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RESEARCH ARTICLE

Removal of Cu (II) and Pb (II) from Aqueous Solution Using treated Rice straw

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Abstract

The present study deals with the application of treated rice straw, as low-cost agricultural residues, for the adsorptive removal of Cu (II) and Pb (II) from its aqueous solutions. Effects of adsorbent dosage, initial metal ions concentration, and pH as well as contact time on the adsorption of Cu (II) and Pb (II) were investigated.
Data obtained from column experiment showed that values of breakthrough capacity was calculated and found to be 6 and 32 mg g^{-1} for $Cu^{+2}$and Pb^{+2}, respectively.

Scanning Electron Microscope (SEM) of RS powder samples were recorded to explore the morphology of the studied adsorbent. It was clearly seen that the external surface of rice straw is full of cavities. Practical separation experiments for the above-mentioned cations on rice straw column from aqueous waste solutions were carried out. Adsorption increases with increasing the pH of the solution for the studied metal ions and also increases with increasing the amount of adsorbent and stay nearly constant for Cu^{2+} and Pb^{2+} metal ions with no significant increase in percentage removal above 0.05 g / 5ml.

INTRODUCTION

Heavy metals are one of the most persistent pollutants in water. Unlike other pollutants, they are non-degradable, but can accumulate throughout the food chain, producing potential human health risks and ecological disturbances. Their presence in water is due to discharges from residential dwellings, groundwater infiltration; fertilize industries, tanneries, batteries, paper industries, pesticides and industrial discharges etc. **(Celik et al., 2005 and Pastircakova et al., 2004)**. In Egypt, industrial wastewater is considered the main source of pollution that leads to serious environmental problems **(Nasr, 2015)** unfortunately; more than 350 factories are discharging their industrial wastewater directly, or with no appropriate treatment, into the Nile **(Nasr et al., 2015).**

These heavy metals pose serious health hazard, including cancer, organ damage, disorders of nervous system, and in extreme cases, death **(Sud et al., 2008).** The danger of heavy metal pollutants in water lies in two aspects of their impact. Firstly, heavy metals have the ability to persist in natural ecosystems for an extended period. Secondly, they have the ability to accumulate in successive levels of the biological chain, thereby causing acute and chronic diseases. For example, copper toxicity causes itching and dramatization, keratinization of the hands and soles of feet **(Huang et al., 2007 and Al-Asheh et al., 2002).** Severe gastro-intestinal irritation and possible changes in the liver and kidney occur due to intake of excessively large doses of copper **(Ajmal et al., 1998).**

In order to remove Cu (II) and Pb (II) from effluents to the permissible level, copper and lead are conventionally removed by several techniques namely: precipitation **(Patterson, 1977)**, ion exchange **(**Tiravanti **et. al., 1997)** and adsorption methods **(Dahbiet al., 1999)**. The commercially available activated carbon in granular or powder form is effective for the removal of various heavy metal ions. However, due to prohibitive cost their use is limited in developing countries like

Egypt. So there is a crucial need to develop low cost and easily available adsorbents for the removal of heavy metal ions from the aqueous environment.

Several types of biomasses have been investigated for their usage in wastewater treatment for heavy metal removal **(Zhang et al., 1998 and Kapooret al., 1999).** An abundant source of potentially metal-sorption biomass is cellulosic agricultural residues. Although their sorption capacity is usually lesser than activated carbons but these materials could be an inexpensive substitute for the heavy metal laden wastewater's treatment (**Altundogan et al.,2005).**

Rice straw is considered as an agriculture residues material, at harvesting time, it is burnt to release nutrients for the next growing season and to get rid of its huge quantities. The burning process of rice straw leads to emission of choking smoke which causes the 'black cloud' phenomenon and its effects on visibility, human health and global climate by emitting particulate matters and other gaseous pollutants. The rice straw contains cellulose (32-47%), hemicellulose (19-27%) and lignin (5-24%) **(Saha, 2003)** In the present study an attempt has been made to explore the use of rice straw as sustainable adsorbents for Cu and Pb removal from aqueous systems under different experimental conditions.

In this work, laboratory studies to produce activated carbon from rice straw (RS) by thermal activation are presented. The prepared RS powder was characterized using different analytical techniques such as chemical stability, scanning electron microscope (SEM) and FTIR spectra. It is essential to study the thermodynamics parameters ($\Delta G°$, $\Delta S°$, and $\Delta H°$) for the adsorption of Cu2+ and Pb2+ on rice straw activated carbon, equilibrium distribution coefficients of metal ions on the prepared activated carbon were determined to explore the removal efficiency of the studied cations.

2. MATERIALS AND METHODS

2.1. Preparation of Adsorbent

Rice straw (RS), as low-cost agricultural residues, were collected from Soil & Water Research Department experimental farm, Nuclear Research Center, Atomic Energy Authority, Inshas, Egypt. RS samples were washed repeatedly with tap water then washed with distilled water to remove dust and soluble impurities and were allowed to dry at sun light in a green-house for 48 hours. The rice straw samples were dried in an air frost oven at 333–343 K for 24 hours. The dried rice straw was then converted into fine powder using mechanical grinder. Then powder was sieved to get fine particulates with size range between 150 to 370 µm. After drying for several hours at room temperature, the rice straw powder was preserved in air tight glass bottles for use as sorbents materials.

2.2. Physical and chemical characteristics of the adsorbent

Particle size was determined using sieves of different particle size. Packed and apparent densities were determined by a tamping procedure using a 25 mL graduated glass cylinder. SEM image of the particles were identified using Jeol scanning electron microscope of JSM-6510A Model, Japan, operating with beams of primary electrons ranging from 5 to 30 keV.

The chemical composition of the studied sorbent was performed by X-ray fluorescence (XRF) of solid samples with Philips XRF detector, Holland, while, the chemical composition of the organic part was performed by the Flash EA Analyzer, Italy (Elemental analysis, C, H, and N concentrations). The IR spectra of the prepared RSP were measured by the KBr disk method by mixing the solid with potassium bromide in the ratio 1:4 and ground to a very fine powder. A transparent disk was formed in a moisture-free atmosphere. The IR spectra were recorded using a Shimadzu infrared spectrometer (BOMEM-FTIR) obtained from Shimadzu Kyoto "Japan", in the range 400–4,000 cm^{-1}.

2.3. Batch technique

The sorption of Cu^{2+} and Pb^{2+} ions by the rice straw was carried out using a batch technique where 0.1 g of rice straw powder was contacted with 10 ml (at a V/m ratio of 100 ml g^{-1}) of 50 mg l^{-1} initial metal ion concentration of the above mentioned metal ions solution. The amount of rice straw powder and the volume of aqueous solution in all sorption experiments were kept constant where otherwise specified. In all cases, the pH of the solution was adjusted using solution of hydrochloric acid and was measured before and after equilibration by using a pH meter of the bench, model 601A, USA. The mixture was placed overnight (time within an equilibrium was attained) in a shaker thermostat adjusted at 25±1°C; agitating rate, 400 rpm; after equilibrium, the solutions were separated by centrifugation and the concentration of metal ions in the supernatant were determined using atomic absorption spectrophotometer (AAS). All tests were repeated two or three times and the total experimental error were about ± 3%.

Experiment to obtain the effect of initial concentrations of metal ion was conducted using initial metal ion concentrations ranged from 50 to 600mg L^{-1} for both of Pb and Cu. To determine the effect of contact time, shaking time was ranged from 5 to 240 minutes. Sorbent amount was ranged from 0.02 to 0.20 g mixed with 5.0 ml of metal ion solution to determine effect of sorbent amount. Varied initial pH of metal ion solution was ranged from 1.5 to 6.5 to determine effect of pH on removal process.

2.4. Continuous flow experiment

Chromatographic column breakthrough investigations were conducted as follows; 1 g of the rice straw powder (of particle size 0.375 mm) was packed in a glass column (1.3 cm diameter and 4 cm heights) to give bed heights of 5.3 cm^3 volume. 500 ml of the desired neutral solutions (pH = 6.5) containing 100 mg L^{-1} of metal chloride [$M (Cl)_x$ where M = Cu^{2+} or Pb^{2+}] were passed through the column beds at a flow rate 0.5 ml min^{-1}, equal fractions were collected and the concentrations were continuously measured using atomic absorption spectrophotometer.

3. CALCULATIONS

$$\textbf{Removal\%} = \frac{A_o - A_f}{A_o} x100 \qquad (1)$$

$$\textbf{Distribution coefficients } (\mathbf{K_d}) = \frac{[A_o - A_f]}{A_f} x V/m \quad \text{ml}/g \qquad (2)$$

Where;

$A_o$and A_f are the concentrations of the ions in solution before and after equilibration, respectively, V is the solution volume (ml) and m is the exchanger mass (g).

$$\textbf{Breakthrough capacity} = V_{(50\%)} x \frac{C_o}{m} \text{ (mg /g)} \qquad (3)$$

Where;

$V_{(50\%)}$: is the effluent volume at 50% breakthrough (ml).
C_o: is the concentration of feed solution.
M : is the amount of the column bed per gram.

The Van’t Hoff relation:

$$LnK_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (4)$$

Where ΔS^o is the entropy change, ΔH^o is the enthalpy change, R is the gas constant, and T is the absolute temperature. (**Mohan and Singh, 2002)**

The free energy change of specific adsorption (ΔG^o)

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (5)$$

and

$$\Delta G^o = -RT \ln K_d \qquad (6)$$

$$\textbf{Breakthrough capacity} = V_{(50\%)} x \frac{C_o}{m} \text{ (mg /g)} \qquad (7)$$

Where;

$V_{(50\%)}$: is the effluent volume at 50% breakthrough (ml).
C_o: is the concentration of feed solution.
M : is the amount of the column bed per gram.

4. RESULTS AND DISCUSSION

4.1. Characterization of material

The physico-chemical characterization of rice straw is shown in Table 1. The solubility experiments show that the studied RS powder as a sorbent material has reasonably good chemical stability. As the results indicate that, the material is resistant to HNO_3 and HCl media.

Table1. The characteristic of treated rice straw powder

Parameter	**Value**
Moisture content (%)	4.62
Bulk density (g/ml)	0.285
Apparent density (g/ml)	0.154
Ash content	46.6
pH	5.78
Surface area (m^2/g)	275.5
Particle size (mm)	0.168-0.370
Solubility in water (%)	0.00
Solubility in 0.5 M HCl (%)	0.06
Solubility in 5 M HCl (%)	0.16
Solubility in 0.5 M HNO_3 (%)	0.071
Solubility in 5 M HNO_3 (%)	0.18

To determine the functional groups of modified and unmodified rice straw, the unmodified rice straw was analyzed by FTIR spectroscopy (Fig. 1) and the modified rice straw with gamma radiation was analyzed by FTIR (Fig.2 and 3) respectively. The results represented the information about the functional groups on the surface of the cell wall of the biomass and the possible interaction between metals and the functional groups. Usually, the cell wall of rice straw compromise of carboxyl (COOH), lignin, carbonyl(C=O) and hydroxide (OH) which are important functional groups during heavy metal ions binding. (Adel et al., 2013). The FT-IR spectrum of the unmodified rice straw is shown in Fig. 1.and represented that the strong broad adsorption at 3401.58 cm^{-1} from vibration of –OH groups medium (Hassan et al., 2013) adsorption at 2918.31 cm^{-1} from $–CH_2$ groups , and adsorption at 1104.29 cm^{-1} from C–O–C bond of glycoside group (Pradhan et al., 1999). These sorption bands indicated the presence of cellulose component in rice straw. Furthermore, absorption at 1514.85 cm^{-1} can be attributed to the vibration of aromatic units in lignin component in rice straw (Adel et al., 2013). And the band that appeared at 1644.15 cm^{-1} represents C=O stretching of carbonyl group.and, the peak displayed at 1372 cm^{-1} is possibly due to carboxylate group (–COO) stretching (Hassan et al., 2013). Also the band at 867.78 cm^{-1} is characteristics of out of plane deformation vibration of C–H in aromatic structure (Castilla et al., 2000). The peak at 784.89 cm^{-1} is considered to be the bonding between C and Si, or the overlapping of the Si–O and Si–OH. The bands at 668 and 467 cm^{-1} are assigned, respectively, to Si–O–Al and Si–O–Si bending vibrations (Madejova.j. 2003).

Thus the morphology of this material can facilitate the adsorption of metals, between its cavities which make it a potential material for the adsorption of metals from aqueous solutions. In other word, based on the morphology of RS powder, it can be concluded that this material presents an adequate morphological profile to retain metal ions.

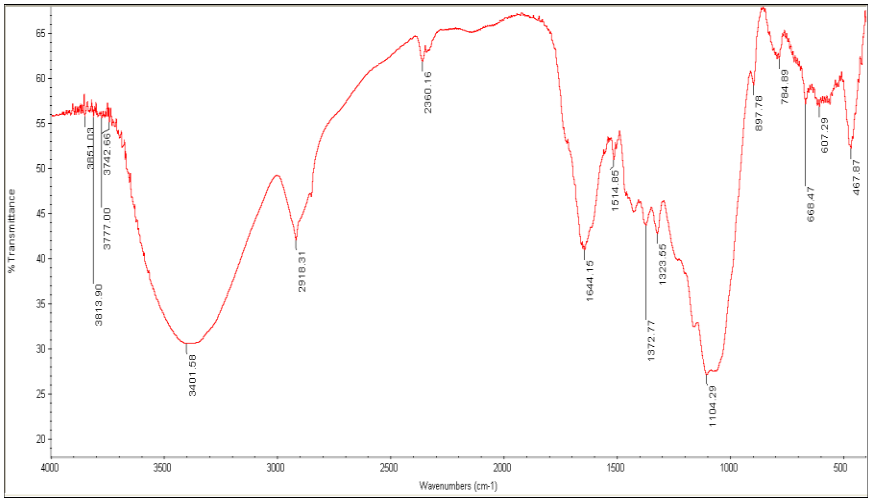

Fig.2: FT-IR spectrum of unmodified rice straw.

4.2. Adsorption dynamics

4.2.1 Effect of contact time

The agitation time was evaluated as one of the most important factors affecting the adsorption efficiency Equilibrium time is one of the most important operational parameter for an economical wastewater treatment process. Fig. 4 depicts Pb (II) and Cu (II) removal percentages as function of contact time..

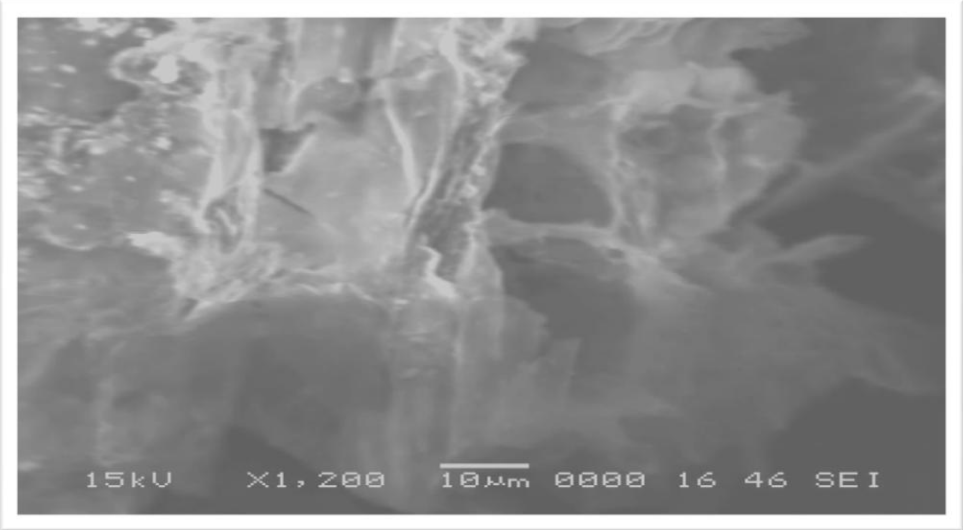

Fig. 3.SEM analysis of rice straw sample.Magnitude of 1200x.

Fig.4 shows Pb(II), Cu(II) and Co(II) removal percentages as a function of contact time. Results indicated that with increasing contact time from 5 to 240 min, the removal percentage increased until adsorption equilibrium was established. The metal uptake was rapid for all studied elements at the said concentration in first 25 min of contact. As shown in Fig. (4) the adsorption equilibrium was established within 50 min, this hold true for removal % of Pb(II), Cu(II) and Co(II) ions, whereas the removal percentages were (91.2 , 74.2 and 78.2%), for Pb(II), Cu(II) and Co(II) respectively.

Sevil Veli, and Bilge Alyuz (2007) indicated that the optimum time for copper and zinc removal were determined at 10 and 5 min, respectively. Their experimental studies indicated that high efficiency for copper and zinc adsorption can be obtained at short time periods. Jiang Kan et. al., (2006) indicated that time required for attaining equilibrium for Pb(II), Cu(II), Zn and Cd(II) was about 60 min. Similar trend found by **(Mousa et. al. 2010).** Therefore, 60 min shaking time was selected for all further studies.

4.2.2. Effect of pH on metal adsorption by Rice Straw.

The effect of pH on the adsorption of Pb(II), Cu(II) and Co(II) by Rice Straw is presented in Fig. 5. The pH of the aqueous solutions is an important operational parameter in the adsorption process because its effects on the metal ions solubility, the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction (Nomanbhay and Palanisamy, 2005 and Amuda et al., 2007).

The role of hydrogen ion concentration was examined on the Pb (II) and Cu (II) removal efficiencies. It is clear that the removal% was 44.78% for Cu (II) and 78.26% for Pb(II) at pH=2. Increasing the pH up to 6.5 resulted in an increase in the metal removal% until it reached the maximum value 73.32% for Cu (II) and 88.3% for Pb (II). Therefore, batch and column experiments in this investigation were carried out at pH 6.5. The decrease of the ion mobility's may be explained by the increase of the frictional forces exerted on the ions due to the change of the nature of hydrogen bonds in water.

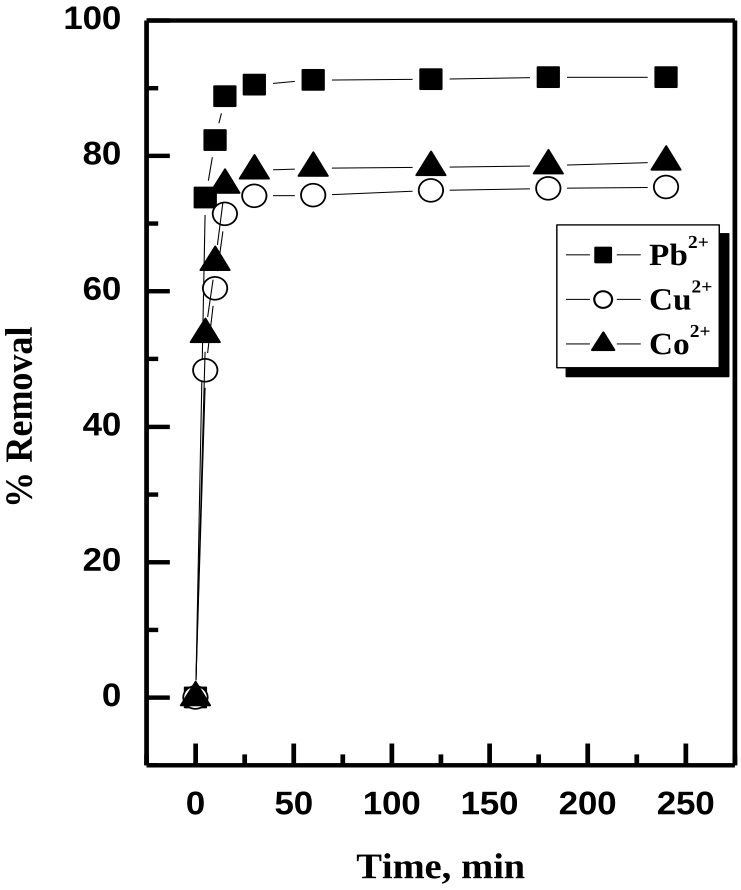

Fig.4. Effect of contact time on Cu^{2+} and Pb^{2} removal by rice straw.

Extensive research has assessed the metal adsorption characteristics of natural or modified clays and several organic/nonorganic residues and has demonstrated that pH variation influences heavy metal adsorption. In this experiment the role of hydrogen ion concentration was examined on the Pb(II), Cu(II) and Co(II), removal efficiencies by RSP. The results exhibited that the adsorption% increases with increasing the pH of the solution for the studied metal ions. The increase in adsorption is probably due to cation hydrolysis, since hydroxyl complexes are adsorbed preferentially over un-complexed cations or to the increase in the negative surface charge of the adsorbent related to the increase in the concentration of hydroxyl ions, leading to an increase in attraction for cation in solution (Zhu et al., 1998). Also, as the proton concentration increases, the following water cluster ions H_3O^+, $H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$ modifying the structure of water and thus the ion-water interaction.

Juan and Liliana (2012) indicated that pH values affected species of heavy metals in aqueous solutions and heavy metals removal increases as pH value rises, reaching a maximum around 5.0. Solution pH also makes effects on the adsorbent and the surface charge of the Activated carbon obtained from orange peel changes. Lacin *et al (2005)*. has found that the pH has positive effects on zinc adsorption by bentonite clay. Usually, raising the pH increases the capacity for zinc adsorption (Casagrande et al., (2004) and Sanchez et al.,(1999)). In the same way, the surface area of the adsorbent can influence in the adsorption process. Moloukhia, (2010) reported that upon increasing the pH, the percentage adsorption increased substantially. This increase was considered to be due to hydrolytic adsorption of ions. It is well known that most of heavy metals ions in aqueous solution tend to precipitate as solution alkalinity increases. For example, Juan and Liliana (2012) determined Cr3+, Cd2+, and Co2+ uptake as a function of hydrogen ion concentration for pH values from 2 to 14. They indicated that pH between 5.0-6.0, hydrogen ions are likely to compete with chromium, cadmium and cobalt ions. At pH values above 4 Cr3+, Cd2+, and Co2+ might precipitate as hydroxides.

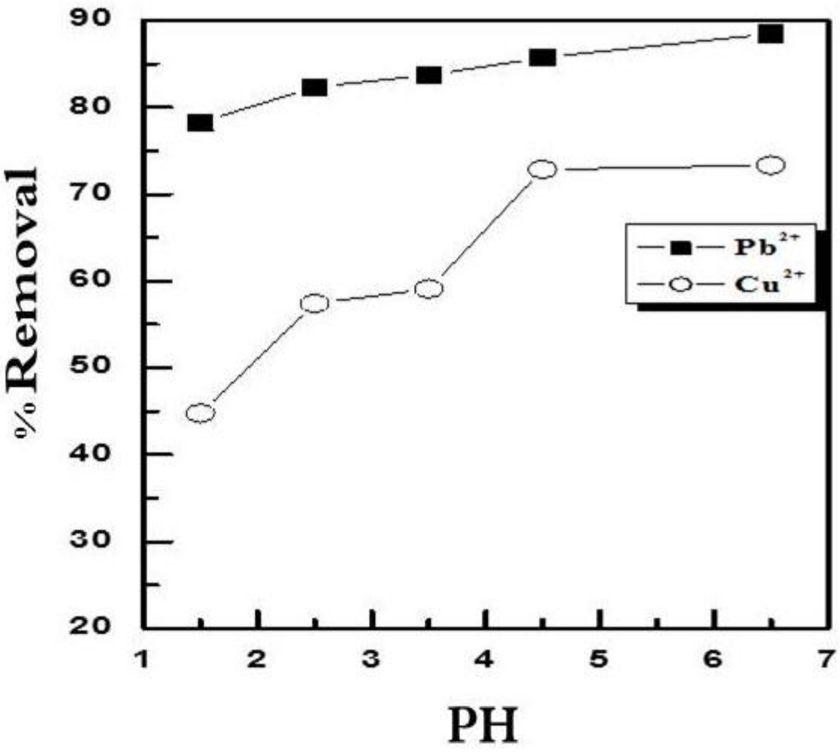

Fig.5: Effect of pH on Pb(II), Cu (II) and Co (II) removal% by rice straw.

Also,as the proton concentration increases, the following water cluster ions are formed H_3O^+, $H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$ modifying the structure of water and thus the ion-water interaction Also, the sorbent takes up the H^+ ions from the solution, hence, the surface becomes positively charged, which eventually restricts the uptake of Pb^{2+} and Cu^{2+}ions**.** Upon increasing the pH, the percentage adsorption increased substantially. This increase was considered to be due to hydrolytic adsorption of ions **(Moloukhia, 2010).**

In general, results indicated that the adsorption is highly pH dependent. Similar results have been reported in literature(Kavitha and Namasivayam (2007).

4.2.3 Effect of adsorbent dosage

The Influence of adsorbent (RSP) dose on adsorption of Pb, Cu and Co at constant adsorbate concentration was studied for the purpose of determining the right RSP mass that will bring about a better decontamination of metal contaminated effluent. The effect of adsorbent dosage on removal percentage of the two studied ions is shown in Fig. 6 with increase rice straw dosage from 0.02 to 0.2 g. The removal percentage increased from 57.42% to75.52% for Cu (II) and 65.05% to 89.9% for Pb(II). This is expected because more binding sites for ions are available at higher dose of adsorbents **(Amuda et al., 2007).** The increase in removal with increase sorbent dosage could be attributing to increase in surface area and the availability of more binding sites **(Abdel –Aty et al., 2012).** In addition, the results have been showed that the removal efficiencies stay nearly constant for the both metal ions with increasing the adsorbent dosage from 0.05 g Up to 0.2 g. Hence, the optimum dose from rice straw was found to be 0.05 g/ 5 ml (i.e., 10 g rice straw per liter of Pb (II) and Cu (II) solutions).

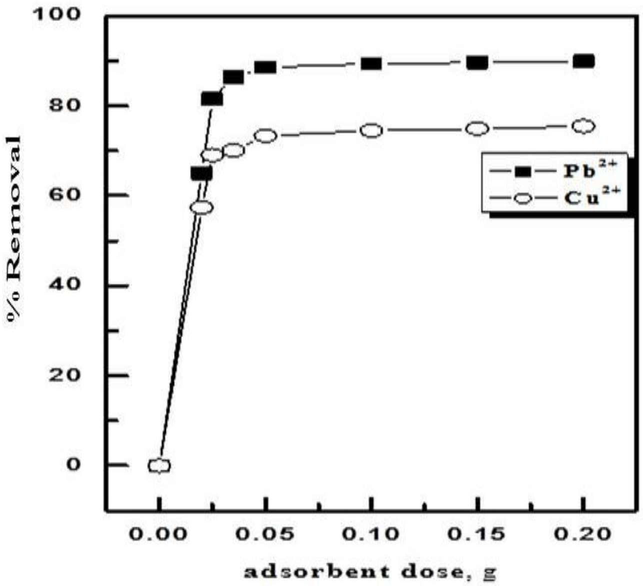

Fig. 6. Effect of adsorbent dosage on removal of Cu^{2+} and Pb^{2+}, agitating rate, 400 rpm; temperature, 25±1°C; initial metal concentration, 50 mgl^{-1}.

The shape of the isotherm (assuming the (x) axis represents the concentration of adsorbing material in the contacting liquid) is a gradual positive curve that flattens to a constant value.

4.2.4 Effect of initial metal ion concentration on removal percentage

The heavy metal ion solutions with different initial concentration were investigated in the range of 50–600 mg L^{-1}. Fig. 7 shows the effect of initial concentrations on heavy metal uptake efficiency. According to the results, removal percentage was decreased with increased initial concentration by using 0.05 g of biomass. The heavy metal uptake efficiency decreased from 88.46 to 51.60% and 73.32 to 34.53% for Pb^{2+}, and Cu^{2+}, respectively, due to concentration increase from 50 to 600 mg L^{-1}.Similar trend reported by **(Sud et al, 2008)** for removal of Pb using rice straw. (**Asci et al., 2007)** reported that sorption of metal ion onto sorbent material related to number of binding sites available to the metal ion would reduce as the concentration of the metal ion was increased, especially when the adsorbent was nearly saturated at high initial concentrations.

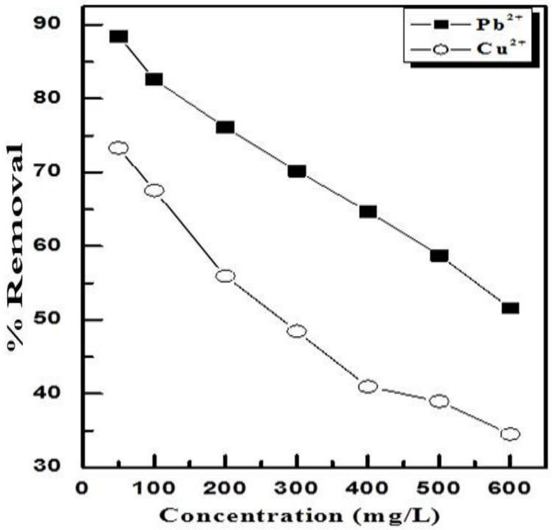

Fig.7. Effect of initial concentration on the removal of Cu^{2+} and Pb^{2+} by rice straw.

(Horsfall and Spiff, 2005) reported that at low concentrations, possible heavy metal binding sites of biomass were available for quick binding. At higher concentrations decreased binding sites of biomass and slow diffusion of heavy metals to the biomass surface due to inter particle interactions caused to decreasing removal efficiency of heavy metal ions.

4.2.5 Adsorption thermodynamic modeling

The values of thermodynamic parameters are relevant for the practical application of adsorption process **(Singhaet al., 2009 and Ozcan et al., 2006)**.

Parameters according to the Van̓t Hoff relation; it was found that the distribution coefficient (K_d) of Cu^{2+} and Pb^{2+} ions for rice straw powder increased with increasing temperature from 298°K to 338°K (i.e. the distribution coefficient decreased with increasing T^{-1}). This trend can be attributed to acceleration of some originally slow adsorption steps and creation of some new active sites on the adsorbent surfaces (**El-Naggar et al., 2010 and El-Naggar et al., 2014).** Linear relation between T^{-1} and ln K_d is illustrated in Fig. 8 and the enthalpy change (ΔH^o) and entropy change (ΔS^o) are summarized in Table 2.

The positive values of (ΔH^o) indicate the endothermic nature of the adsorption process **as reported by El-Naggar et al., 2010 and El-Naggar et al., 2014,** while the positive values of ΔS^o for Cu^{2+} and Pb^{2+} indicate the increased Uniformity at solid-solution interface during the adsorption of these cations by the rice straw.

The magnitude of ΔG decreased with rising of temperature, indicating that the adsorption is favorable at high temperatures. The positive values confirm the feasibility of the process and the non-spontaneous nature of adsorption of Cu (II) and Pb (II) on the studied sorbent **(El-Naggar et al., 2010 and El-Naggar et al., 2014).**

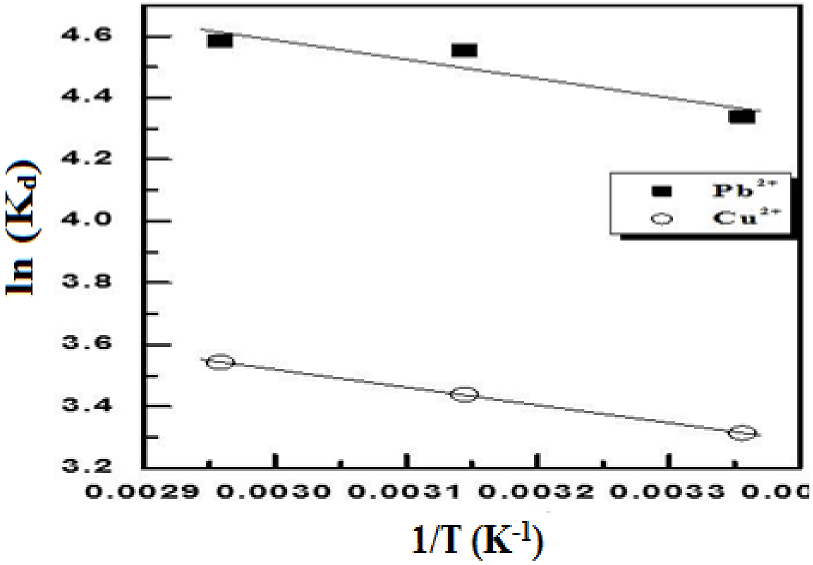

Fig. 8. Van,t Hoff plot of the adsorption of Cu^{2+} and Pb^{2+} ions by rice straw.

Table 2. Thermodynamic parameters for adsorption of Pb (II), and Cu (II) ions by rice straw.

Metal ions	Temp., (K)	ΔG^o, (KJ mol^{-1})	ΔH^o, (J mol^{-1})	ΔS^o, (J mol^{-1} K^{-1})
Pb^{2+}	298	0.658	65.14	1.991-
	318	0.140		0.374-
	338	0.060		-0.304
Cu^{2+}	298	3.200	21.43	10.520-
	318	3.083		9.629-
	338	2.985		-8.349

4.2.6 Fixed-bed experiment

The main theory which explains separation by column chromatography is plate theory. According to this theory, the column is considered to be divided into a number of equal units called theoretical plates. These units, although entirely hypothetical, give rise to a very useful way for the practical measurements of column efficiency. Investigation were conducted to explore suitable conditions for quantitative loading and sorption of Cu^{2+} and Pb^{2+} ions in neutral media (pH = 6.5) by chromatographic column procedures at room temperatures (25±1°C) at flow rate (0.5ml/min). As far as the break-through capacity of the column is concerned (Fig. 7) shows curves for $Cu^{2+}$and Pb^{2+} ions (100 mg L^{-1} for each) from rice straw column in the feed solutions. Each break-through curve reflects the percent concentrations of the respective metal ion in the effluent to the feed solution (C_e/C_o) Vs. effluent volume (V ml) as shown in Fig. 7.

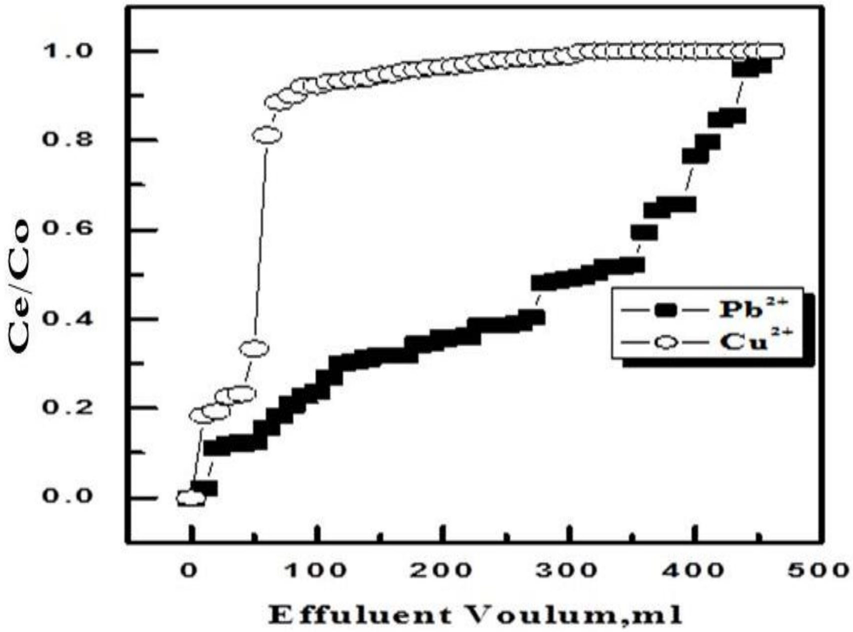

Fig. 7. Break-through curves of $Cu^{2+}$and Pb^{2+} ions uptake by rice straw powder (pH = 6.5 and 25±1˚C and (0.5ml/min)).

The values of breakthrough capacity under the conditions of the experiment can be easily estimated from Fig. 7 and was calculated and found to be 6 and 32 mg g^{-1} for $Cu^{2+}$and Pb^{2+}, respectively.

5. CONCLUSIONS

- The aim of this work was to explore the possible use of rice straw; which is agricultural residues; as sorbents for the removal Cu(II) and Pb(II) from aqueous solutions.
- Characterization of rice straw indicated that its surface was full of cavities as shown by SEM. It was found that it has good chemical stability.
- The percentage removal of Cu^{2+} and Pb^{2+} ions were found to be up to 88.46 and 73.32% for Pb and Cu, respectively. Equilibrium time was about 60 minutes; maximum removal was at pH 6.5, best adsorbent dosage was 0.05g with 5ml.
- The break-through capacity for the studied metal ions was calculated and it is found to be 5.56 and 32 mg g^{-1} for $Cu^{+2}$and Pb^{2+}, respectively.

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