, it is known as an excellent conductor of electricity, widely used in the electrical industry in all gauges of wires for circuitry. Copper is also utilized in analytical reagents, in paints for ship keels, in pigments, in electroplating, in fertilizer industry, etc. [5]. In addition, copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate [6]. The maximum recommended concentration of Cu^{2+} for drinking water by EPA is 1.0 mg/L [7]. Cost-effective treatment technologies, therefore, are needed to meet these requirements.

Various treatment technologies such as precipitation, ion exchange, adsorption, and solvent extraction have been commonly employed to remove metal pollutants from aqueous solutions. Apart from being expensive, these technologies create secondary problems with metal bearing sludges [8]. This has encourages researcher into discovering materials that are efficient, cheap and available in nature. One of the promising techniques for the removal of metals is the use of environment-friendly natural materials as adsorbent. Recently the use of agricultural bioproducts (waste) has been widely investigated as adsorbent materials (Table 1) to remove trace metals from aqueous systems.

Adsorption and desorption at the solid/liquid interface play an important role in the transport process. Sarwar and Islam [9] have reported that adsorption of cations on a solid/liquid interface may be related to several mechanisms, namely (1) electrostatic inter-

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Table 1
Comparison of Cu(II) ions uptake of selected similar nature sorbents.

Adsorbent	Maximum Cu(II) uptake	Optimum pH value	References
Cellulose pulp waste	4.98 mg/g	<6.0	[31]
Sugar beet pulp	20.96 mg/g	5.5	[21]
Aquatic plant	15.59 mg/g	<6.0	[32]
Rice husk	29 mg/g	5.3	[20]
Wheat bran	51.5 mg/g	5.0	[33]
Cotton ball	11.40 mg/g	5.0	[34]
Sunflower stalks	25.11 mg/g	4.25	[35]
Canola meal	9.8 mg/g	6.0	[17]
Pine bark	6.4–15.6	4.0	[18]
Olive shale	9.8 mg/g	6.0	[19]
Crab carapace (*Cancer pagurus*)	79.4 mg/g	5.0	[36]
Anaerobic granular biomass	55 mg/g	4.5–5.5	[37]
Marine biomass	63–75 mg/g	5.0	[38]
Peat biomass	34.06 mg/g	6.0	[39]
Black gram husk	25.5 mg/g	5.0	[40]
Carrot residue	32.74 mg/g	5.0	[41]
Marine algal biomass	72.43 mg/g	5.0	[42]

actions, (2) van der Waals interactions, (3) non-polar chain–solid interactions, (4) covalent bonding, (5) hydrogen bonding, and (6) solvation and desolvation of the adsorbates. The most widely used adsorption isotherm equations for modeling equilibrium are the Langmuir and the Freundlich equation. Equilibrium studies on adsorption give information about the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. These mechanisms have been elaborated by Rahman [10].

There are 13 native maple species in North America. Maple trees have played a meaningful role in the historical development of Canada and continue to be of commercial, environmental and aesthetic importance to all Canadians. Maple wood, which varies in hardness, toughness and other properties, is in demand for flooring, furniture, interior woodwork, veneer, small woodenware, and supports several flourishing industries in eastern Canada. Every year a huge amount of maple wood sawdust is produced as a byproduct of wood furniture industries. In this paper, maple wood sawdust is introduced as an unconventional adsorbent that reduces copper ions concentration significantly from aqueous solutions. The adsorption isotherms and the probable mechanisms have been explained in this study.

2. Materials and methods

2.1. Instrumentation

In this study, scanning electron microscope (Hitachi S-4700, Japan) was used to characterize the surface of the maple wood sawdust at very high magnification. The maple wood sawdust was coated with gold and palladium by a sputter coater (Hitachi E-1030, Japan) with conductive materials to improve the quality of micrograph. The thickness of the coating was 30.00 nm, and the density was 19.32 g/cm^3.

Functional groups in maple wood sawdust were determined by the Fourier transform infrared (FTIR) spectroscopy. Spectra were collected with a spectrometer using KBr pellets. In each case, 1.0 mg of dried maple wood sawdust sample and 100 mg of KBr are homogenized using mortar and pestle thereafter pressed into a transparent tablet at 200 kgf/cm^2 for 5 min. The pellets are analyzed with a FTIR Spectrometer (VECTOR 22, Bruker Co.) in the transmittance (%) mode with a scan resolution of 4 cm^{-1} in the range 4600–500 cm^{-1}.

Flame atomic absorption spectrophotometer (Spectr*AA* 55B, Varian, Australia) was used for the analysis of copper (Cu^{2+}) in aqueous solution. Concentrations were determined after calibrating the instrument with standards within the concentration range of 0.5–10 mg/L for Cu^{2+}. To measure the unknown Cu(II) ions concentration in aqueous solution, we diluted the solution to bring the concentration within the calibration range. The light source was a hollow-cathode lamp of the element that was being measured.

The pH measurements of all aqueous samples were performed following standard methods with SP21 pH meter manufactured by VWR scientific product. The meter was standardized using buffer solutions with the following pH values: pH 4.0, pH 7.0 and pH 10.0.

All glassware used in the experiments were first washed with detergent and properly rinsed with tap water, this was followed by the addition of 10% nitric acid to eliminate any trace of residual metals. The glassware was then washed three times with tap water and then finally washed three more times with de-ionized water.

2.2. Adsorbent

Maple wood sawdust samples were collected from a local saw mill “Hefler Forest Products Ltd.”, 230 Lucasville Road, Halifax, NS, Canada. The maple wood sawdust samples were sieved through 20–50 mesh and it was used directly for adsorption experiments without any physical and chemical treatments. The proximate analysis of maple wood sawdust was performed following the procedure reported in the literature [11].

2.3. Chemicals

The standard solutions of Cu(II) was prepared from the 1000 mg/L reference solution manufactured by Fisher Scientific Limited, England. The required concentrations were obtained by diluting with distilled de-ionized water to the concentrations of 5.0 mg/L, 10.0 mg/L, 25 mg/L, 50 mg/L and 100 mg/L. These Cu(II) ions solutions were used in adsorption experiment using maple wood sawdust. The standard solutions were freshly prepared before every metal ions determination of the analysis of the present work.

2.4. Batch adsorption studies

The adsorption of copper onto maple wood sawdust was studied by batch technique. A known weight of adsorbent (e.g. 0.5–30 g adsorbent) was equilibrated with 100 mL of the copper ions solution of known concentration (5–100 mg/L) in 250 mL of Erlenmeyer flasks at a room temperature of 23 °C for a known period (5–360 min) of time. To keep high adsorption capacity and free of precipitation effect, pH of the solutions was adjusted with 0.1 M NaOH or 0.1 M H_2SO_4. After equilibration, the suspension of the adsorbent was separated from solution by filtration using Whatman No. 42 filter paper. Blank experiments were conducted to ensure that no adsorption was taking place on the walls of the apparatus used. The concentration of heavy metal ions remaining in solution was measured by AAS using flame method.

All experiments were conducted in triplicate and mean values were used. The results of these studies were used to obtain the optimum conditions for maximum heavy metals removal from aqueous solution. The percentage of heavy metal removal was calculated using the following equation:

$$\text{Sorption}\ (\%) = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

where C_o is the initial concentration (mg/L) of the test solution and C_e is the equilibrium concentration (mg/L) of the test solution.

The amount of metal sorbed by weight of maple wood sawdust was calculated using the following equation:

$$q_e\ (\text{mg/g}) = \frac{(C_o - C_e)V}{m} \tag{2}$$

where q_e is the equilibrium adsorption capacity (mg/g), C_o is the initial concentration (mg/L) of copper ions in solution, C_e is the equilibrium concentration (mg/L) of copper ions in solution, V is the volume of aqueous solution (mL) and m is the dry weight of the adsorbent (g/L).

2.5. Adsorption isotherm models

2.5.1. The Langmuir isotherm model

The Langmuir isotherm model is valid for monolayer adsorption onto surface containing finite number of identical sorption sites which is presented by the following equation [12]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where q_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration of the solution (mg/L), and q_m is the maximum amount of metal ions required to form a monolayer (mg/g). The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants (K_L) as below. The values of q_m and K_L can be determined from the linear plot of C_{eq}/q_{eq} versus C_{eq}:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{4}$$

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using the separation factor or dimensionless equilibrium parameter, "R_L", expressed as in the following equation [13]:

$$R_L = \frac{1}{1 + K_L C_o} \tag{5}$$

where K_L is the Langmuir constant and C_o is the initial concentration of metal ion. The value of separation parameter R_L provides important information about the nature of adsorption.

2.5.2. The Freundlich isotherm model

The Freundlich equation is purely empirical based on sorption on heterogeneous surface, which is commonly described by the following equation [14]:

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

where K_F and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Freundlich equilibrium constants evaluated from the intercept and the slope, respectively, of the linear plot of $\ln q_e$ versus $\ln C_e$ based on experimental data. The Freundlich equation can be linearized in logarithmic form for the determination of the Freundlich constants as shown below:

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

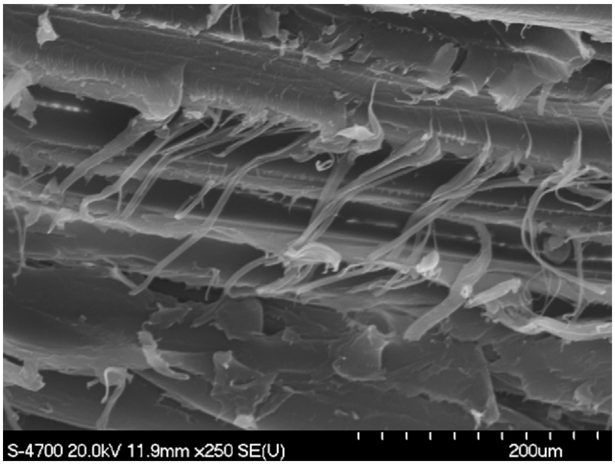

Fig. 1. SEM microphotograph of the untreated maple wood sawdust.

3. Results and discussions

3.1. Characterization of maple wood sawdust

The cell wall of maple sawdust mainly consists of dry matter (96.93%). The proximate composition of maple wood sawdust is 65.12% crude fiber, 31.05% of acid detergent fiber, 1.2% of crude protein, and 1.7% of ash. Cellulose, hemicellulose and lignin are the main components of acid detergent fiber. All those compounds are active ion exchange compound [15].

The surface structure of maple wood sawdust was analyzed using a scanning electron microscope (SEM) before and after copper (II) ions adsorption (Figs. 1 and 2). The microphotographs of before metal ions adsorption revealed clearly the presence of asymmetric pores and open pore structure in maple wood sawdust that might be the reason of high metal ions adsorption due to providing high internal surface area (Fig. 1). However, after metal ions

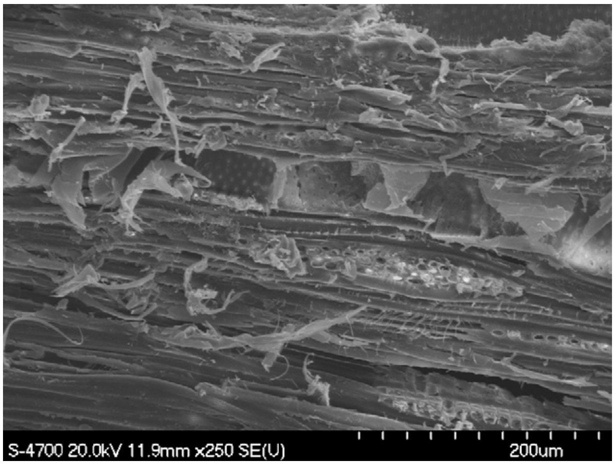

Fig. 2. SEM microphotograph of the treated maple wood sawdust with Cu(II) ions in solution.

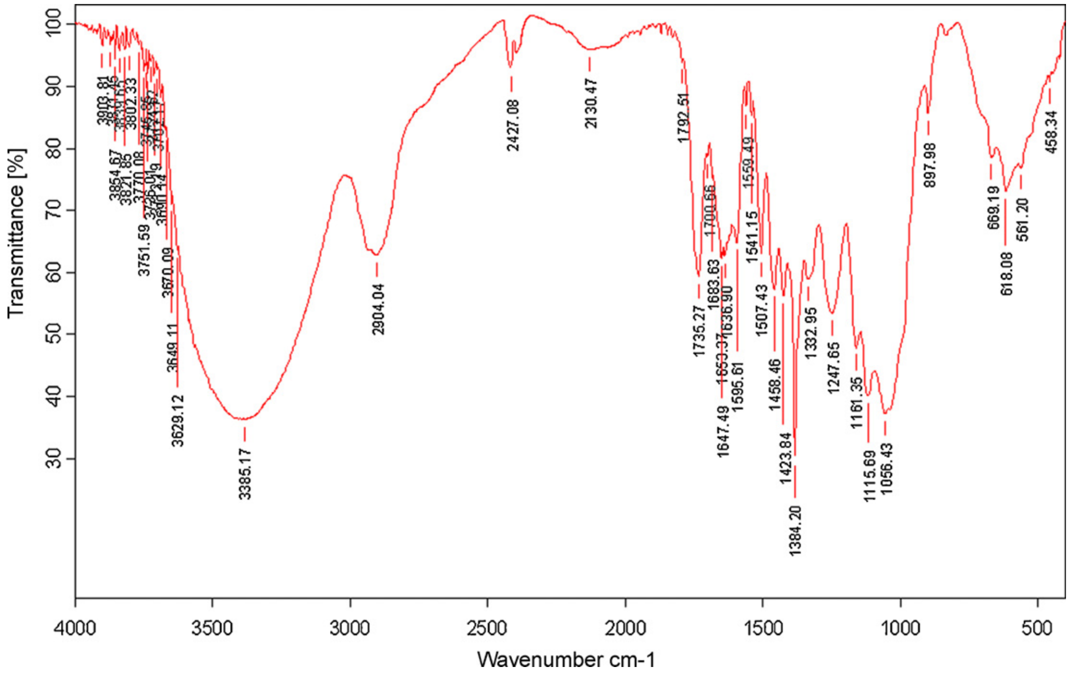

Fig. 3. FTIR spectrum of maple wood sawdust.

adsorption the micrographs revealed the presence of more dense of closed pore structures, the presence of pellets and pellets inside layers of sawdust particles (Fig. 2). The change of the structure of the cell materials in the adsorbent particle was probably influenced by the metal ions.

The metal adsorption capacity is influenced strongly by the surface structures of carbon–oxygen (functional groups) and surface behavior of carbon [16]. Functional groups in maple wood sawdust were determined using FTIR spectroscopy. The maple wood sawdust FTIR spectrum showed six major intense bands, around 3385 cm^{-1}, 2904 cm^{-1}, 2427 cm^{-1}, 1735 cm^{-1}, 1384 cm^{-1} and 1056 cm^{-1} (Fig. 3). The broad band around 3385 cm^{-1} is attributed to the surface of hydroxyl groups. The peaks at around 2904 cm^{-1} represented C–H stretching vibrations and $-\text{CH}_3$. The FTIR spectra at around 2427 cm^{-1} is characteristic of the carboxyl acid groups. The band around 1735 cm^{-1} might be assigned to the carbonyl (C=O) stretching vibration. The peaks at 1647 cm^{-1} and 1596 cm^{-1} in maple wood sawdust spectrum were caused by the stretching band of carboxyl groups. A narrow band spectrum was observed at around 1384 cm^{-1}. This can be attributed to the aromatic CH and carboxyl–carbonate structures. In addition, the intensity of the band at 1241 cm^{-1}, related to C–O stretching vibration of the acetate function, was observed. The strong peaks at 1115–1056 cm^{-1} represented C–OH stretching vibration [10]. FTIR studies reveal that several functional groups, which are able to bind with heavy metal ions, in particular Cu(II) ions were are present in the maple wood sawdust.

3.2. *Batch studies*

3.2.1. *The effect of maple wood sawdust dose on adsorption*

The effect of maple wood sawdust dose was studied for a by varying the dose between 0.5 g/L and 30 g/L. These tests were conducted at a room temperature of 23 °C, with a pH value of 5.0. The initial metal ion concentration was 25 mg/L. The pH value of the solution was adjusted with 0.1 M NaOH or 0.1 M H_2SO_4. It was observed that the adsorption percentage of copper (II) ions onto the maple wood sawdust increased rapidly with the increasing of adsorbent concentration (Fig. 4). This result is expected because the increase of adsorbent dose leads to greater surface area. When the adsorbent concentration was increased from 0.5 g/L to 10 g/L, the percentage of Cu(II) ions adsorption increased from 61.75% to 82.27%. At higher concentrations, the equilibrium uptake of copper (II) ions did not increase significantly with increasing maple wood sawdust concentrations. Such behavior is expected due to the saturation level attained during an adsorption process [10]. For subsequent studies, a dose of 10 g/L of maple wood sawdust was selected.

3.2.2. *Effect of contact time*

Fig. 5 shows the effect of contact time on adsorption of copper (II) ions using maple wood sawdust. For these cases, initial Cu(II) ions concentration of 25 mg/L, pH of 5.0 and sawdust dose of 10 g/L were used. It was observed that the copper adsorption increased rapidly for the first 30 min and an equilibrium uptake of copper ions 2.06 mg/g maple wood sawdust (Table 2) was nearly reached after 60 min that was equivalent to 82.21% copper ions adsorption. Furthermore, there was significant difference of adsorption among the obtained data for 120 min, 240 min, and 360 min. As a conse-

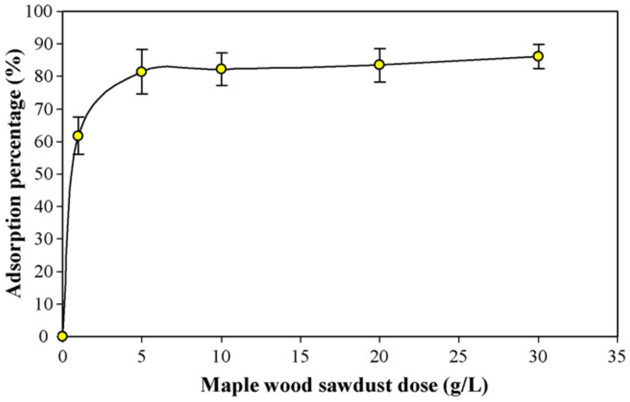

Fig. 4. The effect of sawdust dose on adsorption.

Table 2
The adsorption percentage (%) and equilibrium uptake (q_e) of copper ions mg/g maple wood sawdust for the different contact time.

Contact time (min)	Equilibrium concentration C_e (mg/L)	Adsorption percentage (%)	Metal uptake mg/g adsorbent
10	10.43	58.29	1.46
30	5.29	78.86	1.97
60	4.45	82.21	2.06
120	4.44	82.26	2.06
240	4.28	82.89	2.07
360	4.43	82.27	2.06

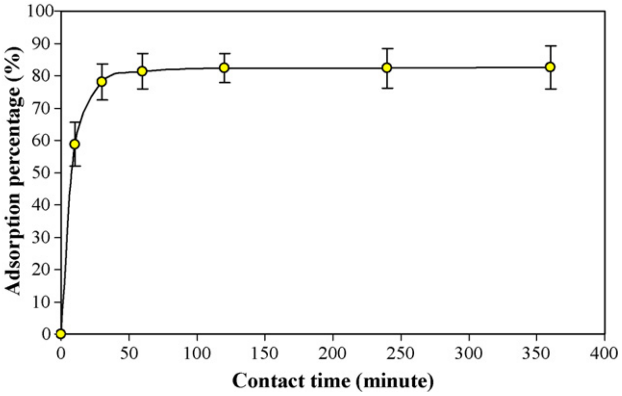

Fig. 5. Effect of contact time on copper ions adsorption using maple wood sawdust.

quence, 60 min contact time was chosen as an optimum time in each experiment.

3.2.3. The effect of initial concentration

The metal uptake is particularly dependent on initial heavy metal ions concentration. At low concentration values, metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and exchange sites are filled [10]. Different concentrations for copper ions solutions of 5 mg/L, 10 mg/L, 25 mg/L, 50 mg/L and 100 mg/L were used and the experiments were carried out at room temperature (23 °C) with contact time of 60 min. From the experimental studies, it was shown that the percentage of copper ion adsorption decreased from 85.51% to 62.5% with the increment of the initial copper ions concentration (Fig. 6). The experimental results are very close to those found by other researchers that studied the effect of initial sorbate concentration on sorption of heavy metals using different biomass [17–20]. At the beginning of initial concentrations (5 mg/L), the copper removal percentage was higher due to a larger surface area of the maple wood sawdust being available for the adsorption of copper ions. When the concentration of the metal ion solution became higher, the copper removal percentage was lower because the available sites of adsorption became less. At a higher initial concentration, the ratio of initial number of moles of copper (II) to the available adsorption surface area was higher and as a result adsorption percentage was less. This might be the major mechanism of the effect of the initial metal ions concentration in aqueous solution on the adsorption process.

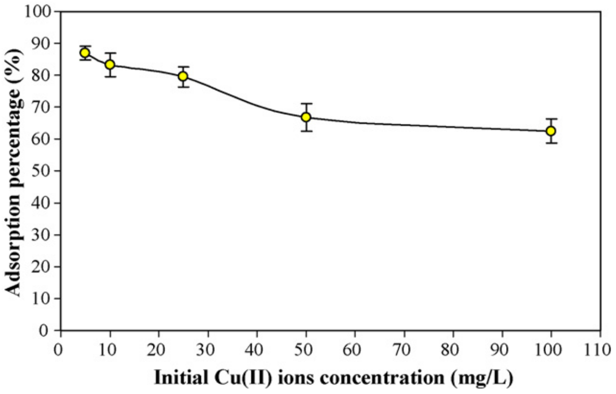

Fig. 6. The effect of initial Cu(II) ions concentration on adsorption.

3.2.4. The effect of pH

The pH value of the aqueous solution is an important controlling parameter in the adsorption process. These pH values affect the surface charge of adsorbent, the degree of ionization and speciation of adsorbate during adsorption. Thus the effect of pH (H^+ ion concentration) in the solutions on the adsorption percentage of copper ions was studied at different pH ranging from 2.0 to 8.0. The experiment was performed with an initial copper ions concentration of 25 mg/L, temperature of 23 °C with contact time of 60 min. Results are shown in Fig. 7. It was observed that the biosorption was very less (28.66%) at an initial pH value of 2.0. A sharp increase in the biosorption of copper ions from 28.66% to 83.25% occurred in the pH range of 3.0–4.0. It was observed that the adsorption capacity was very low at strong acidic medium and the adsorption capacity increases with increasing pH values, until a certain pH value was reached. This can be explained on the basis of decrease in competition between positively charged H^+, H_3O^+ and Cu^{2+} for the same functional groups. As the pH value was increased, more ligands were exposed and the number of negatively charged groups on the adsorbent matrix probably increased, enhancing the removal cationic species [21]. It was observed that the optimum copper (II) ions removal occurred between the pH values of 5.0–6.0. It was also observed that the adsorption capacity was increased again at pH value from 6.0 to 7.0, which might be due to the onset of precipitation of copper ions as insoluble $Cu(OH)_2$ and not due to adsorption. As a result, the maximum adsorption was observed at pH of 7.0 and it might be due to interaction of the species of Cu(II) ions, i.e. Cu^{2+},

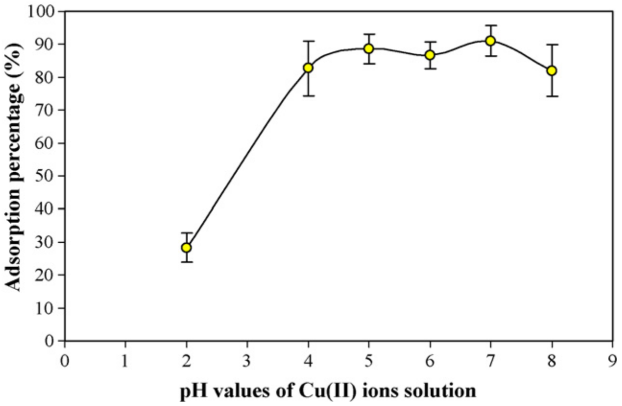

Fig. 7. The effect of pH values on adsorption of copper ions using maple wood sawdust.

$Cu(OH)^+$, and $Cu(OH)_2$ with the surface functional groups present in maple wood sawdust. However, a pH value of 6.0 was chosen as being the optimum for further experiment to avoid the precipitation of $Cu(OH)^{2+}$ as Cu^{2+} precipitates above pH 6.5 in the form of $Cu(OH)_2$ [10].

The metal uptake depends on the active sites of the adsorbent as well on the nature of the metal ions in solution. At a pH value of 6.0 there are three species of Cu(II) ions present in solution as suggested by several authors [22,23]. $Cu(OH)^+$ and $Cu(OH)_2$ in large quantities and Cu^{2+} is very small quantity. These species were adsorbed at the surface of the maple wood sawdust either by ion exchange mechanism or by hydrogen bonding for the adsorption process due to the –COOH groups and –OH groups present in the most adsorbents [10,24,25]. Copper may most likely bind on polar functional group by the following mechanisms:

$$(\text{–ROH}) + \text{Cu}^{2+} \rightarrow (\text{RO})\text{Cu} + \text{H}^+ \quad [\text{ionexchange}]$$

$$(\text{–RCOOH}) + \text{Cu}^{2+} \rightarrow (\text{RCOO})\text{Cu} + \text{H}^+ \quad [\text{ionexchange}]$$

$$\text{–ROH} + \text{CuOH}^+ \rightarrow (\text{–RO})\text{CuOH} + \text{H}^+ \quad [\text{ionexchange}]$$

$$\text{–RCOOH} + \text{CuOH}^+ \rightarrow (\text{–RCOO})\text{CuOH} + \text{H}^+ \quad [\text{ionexchange}]$$

$$(\text{ROH}) + \text{Cu(OH)}_2 \rightarrow (\text{–ROH})_2\text{Cu(OH)}_2 \quad [\text{H-bonding}]$$

$$(\text{RCOOH}) + \text{Cu(OH)}_2 \rightarrow (\text{–RCOOH})_2\text{Cu(OH)}_2 \quad [\text{H-bonding}]$$

(where –R represents the matrix of sawdust).

3.2.5. Analysis of the maximum adsorption capacity using isotherms

The adsorption isotherm is based on the assumption that every adsorption site is equivalent and independent of whether or not adjacent sites are occupied. Isotherms show the relationship between metal concentration in solution and the amount of metal sorbed on a specific sorbent at a constant temperature.

The amount of copper ions adsorbed per specific amount of adsorbent (q_e) was calculated according to the linearized form of Eq. (2). The dependence of the metal uptake data (q_e) on the equilibrium concentration of copper (C_e) in aqueous solutions for different pH values is shown in Fig. 8. When equilibrium solid phase concentration of an adsorbate increases sharply from a low to a high equilibrium concentration, the adsorption is said to be favorable and results in a convex-shaped isotherm. Isotherms of concave shape indicate an unfavorable adsorption process and when the equilibrium solid phase concentration of an adsorbate increases linearly with equilibrium concentration of an adsorbate in the liquid phase, the isotherm obtained is called a linear [26]. The convex-shaped isotherms were observed at pH 4 and 6 that indicated favorable adsorption. However, adsorption isotherms were unfavorable at pH value 8.0 showing concave shape isotherm for this study.

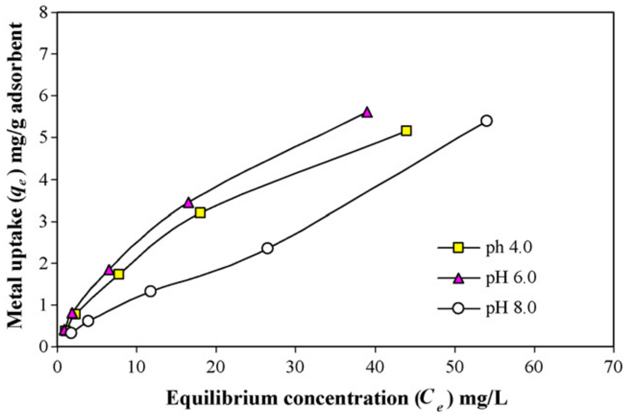

Fig. 8. Equilibrium concentration versus equilibrium metal uptake (C_e) mg/g maple sawdust.

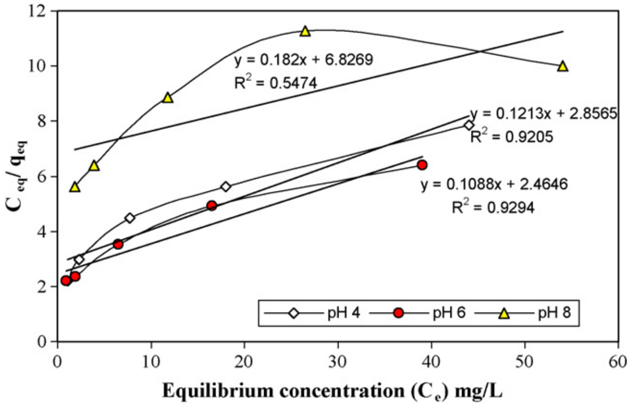

Fig. 9. The Langmuir isotherm plots for the adsorption of Cu(II) ions onto maple wood sawdust sample at different pH values.

3.2.6. The Langmuir isotherm

The equilibrium data were analyzed using the linearized form of the Langmuir adsorption isotherm Eq. (4). The Langmuir constants, K_L and monolayer sorption capacity, q_m were calculated from the slope and intercept of the plot between C_e/q_e and C_e (Fig. 9). The Langmuir adsorption isotherm was determined at different pH values ranging from 4.0 to 8.0 for copper (II) ions concentration range of 5–100 mg/L. All solutions contain a fixed specific mass of maple wood sawdust (10 g/L). The isotherm constants were calculated from the isotherm equations for the different pH values. The values of Langmuir adsorption isotherm parameters are presented in Table 3.

The linear plot of C_{eq}/q_e and C_e demonstrates that the experimental data fit the Langmuir isotherms reasonably well over the whole copper concentration range studied. The regression coefficient values (r^2) in the case of the Langmuir isotherm for different pH values were varied from 0.54 to 0.92. The r^2 value near unity indicates an excellent fit to the isotherm equation and near zero indicates a very poor fit. Therefore, the equation that gives maximum coefficient of correlation is the best fit equation and this equation is used to determine the amount of metal ions required to form a monolayer on adsorbent (q_m) and the Langmuir equilibrium constant (K_L) [27]. The values of both the Langmuir isotherm parameters are calculated from the linearized equation and the results are presented in Table 3. It is observed that the maximum metal adsorption capacity varied with the change of pH value and the maximum metal adsorption was found to be at a pH of 6.0. Sing and Yu [28] have been reported that the higher value of K_L, the higher is the

Table 3
The Langmuir adsorption isotherm parameters and equation for adsorption of copper (II) on maple wood sawdust.

pH value	q_e (mg/g)	The Langmuir isotherm constants				Equation
		q_m (mg/g)	K_L (L/mg)	r^2	R_L	
4	5.6	8.244	0.043	0.9205	0.823	$q_e = \frac{0.354C_e}{1+0.043C_e}$
6	6.1	9.191	0.044	0.9294	0.819	$q_e = \frac{0.404C_e}{1+0.044C_e}$
8	5.4	5.494	0.026	0.5474	0.885	$q_e = \frac{0.142C_e}{1+0.026C_e}$

Table 4
Use of the Langmuir isotherm dimensionless constant separation parameter, R_L in getting information about the nature of adsorption [13].

Serial no.	Value of R_L	Information about the adsorption
1	$R_L > 1$	Unfavorable
2	$R_L = 1$	Linear
3	$0 < R_L < 1$	Favorable
4	$R_L = 0$	Irreversible

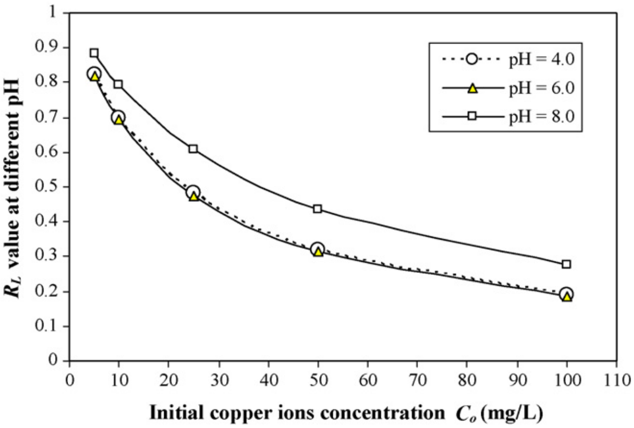

Fig. 10. The mean values of Langmuir separation factor, R_L on adsorption of copper ions onto maple wood sawdust for different pH values.

affinity of adsorbent for the metal biosorbed. It is evident from the values of K_L for various pH values (Table 3) that the affinity of maple sawdust to biosorb copper ions is greater at a pH value of 6.0 than that the pH values of 4.0 and 8.0. From Table 3, it can be seen that the value of q_e is smaller than q_m for all pH values. This indicates that the adsorption of copper ions onto maple wood sawdust is of a monolayer type, with still unsaturated surface of the maple wood sawdust. The variation of the Langmuir isotherm constant K_L according to pH values indicates the fact that the affinity of metal ions onto maple wood sawdust is pH dependent.

The Langmuir isotherm dimensionless constant separation parameter (R_L) provides important information about the nature of adsorption (Table 4) and it was calculated using Eq. (6) for the different pH values ranging from 4.0 to 8.0. The values of R_L between 0 and 1.0, indicating more favorable sorption of copper ions onto maple wood sawdust for the pH values of 4.0 and 6.0. However, the Langmuir separation parameter R_L is dependent on concentration and according to Bhattacharyya and Sharma [29], this indicates that the sorption of copper onto maple wood sawdust is also feasible at the concentrations studied (Fig. 10).

3.2.7. Freundlich isotherm

K_F and $1/n$ are the Freundlich isotherm constants, which indicate the adsorption capacity and the adsorption intensity, respectively. Both values were determined from the linear plots of $\log q_e$ and $\log C_e$; and presented in Table 5. The slope and the intercept correspond to $1/n$ and K_F, respectively [10]. The linearized isotherm for copper (II) ions adsorption onto maple wood sawdust is presented in Fig. 11 and it was revealed that the plot of $\log q_e$ and $\log C_e$ yields a straight line. The values of regression coefficient (r^2) regarded as a measure of the quality of fit of experimental data on the isotherm models [17–19]. For copper solutions, the values of r^2 in the case of the Freundlich isotherms were 0.995, 0.944 and 0.21 for pH values of 4.0, 6.0 and 8.0, respectively. On the basis of the considerations of regression coefficient (r^2), it may be concluded in the case of the Freundlich isotherms that the data on sorption of copper (II) ions by maple wood sawdust represented more acceptable fit at pH 4.0.

Table 5
The Freundlich adsorption isotherm parameters and equation for adsorption of copper (II) ions onto maple wood sawdust.

pH value	q_e (mg/g)	The Freundlich isotherm constants			Equation
		K_F	$1/n$	r^2	
4	5.6	0.7439	0.5442	0.9949	$q_e = 0.7439C_e^{0.5442}$
6	6.1	0.3806	0.7256	0.9441	$q_e = 0.3806C_e^{0.7256}$
8	5.4	1.047	0.2771	0.2101	$q_e = 1.047C_e^{0.2771}$

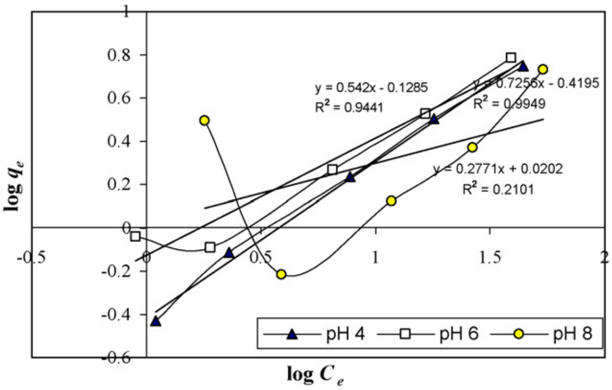

Fig. 11. The Freundlich isotherm plots for the adsorption of copper ions onto maple wood sawdust sample for different pH values.

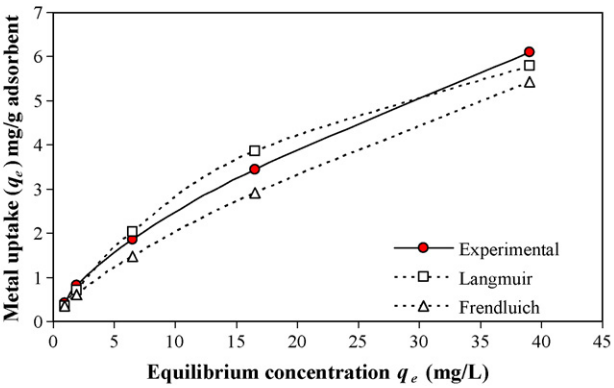

Fig. 12. Equilibrium curves of the Langmuir isotherm, the Freundlich isotherm and the experimental values for copper adsorption onto maple wood sawdust.

From the adsorption isotherm modeling, it was revealed that the adsorption of copper ions followed both the Langmuir and the Freundlich type isotherms. However, a comparison of the correlation coefficients indicates that the experimental data are fitted somewhat better by the Freundlich isotherm model than the Langmuir isotherm model. Fig. 12 also shows that the curve generated by the Langmuir isotherm data are very close to experimental data. This was supported the assumption that the Langmuir isotherm was well fitted [30] to this study. The maximum copper adsorption capacity (q_m) on maple sawdust was determined (9.191 mg/g) using the Langmuir linearized equation. Similar adsorption capacities have been found by other researchers who have applied lingocellulosic materials for copper adsorption (Table 1).

4. Conclusions

Adsorption studies on maple wood sawdust have been shown to be highly effective in removing of copper (II) ions from aqueous solution. This adsorbent is widely available as a waste material, is mechanically stable, and most importantly it is environmentally appealing. In addition, this adsorbent does not mix with water and it can be separated very easily from water. The maximum copper (II) ions adsorption capacity of maple wood sawdust is very close to other adsorbents. Therefore, it may be used as an alternative adsorbent, replacing costly materials, such as activated carbon, resins, etc. The maximum Cu(II) ions adsorption capacity (q_e) obtained from the Langmuir isotherm equation is 9.19 mg/g maple wood sawdust that is higher than the experimental value of 6.1 mg/g maple wood sawdust. This supported the assumption that only monolayer coverage occurred on the outer surface of maple wood sawdust. The variation of the Langmuir isotherm parameters indicate the fact that the affinity of metal ions onto maple wood sawdust is pH dependent and the sorption data can be used for the modeling of both the Langmuir and the Freundlich isotherms. However, a better fit is observed for the Langmuir isotherms.

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