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Removal of Pb (II) ION from Aqueous Solutions using Raw and Modified *Pinus Sylvestris* Sawdust

KEYWORDS

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ABSTRACT *The present study describes the adsorptive removal of Pb(II) ions from aqueous solutions by raw sawdust (R-SD) and sawdust modified with urea (U-SD) or thiourea (TU-SD). Adsorption experiments were carried out using a batch technique. The influences of solution pH, contact time, initial lead concentration, and adsorbent dose on the removal efficiency have been investigated. Langmuir and Freundlich adsorption isotherms fit well in the experimental data and their constants were evaluated. The results obtained in this study showed that sawdust modified with urea or thiourea has higher removal efficiencies (97.0-98.3%) for removal of Pb(II) from aqueous solutions in the Pb(II) concentration range of 10-50 mg/L compared to those of raw sawdust (86.7-95 %) used in this study. The results of treatment of some polluted water samples showed that the amount of lead reduced from 1.10 ± 0.02 mg/L to 0.55 ± 0.02; 0.46 ± 0.02 and 0.36 ± 0.02 by application of raw sawdust (R-SD), urea modified sawdust (U-SD) and thiourea modified sawdust (TU-SD), respectively. These facts suggest that the raw and modified sawdust present high potential to remove heavy metals from wastewaters.*

1. Introduction

Fresh water is already a limiting resource in Egypt and many parts of the world. In the next decades, it will become even more limiting due to increased population, urbanization, and climate change. This limitation is caused not just by increased demand for water, but also by pollution in freshwater ecosystems. Pollution decreases the supply of usable water and increases the cost of purifying it. Major water pollutants include a variety of organic and inorganic chemicals such as heavy metals, dyes and industrial compounds. They can affect human health and/or interfere with industrial or agricultural water use. If the level of a pollutant in the water supply exceeds an acceptable level for a given water use, the water is considered unsafe or too degraded for that use. Solutions to such pollution problems, therefore, usually focus on reduction of pollution at the source and/or treatment of the polluted water prior to use [1-5].

Heavy metals are widely distributed in the environment and are ecologically important due to their high toxicity for living organisms including human beings [6]. Several industrial activities are important sources of environmental pollution due to their high content of several heavy metal ions. In particular, Pb(II) is a common metal ion found in effluents of a large number of industries. Many human activities such as mining, metallurgy and industrial wastewater implications cause heavy metal contamination of surface and ground water and increase the risk of water crises in the country. These metals have large significance effects on the economic and public health of ecosystems [7]. The large affinity of Pb(II) for thiol and phosphate-containing ligands inhibits the biosynthesis of heme and thereby affects membrane permeability of kidney, liver and brain cells. This results in either reduced functioning or complete breakdown of these tissues [8]. On the other hand, properly treated wastewater may be applied as water for irrigation or it may be discharged to ground water sources, which in both cases, it lowers the water shortage. The removal of metal ions from effluents is important to many countries of the world both environmentally and for water re-use.

There are many methods for the removal of metal ions from solutions including, chemical precipitation, complexation, solvent extraction, and membrane processes. However, most of these methods are either economically prohibitive or too complicated for the treatment of metals [1,2]. Among the physicochemical treatment processes, adsorption is found to be highly effective, cheap and easy to adapt. It is quite selective, effective, and able to remove various levels of soluble heavy metals in solution. In recent years, considerable attention has been focused on the removal of heavy metals using biosorbents derived from low-cost materials. Several biosorbents such as peat, sawdust, sewage sludge, and crop waste have been used for the treatment of metals in aqueous solution [9]. Sawdust is one possible material because it is produced in large quantities at sawmills as a solid waste. Sawdust contains primarily lignin and cellulose. In this context, sawdust of Pinus sylvestris is particularly interesting in Egypt because of its high availability and low-cost. In addition, it is a renewable resource, and does not need to be regenerated after it has been used to remove the metals. The main objective of this study was to investigate the feasibility of using raw and modified sawdust (Pinus sylvestris) for the maximum removal of Pb(II) ion from aqueous solutions and polluted water samples at optimized process parameters such as initial concentration, adsorbent dose, contact time and pH. The treatment of sawdust by urea or thiourea was performed to increase the power of Pb(II) ion removal from aqueous samples. In this work, the adsorption of Pb(II) ion on raw and modified sawdust was studied using a batch equilibrium technique, and the equilibrium adsorption data was described by Langmuir and Freundlich isotherm models.

2. Materials and methods

2.1. Preparation and modification of sawdust

The sawdust, originating from Pinus sylvestris, was first sieved (20-30 mesh), then washed with distilled water, and dried in an oven at 80° C, until constant weight (raw sawdust, R-SD). Next, 15 g of R-SD was mixed in a beaker with 1000 ml of 0.25 M urea (U) or thiourea (T) solution, and allowed to soak for 24 hours. Then, the mixture was filtered to remove the adsorbent, which was washed several times with distilled water to provide neutral pH. The adsorbents were then oven-dried at 80° C for 2 h. The sawdust treated

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with urea is denoted (U-SD) and that treated with thiourea is denoted (T- SD). The materials were kept in an airtight container for further use.

2.2. Adsorbate and Reagents
All the chemical compounds used to prepare the reagent solutions were of analytical grade and were obtained from Sigma-Aldrich ((Germany). The stock solution of Pb(II) in this study (1000 mg/L) was prepared by dissolving weighed quantity of $Pb(NO_3)_2$ in double distilled water. The solution was further diluted to the required concentrations before use.

2.3 Polluted water samples
Polluted water samples were obtained from the drain point of El-Bashteer sea in Bahr El-Baker drain, and the connection canal between El-Manzala lake and the Suez canal, Port Said, Egypt. The samples were filtered by Wattman 42 filter paper to remove any suspended materials and kept in fridge (<4 °C) for adsorption experiments.

2.4. Scanning electron microscopy and Fourier Transform Infrared study
Surface morphology was studied using scanning electron microscopy (SEM, JEOL JXA- 840 Electron Probe Microanalyzer- Japan). All samples were coated with gold prior to testing. For the main functional groups that might be involved in metal adsorption, a Fourier Transform Infrared (Nicolet, AVATAR FTIR- 360) analysis was done on the raw sawdust and modified sawdust to determine the surface functional groups, and the spectra were recorded from 4000 to 400 cm^{-1}.

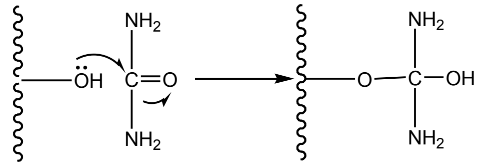
2.5. Batch adsorption studies
Batch adsorption studies were performed by agitating 1 g of raw or modified sawdust with 50 mL of synthetic Pb(II) solutions or polluted water samples. pH of the solution was adjusted by adding 0.1 M HCl or 0.1 M NaOH solution as per required pH value. The contents in all adsorption experiments were shaken for desired contact time at room temperature (25±2 °C) and then filtered through Whattman 42 filter papers. In this study, the contact time was varied from 15 to 90 min, the pH of the solution from 2 to 9 , the initial concentration from 10 to 50 mg/L and the amount of adsorbent from 5 to 30 mg/L. A Perkin-Elmer model 2380 atomic absorption spectrometer (AAS) was used for lead analysis. The results are expressed in terms of removal efficiency (%) of Pb(II) ion and adsorption capacity (mg/g) of the raw and modified sawdust for lead ion, according the following relationships:

Removal efficiency (%) $= \frac{C_0 - C_e}{C_0} \times 100$ (1)

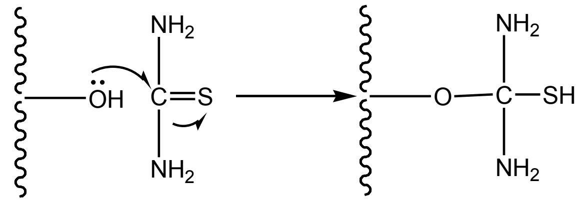
Adsorption capacity (mg/L) $= \frac{C_0 - C_e}{m} \times V$ (2)

Where, C_0 and C_e are the initial and final Pb(II) concentrations (mg/L) respectively, V the volume of lead solution (L) and m the weight of adsorbent(g).

3. Result and Discussion
3.1. Characterization of raw and modified sawdust
One strategy to improve the adsorption of metal ions from wastewater and the dimensional stability of wood is to chemically modify the cell wall. Sawdust can be modified as esters, isocyanates, acetals, epoxides etc., by using appropriate reagents. In this work sawdust is modified by using urea and / or thiourea, the modification reaction is suggested to take place through the hydroxyl group of sawdust on the carbonyl group (C=O) of urea or thion group (C=S) of thiourea. A schematic representation of chemical treatment of lignocellulose with urea and thiourea is depicted in Figure 1.



Lignocellulose- Urea **(A)**



Lignocellulose- Thiourea **(B)**

Fig. 1. Modification of sawdust by urea (A) and thiourea (B)

Infrared spectroscopy (IR) is a useful technique for studying wood chemistry [10], as well as characterizing the chemistry of wood [11-13] and analyzing chemical and structural changes that occur in wood components due to different treatments [14-16]. In this work we used IR spectra to clarify the modification of sawdust with urea and / or thiourea.

The spectrum of free saw dust shows the same basic structure as all wood samples: strong broad OH stretching centered at 3405 cm^{-1} and a strong broad superposition with sharp and discrete absorptions in the region from 1000 to 1742 cm^{-1} [17].

Comparing the spectra of holocellulose and lignin reveals that, the absorptions situated at 1510 and 1651 cm^{-1} (aromatic skeletal vibrations) are caused by lignin, and the absorption located at 1742 cm^{-1} is caused by holocellulose; this indicates the presence of C=O stretch in non-conjugated ketones, carbonyls and ester groups [17, 18].

Fig. 2. shows the FT-IR spectra of unmodified saw dust and that modified with urea and thiourea. The spectra show in the fingerprint region between 1800 and 1100 cm^{-1} bands assigned to the main components of wood: cellulose, hemicelluloses and lignin, the spectra being very complex, slight differences can be detected in the infrared spectra, both in the different absorbance values and shapes of the bands and in their location. A decrease in the intensity of the O–H absorption band at 3405 cm^{-1} and a shift in its center were observed, indicating that the hydroxyl group contents in wood were reduced after the modification reaction [19]. The higher xylan content in hardwood is evidenced by a stronger carbonyl band at 1740 cm^{-1}, for chemically modified sawdust this band remains unaltered on modification. The band at 1651 cm^{-1} is assigned to the aromatic moiety of lignin, in the spectra of sawdust this band is shifted to higher wave-number after modification, indicating the presence of an increase in the electron flow to the ring. This behavior is taken as an evidence that modification takes place on the hydroxyl group of lignin.

A new shoulder band in the region 1628-1634 cm^{-1} appears on the modified sample which could be attributed to the in-plane-bending of NH_2 group of urea or thiourea [20]. This band is taken as evidence that the modification process has taken place. Another new shoulder band is observed in the spectra of modified sawdust at 1228 cm^{-1} [17]. This band is assigned to the stretching vibration of C-N of urea or thiourea molecules.

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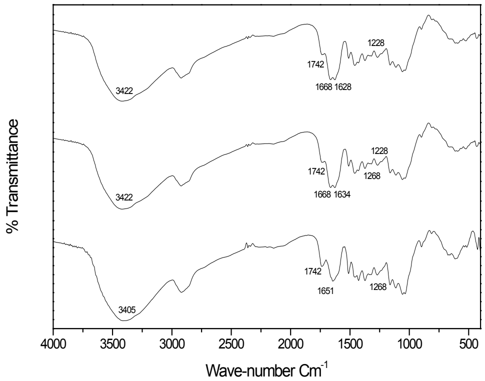
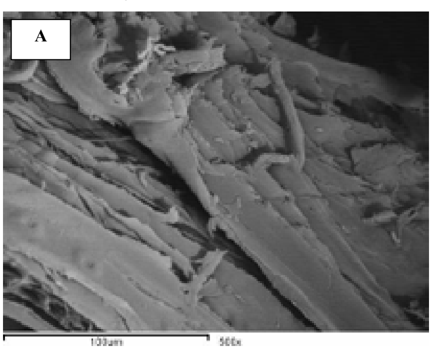
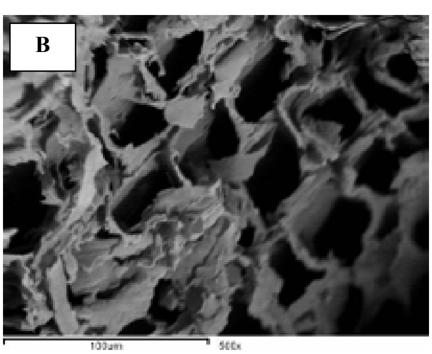


Fig. 2. FTIR spectra of raw , urea modified and thiourea modified sawdust

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography. The fracture surfaces of the flexural test specimens were characterized with scanning electron microscopy. The scanning data are analyzed at magnifications of 500 X , 1000 X and 1500 X. Approximately 9 SEM images are taken and analyzed for pure sawdust and saw dust modified with urea and thiourea.

Fig.3. (a), b and (c) show SEM images at magnification of 500 x of fracture surface of the pure sawdust, sawdust modified with urea and that modified with thiourea, respectively. SEM images show that the surface of sawdust is smoother than that of the sawdust modified with urea or thiourea because of heterogenity in the distribution of urea or thiourea on the surface of saw dust. The SEM images show also that, there are clear gaps between sawdust and the modifying agents indicating the weak interface bonding. In general, modifying agents are randomly distributed on the surface of sawdust and randomly reacted with the surface.





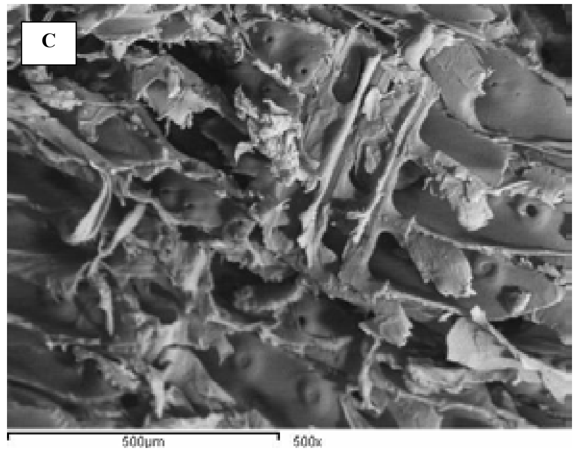


Fig.3. SEM micrograph of sawdust (magnification, 500): (a) raw sawdust, (b) urea modified sawdust and (c) thiourea modified sawdust.

3.2. Adsorption studies using raw sawdust(R-SD)

3.2.1. Effect of pH

pH of the solution is the most important parameter affecting metal ion adsorption. At high pH, heavy metal ions precipitate as metal hydroxides, and at low pH they compete with hydrogen ions for available adsorption sites [4, 21-23]. The effect of pH on the adsorption of Pb(II) ion from synthetic solutions on raw sawdust has been studied by varying it in the ranges of 2-9 as shown in Fig. 4. As shown in Fig. 4. The removal efficiency of Pb(II) ion depends on pH, it increases with the increase in pH value reaching the maximum removal at pH 5 and then remains almost constant. Hence, pH 6 was considered to be the optimum pH for further studies. The effect of pH can be explained considering the surface change on the adsorbent material. At pH value lower than 4, the removal efficiencies were found to be low due to the competitive adsorption of H_3O^+ ions and Pb(II) ions for the same available adsorption sites. As the pH increased, the adsorption surface becomes less positive and therefore electrostatic attraction between the lead ions and sawdust surface is likely to be increased.

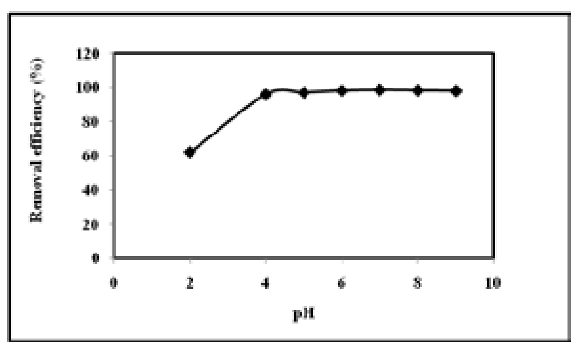


Fig. 4. Effect of pH on the adsorption of Pb(II) ion on raw sawdust (initial concentration = 30 mg/L, contact time = 90 min, adsorption dosage = 20 g/L).

3.2.2. Effect of initial metal ion concentration

In batch adsorption processes, the initial metal ion concentration in the solution plays a key role and a driving force to overcome the mass transfer resistance between the solution and solid phases [24]. Therefore, the amount of metal ions adsorbed was expected to be high with a higher initial concentration of metal ions. The effect of initial concentration of Pb(II) ions while, keeping the other parameters constant, on the adsorption process is shown in Fig. 5, it is apparent that the adsorption capacity, q_e (mg/g), increased with the increase of initial metal ion concentration. While, by increasing

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the initial concentration of Pb(II) solution from 10 to 50 mg/L, the lead removal reduced from 95.0 % to 86.7%. An explanation for this result is that at low metal ion/adsorbent ratio, metal ion adsorption involves higher energy sites. As the meal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sits, resulting in decrease in the removal efficiency.

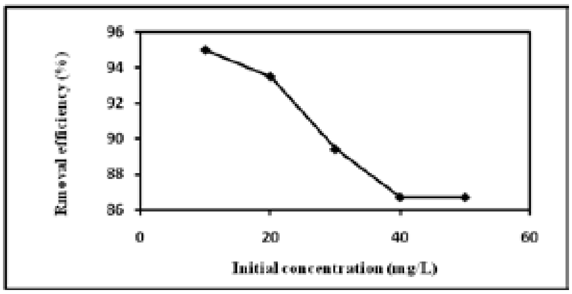

Fig. 5. Effect of initial Pb(II) ion concentration on the adsorption (contact time = 90 min, pH 6.0 and adsorbent dose = 20 g/L). 3.2.3.. Effect of contact time

The results of the experimental test measuring the effect of contact time on the batch adsorption of 30 mg/L Pb(II) at initial pH value 6 and adsorbent dose of 20 g/L are listed in Table 4 and represented in Fig. 6. The adsorption rate was relatively fast in the initial stage, showing 91 % equilibrium attained within 30 min. This result indicates that adsorption of Pb(II) ion is mainly occurring at the surface of the sawdust. As the surface adsorption sites become exhausted, the rate of uptake is controlled by the rate of transportation from the exterior to the interior sites of the sawdust particles. In addition, the removal efficiencies decreased slightly with increasing contact time after equilibrium had been reached. This probably resulted from saturation of sawdust surface with metal ions followed by adsorption and desorption processes that occur after saturation [25].

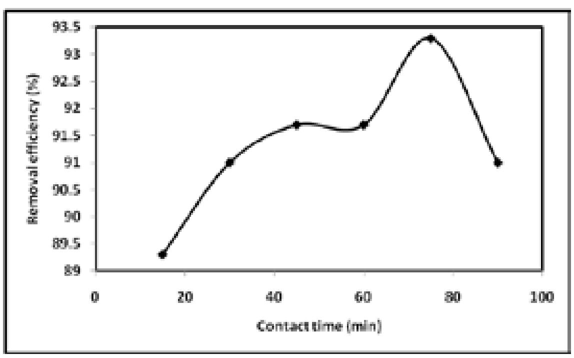

Fig. 6. Effect of contact time on the adsorption of Pb(II) ions (initial concentration = 30 mg/L, adsorbent dose = 20 g/L and pH 6)

3.2.4. Effect of adsorbent dose

The adsorption studies of Pb(II) ions on sawdust were done at room temperature (25 ±2 ˚C) by varying the quantity of adsorbent from 5 to 30 g/L, while keeping the other parameters constant. The influence of adsorbent dosage in percent adsorption of Pb(II) ions is shown in Fig. 7. The adsorptive removal of Pb(II) ions by sawdust increased from 76.7 to 97.3 % by increasing the sawdust dosage from 5 to 30 g/L under equilibrium conditions. It is apparent that the percent removal of Pb(II) ions increases rapidly with increase in the dose of the adsorbent due to the greater availability of the exchangeable sites or surface area.

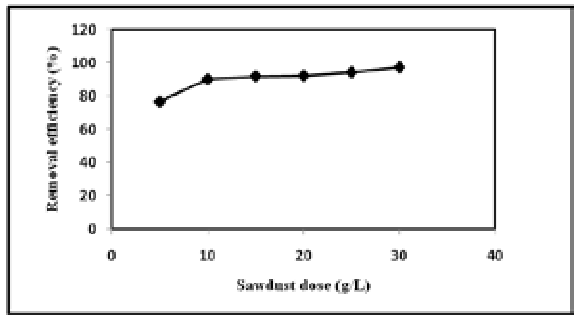

Fig.7. Effect of adsorbent dose on the adsorptive removal of Pb(II) ions by raw sawdust ((initial concentration = 30 mg/L, contact time 90 min and pH 6).

3.3. Adsorption studies using modified sawdust

In these tests, sawdust (Pinus sylvestris) treated with urea or thiourea was used to remove Pb(II) ions from aqueous solutions at nearly the same optimum conditions. In order to have a better comparison, The adsorptive removal of Pb(II) ions by modified sawdust was compared with that of raw sawdust (Table 1). Comparing the results, it appears that the maximum adsorptive removal percent of Pb(II) ions using sawdust modified with urea or thiourea was higher than raw sawdust. These findings may be attributed to the nature of urea and thiourea that provided more binding sites within each of their substrates for lead ions. Based on the obtained data we conclude that either urea or thiourea can be used to enhance the removal of heavy metals from aqueous solutions using sawdust.

Table 1 Removal efficiency (%) of Pb(II) ions using raw sawdust (R-SD), urea modified sawdust (U-SD) and thiourea modified sawdust (TU-SD).

pH	Sorbent dose (g/L)	Initial concentration (mg/L)	Removal efficiency (%)		
			R-SD	U-SD	TU-SD
6-7	20	10	95.0	97.0	97.9
		20	93.5	97.5	97.6
		30	89.4	97.7	97.6
		40	86.7	97.9	97.9
		50	86.7	98.3	98.2

3.4. Adsorption isotherms

Adsorption is usually described through an isotherm. The adsorption isotherms revel the relationship between absorbate concentration and its adsorption degree on the adsorbent surface at a constant temperature. Several models describe the process of adsorption. Although many theories of adsorption have been put forward to explain the phenomena of adsorption, the isotherms of Langmuir and Freundlich had been widely used by several researchers. Therefore, Langmuir and Freundlich isotherms are used to understand the extend and degree of favorability of lead sorption onto raw and modified sawdust (P. sylvestris).

3.4.1 Langmuir isotherm

This model assumes that the adsorption occurs at specific homogeneous sites on the adsorbent surface and is used successfully in many monolayer adsorption process [26]. The linear form of Langmuir isotherm is given by Eq 3.

$$1/q_e = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}}$$

Where:

q_e =
The amount of metal ions adsorbed per mass of adsorbent (mg/g).

C_e =
The metal concentration in aqueous phase at equilibrium

(mg/L)

K_L =
Langmuir isotherm constant related intensity of adsorption.

q_{max} =
Langmuir monolayer sorption capacity.

The parameters were obtained by fitting the experimental data of the plot $1/q_e$ versus $1/C_e$ for lead ions removal at different concentrations. The values of q_{max} and K_L(Longmuir constants) were obtained from the intercept and slope of Eq.(3).

The plot of Eq.(3) is shown in Fig.(8). The values of Langmuir parameters and the coefficient of correlation (R^2) are shown in Table (6). The maximum adsorption capacity (q_{max}) of lead ions removal and intensity of adsorption (K_L) are 2.9 mg/g and 0.34 (L/mg), respectively.

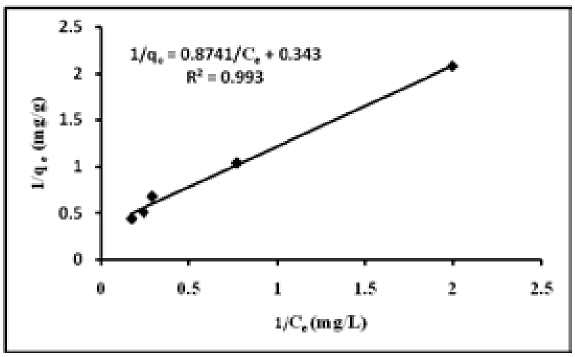

Fig. 8.linear Langmuir isotherm of Pb(II) ion adsorption onto raw sawdust (Pinus sylvestris)

Table 2 Adsorption isotherm model constants and correlation coefficients for the adsorption of Pb(II) ions on raw and modified pinus sylvestris sawdust

Adsorbent	Langmuir			Freundlich		
	K_L (L/mg)	q_{max} (mg/g)	R^2	K_F (mg/g)	1/n	R^2
R-SD	0.34	2.9	0.993	0.76	0.611	0.986

The isotherm data have linerarized using Langmuir isotherm as shown in Fig.(8), the high values of correlation coefficient (R^2 = 0.993) indicates a good agreement between the parameters and confirms the monolayer adsorption of Pb(II) ions onto pinus sawdust surface [27, 28].

3.4.2. Freundlich isotherm
The Freundlich model is an indicator of extent of heterogeneity of the adsorbent surface. For this model, the concentration of solute in solution at equilibrium (C_o) and the amount of solute adsorbed being q_e are connected by the following equation:

$$q_e = K_F C_e^{1/n}$$

Where, K_F and n are the Freundlich constants and represent the adsorption capacity and intensity of adsorption, respectively. The linear form is given by the following:

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

Thus, a plot of ln q_e versus ln C_e (Fig. 9) should be a straight line with a slope 1/n and an intercept of ln K. This model deals with the multilayer adsorption of the substance on the adsorbent. The related parameters were calculated and listed in Table 2. The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent while Langmuir type isotherm hints towards surface homogeneity of the adsorbent. This leads to the conclusion that the surface of sawdust is made up of small heterogeneous adsorption patches which are very much similar to each other in respect of adsorption phenomenon and the values of K_F and 1/n were determined from intercept and slope of the plot and are given in Table 2.

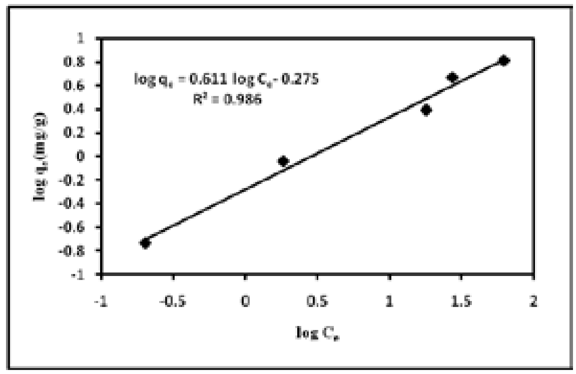

Fig. 9. Linear Freundlich isotherm of lead adsorption onto raw sawdust (Pinus sylvestris)

3.5. Applications
The results obtained in this study demonstrated the potential use of raw and modified sawdust (Pinus sylvestris) for removal of Pb(II) ions from aqueous solutions. Thus, the application of this low-cost material in environmental samples must be followed. Industrial wastewaters present an environmental problem due to their high level of lead. The permissible lead discharge limits in surface water in Egypt is 0.5 mg/L. However ,many of industrial wastewaters in Egypt contained values of heavy metals higher than Egyptian limits.

The results of treatment of some polluted water samples by raw and modified sawdust show that the amount of lead reduced from 1.10 ± 0.02 mg/L to 0.55 ± 0.02; 0.46 ± 0.02 and 0.36 ± 0.02 for application of raw sawdust (R-SD), urea modified sawdust (U-SD) and thiourea modified sawdust (TU-SD), respectively. These facts suggest that the raw and modified sawdust present high potential to remove heavy metals from wastewaters.

4. Conclusions
Batch adsorption experiments were performed for the removal of Pb(II) from aqueous solutions by using raw sawdust and sawdust modified with urea or thiourea. The adsorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time, and adsorbent doses. The pH experiments showed that the removal efficiency of Pb(II) ion depends on pH, it increases with the increase in pH value reaching the maximum removal at pH 5 and then remained almost constant. Increase in mass of adsorbent leads to increase in Pb(II) adsorption due to increase in number of adsorption sites. The adsorptive removal of Pb(II) ions by sawdust increased from 76.7 to 97.3 % by increasing the sawdust dosage from 5 to 30 g/L under equilibrium conditions. The Langmuir and Freundlich adsorption isotherm models were used to represent the experimental data. Both the models were fitted well. The results obtained in this study show that modifying sawdust with urea or thiourea significantly increases the metal ion adsorption capacity, and that modified sawdust could be used as an adsorbent for heavy metal ions removal from aqueous solutions and wastewaters. Moreover, these materials could also be used for purification of water. The removal of metal ions from effluents is important to many countries of the world both environmentally or and for water re-use.

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