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Abstract

In the present study, the potential of the raw (RS) and NaOH-Modified Rice Straw (MRS) to remove copper (II) from aqueous solutions was investigated by batch tests under different experimental conditions. The chemical and morphological structures of adsorbents were investigated by scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDAX), element analyzer and Fourier-Transform Infrared spectroscopy (FTIR). The study also investigated the effects of process parameters such as initial Cu (II) concentration, solution pH and temperature. Results of the present study revealed that, the maximum adsorption was about 39.40% and 46.20% for RS and MRS respectively, at pH 4.3, contact time 210 min. and initial concentration is 381.3 mg L^{-1}. Langmuir and Freundlich adsorption isotherms were applicable to the absorption process and their constants were evaluated. The good correlation coefficient was obtained from pseudo second-order kinetic model, which agreed with conception as the rate-limiting mechanism. Thermodynamic aspects of the adsorption process indicated feasible, spontaneous and endothermic biosorption process. The modified rice straw in comparison, could adsorb Cu (II) ion faster than the unmodified.

Keywords: Rice straw; Adsorption; Copper; Isotherms; Kinetics; Thermodynamics

Introduction

The presence of heavy metals in the water environment is a major concern due to their toxic effects since they cause severe health problems to animals and human beings. According to the World Health Organization (WHO), the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead [1]. Heavy metals as raw materials or catalysts are used widely in many industrial production, such as mining, metallurgy, electrolysis, electroplating and leather [2]. They can be subsequently released into the environment through wastewater, which has become a threat to human and local environment [3]. Because the heavy metals in water are difficult to be biodegraded and tend to accumulate in organisms through the food chain [4], the wastewater containing heavy metals should be treated before discharge..

Various methods for heavy metal removal have been proposed, demonstrated and applied, such as chemical precipitation [5], membrane filtration [6] and ion exchange [7–9]. Compared with treatment methods listed above, adsorption is considered as an efficient method for the removal of heavy metals from waste water with several advantages like no chemical sludge, easy to operate [10] and the process appears to be inexpensive [10–12].

Agricultural wastes are generated in high amounts in Egypt; these products are not used economically. Some of the advantages of using agricultural residues for wastewater treatment include simple technique, little processing requirement, good adsorption capacity, selective adsorption of heavy metal ions which causes environmental issues, low cost, free availability, and easy regeneration [13].

Rice straw is comprised of cellulose, hemicellulose and lignin that can adsorb heavy metals in aqueous solutions validly [14]. Hence the adsorption of heavy metal ions with waste agricultural materials could provide a novel treatment of both crop residues and heavy metal pollution. In several previous reports, many authors have documented the use of the rice straw for the adsorption of heavy metals [15–17]. Whereas, a lot of previous researchers simply modified rice straw by acid or alkali washing, which just improved the adsorption capacity inconspicuously.

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The purpose of this work is to investigate the capability of unmodified (RS) and Modified Rice Straw (MRS) for the removal of Cu (II) from single system. The adsorbents were characterized by Fourier Trans-form Infrared spectra (FTIR), Scanning Electron Microscope (SEM), Energy Dispersive X-ray Analysis (EDXA) and the X-ray Diffraction (XRD). The kinetic and thermodynamic parameters were calculated and the equilibrium data were fitted to some isotherm models to determine the adsorption mechanism.

2. Material and Methods

2.1. Preparation of adsorbent

2.1.a. Rice straw

The natural Rice Straw (RS) used in the present experiments was obtained from a market in Menoufia Country, Egypt. The (RS) was thoroughly washed with a stream of distilled water to remove all dirt and then was dried at 110°C. The dried (RS) were stored in desiccators until used.

2.1.b. Modified rice straw

The Modified Rice Straw (MRS) sample was prepared by alkali treatment. Alkali treatment was carried out by placing the RS sample in contact with NaOH (0.1 M), with constant stirring for 24 h. The liquid/solid ratio was 10 ml/g. It was then filtered, washed OH− free with distilled water, and dried at 110 °C for 24 h to constant weight. And it was ground and sieved. The particles 0.63 mm was selected and preserved at room temperature in a sealed bottle.

2.2. Preparation of metal-solutions

The Cu (II) stock solution containing 1000 mg/L was prepared by dissolving copper chloride (analytical reagent grade) in distilled water. Copper working solutions in different concentrations was prepared by diluting the Cu (II) stock solution with distilled water.

2.3. Analytical technique

The concentrations of the Cu (II) metal ions were performed using Flame Atomic Absorption Spectrophotometer (FAAS) Vario 6. Elements were determined using an air–acetylene flame.

3. Results and Discussion

3.1. Characterization of adsorbents

3.1.1. Chemical composition

The chemical composition of the rice straw was determined at each stage of treatment and the data are summarized in Table 1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical Characterization</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Moisture Content %</td>
<td>RS 7 %</td>
</tr>
<tr>
<td>2</td>
<td>Ash Content %</td>
<td>RS 6 %</td>
</tr>
<tr>
<td>3</td>
<td>Lignin Content %</td>
<td>RS 12.5 %</td>
</tr>
<tr>
<td>4</td>
<td>Holocellulose %</td>
<td>RS 75.5 %</td>
</tr>
<tr>
<td>5</td>
<td>Alpha Cellulose</td>
<td>RS 56 %</td>
</tr>
</tbody>
</table>

3.1.2. FTIR spectra

The rice straw is constituted basically by cellulose, hemicellulose, lignin, extractives, water and mineral ash which are in large amount SiO2. The lignin is promptly available to interact with cations, by firstly exchanging with protons and subsequently by chelating with the metallic ion.

FTIR spectroscopy was applied to identify the functional groups of rice straw responsible for metal adsorption. To reveal then systematic changes in the spectral features upon reaction with metal ions, FTIR spectra were obtained for the sample before reacting with Cu (II). By comparing the FTIR spectra of outer and inner surface for RS and MRS in table 2 (a, b) and figure 1.
Table 2a: FTIR for outer surface of RS and MRS

<table>
<thead>
<tr>
<th>FTIR Peak</th>
<th>Outer surface</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS</td>
<td>MRS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>≈ 3300 cm⁻¹</td>
<td>Shift to ≈26 cm⁻¹</td>
<td>Stretching vibration of –OH groups</td>
</tr>
<tr>
<td>2</td>
<td>≈ 2925±1 cm⁻¹</td>
<td>Vibration of the carbon-hydrogen bonds superimposed onto –OH broad band</td>
<td>[18], [19]</td>
</tr>
<tr>
<td>3</td>
<td>≈ 1738 cm⁻¹</td>
<td>Disappear</td>
<td>The vibration of carbonyl from carboxylic groups in ester linkage</td>
</tr>
<tr>
<td>4</td>
<td>≈ 1626±4 cm⁻¹</td>
<td>Shift slightly</td>
<td>–OH groups</td>
</tr>
<tr>
<td>5</td>
<td>≈ 1539 cm⁻¹</td>
<td>Disappear</td>
<td>The vibration of carbonyl from carboxylic groups in ester linkage</td>
</tr>
<tr>
<td>6</td>
<td>≈ 1217 cm⁻¹</td>
<td>Disappear</td>
<td>Vibration of silica bonds</td>
</tr>
<tr>
<td>7</td>
<td>786±5 cm⁻¹</td>
<td>Disappear</td>
<td>Vibration of silica bonds</td>
</tr>
</tbody>
</table>

Table 2b: FTIR for inner surface of RS and MRS

<table>
<thead>
<tr>
<th>FTIR Peak</th>
<th>Inner surface</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS</td>
<td>MRS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>≈ 3273.5±57 cm⁻¹</td>
<td>Shift to 49 cm⁻¹</td>
<td>Hydrogen bonded –OH in cellulose fibers</td>
</tr>
<tr>
<td>2</td>
<td>≈ 2919±0.5 cm⁻¹</td>
<td>C–H vibration bond</td>
<td>[19]</td>
</tr>
<tr>
<td>3</td>
<td>≈ 1614±19 cm⁻¹</td>
<td>–OH vibration bond</td>
<td>[18], [19]</td>
</tr>
<tr>
<td>4</td>
<td>1201-1156 cm⁻¹</td>
<td>Vibration range of silica bonds</td>
<td>[20]</td>
</tr>
<tr>
<td>5</td>
<td>790 cm⁻¹</td>
<td>Disappear</td>
<td>Vibration range of silica bonds</td>
</tr>
</tbody>
</table>

Figure 1: FTIR spectra for (a) RS and (b) MRS before adsorption.
3.1.3. Scanning Electron

Scanning Electron (SEM) micrographs of untreated and treated rice straws are shown in Fig. 2(a,b). As shown in Figure 2 (a, b) the surface roughness of the outer and inner surfaces of rice straws change significantly after alkali treated with NaOH. Changes started to be substantial when the rice straws were treated with NaOH. These include wearing of asperities on the outer surfaces and particle cracking which suggests the weakening of the rice straws due to increase in brittleness. The result of Scanning Electron Microscopy (SEM) also shows that rice straw is a porous material [22].

Figure 2: SEM image for (a) RS and (b) MRS before adsorption

3.1.4. EDXA Spectra

Figure 3 (a, b) shows the EDXA spectra of RS and MRS adsorbents before adsorption with Cu (II) respectively. Figure 3 (a, b), indicates the presence of major constituents – carbon and oxygen in the two samples adsorbents. It was suggested that toxic metals including Cu (II) had been adsorbed on the surface of MRS successfully. Moreover, after loading with toxic copper, a distinct increase of silica peak intensity could be found. This phenomenon might be derived from the alkali treatment.

Figure 3: EDXA for (a) RS
3.1.5. X-ray Diffraction

Figure 4 (a, b) shows the X-ray diffraction patterns of RS and MRS biosorbents powder. Diffraction peaks corresponding to crystallinity were not observed, whereas, amorphous form is identified in the biosorbtent. The amorphous nature of the biosorbents suggested that the metal ion could more easily penetrate into the surface of the two biosorbents on the amorphous. Optimization of Cu (II) biosorption by chemically modified rice straw.
3.2. Effect of contact time

The rate at which adsorption take place is most important when designing batch adsorption experiments. Consequently, it is important to establish the time dependence of such systems under various process conditions. The experimental runs measuring the effect of contact time on the batch adsorption of metal solution containing 381.3mg/l of Cu(II) at 28ºC and initial pH value 4.3 is shown in Figure 5.

The adsorption of Cu (II) increased with increasing contact time and became almost constant for ~3.5 h for both RS. and MRS. After ~3.5, the % removal was negligible hence all experiments were carried out at equilibrium time of 3.5 h. Higher adsorption efficiency of MRS than RS could be attributed to available absorbing site (Surface functional groups) on the adsorbent surface [23].

**Figure 5:** Effect of contact time on the removal of Cu (II) by RS and MRS

![Figure 5](image_url)

3.3. Effect of adsorbent dosage

The adsorbent weight is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion solution. To study the influence of the liquid to solid ratio on the retention of copper, three different values have been taken by varying the adsorbent amount of both RS and MRS while keeping the volume of the metal solution constant as shown in Figure 6, where it can be seen that the adsorption increases with the increase in the amount of the adsorbents doses from 0.1 to 1.0g. This can be explained by a greater availability of the exchangeable sites or surface area at higher amount of the adsorbent. The RS has adsorption ability for Cu (II), the removal percentage of Cu (II) from 26.8% to 52.5% and for MRS, the removal percentage of Cu (II) is 38.8% and 68.3%, respectively [24,25]. The data clearly shows that the MRS is more effective than RS for removal of Cu (II) from aqueous solution.

**Figure 6:** Effect of amount of adsorbent on the removal of Cu (II)

![Figure 6](image_url)
3.4. Effect of initial metal ion concentration

The metal uptake mechanism is particularly dependent on the initial heavy metal concentration. The adsorption capacity of Cu(II) for RS increased from 12.8 mg/g to 28 mg/g with the increasing initial Cu (II) concentration from 127.1 mg/L to 889.7 mg/L. And the uptake of Cu (II) for MRS increased from 11.5 mg/g to 19.6 mg/g with initial Cu (II) concentration ranging from 127.1 mg/L to 889.7 mg/L (Figures not shown). Actually, as the initial concentrations of Cu (II) increased, the driving force became higher as well, the accessibility of the heavy metal ions to the binding sites of the RS and MRS are relatively high with increased initial concentration, the ions exchange frequently and the uptake of heavy metals becomes more and more [26-29].

This may be due to, at low concentrations, copper ions are adsorbed by specific active sites, while at higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. This appears to be due to the increase in the number of ions competing for the available active sites on the surface. In addition, typical mass-transport controlled kinetics of pollutants removal by the rice straw is another factor which control removal rate of copper and at higher concentrations, more metal ions are left in solution [30].

3.5. Effect of initial pH

The pH of the solutions has been identified as the most important variable governing metal adsorption. This is partly due to the fact that hydrogen ion (H+) themselves is strong competing ions and partly that the solution pH influences the chemical speciation of the functional groups on to the adsorbent surfaces. In order to evaluate the influence of this parameter on the adsorption, the experiments were carried out at different initial pH values. The pH range was chosen as 1.8–4.6 in order to avoid metal hydroxides, which has been estimated to occur at pH > 4.9 for Cu (OH)2.

At higher pH values a slight decrease of adsorption for Cu (II) could be suffering hydrolysis, starting at pH higher than 4.9, forming Cu (OH)2, which promotes a reduction of the adsorption capacity, due to the diminution of the formal charge of the metallic ion.[31]

The effect of pH on adsorption efficiencies are shown in Figure 7. It can observed from Figure 7 that the removal of Cu (II) increase with increasing solution pH and a maximum value was reached at an equilibrium pH of around 4.3 for RS and MRS. The same trend has also been reported in the removal of Cu (II) ions by other vegetable materials [32-34]. The low degree of adsorption at low pH values can be explained by the fact that at low pH values the [H+] ion concentration is high and therefore protons can compete with the lead cations for surface sites, since at low pH, Cu (II) are present in solution as Cu^{2+} free cations. The process involved for Cu (II) adsorption are proposed by Greenwood and Earnshaw, 1997 [35] as the following.

\[ \text{Cu}^{2+} + n\text{H}_2\text{O} = \text{Cu} (\text{H}_2\text{O})_{n}^{2+} \]
\[ \text{Cu} (\text{H}_2\text{O})_{n}^{2+} = \text{Cu} (\text{H}_2\text{O})_{n-1}^{+} \text{OH}^+ + \text{H}^+ \]
\[ \text{Cu}^{2+} + n\text{H}_2\text{O} = \text{Cu} (\text{H}_2\text{O})_{n-1}^{+} \text{OH}^+ + \text{H}^+ \]

On the other hand, as pH increases, there is a decrease in positive surface charge (since the deprotonation of the sorbent functional groups could be occurs, which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of MRS, favoring adsorption than its RS.

**Figure 7:** The effect of pH on the removal of Cu (II) by RS and MRS
3.6. The distribution ratio (D)

Distribution ratio $D$ for copper ions was determined by the batch method at different temperature systems (301, 313 and 323K). The distribution ratio, $D$, is defined as the ratio of metal ion concentration on the adsorbent to that in the aqueous solution and can be used as a valuable tool to study Cu (II) ion mobility. The distribution ratio ($D$) is defined by the following relationship [36, 37]:

$$K_d = \frac{(I-F)}{500 \text{ mg} \times \frac{50 \text{ ml}}{F}}$$

Where $I$ is the volume of EDTA used before treatment of metal ion-exchange. $F$ is the volume of EDTA consumed by metal ion left in solution phase.

High values of the distribution ratio (as in aqueous-MRS systems), indicate that the metal has been retained by the solid phase through sorption reactions, while lower values of D (as in aqueous-RS systems), indicate that a large fraction of the metal remains in solution. Figure 8 shows that the distribution ratio ($D$) values increase with the increase in temperatures of copper solutions. The rapid metal sorption has significant practical importance, as this will facilitate with the small amount of resin to ensure efficiency and economy.

Figure 8: The effect of distribution coefficient on adsorption of Cu (II)

3.7. Adsorption Isotherm

When the adsorption is at the state of equilibrium, the results were then fitted to the Langmuir [38] and Freundlich [39] isotherm model. The Langmuir model is effective in monolayer adsorption on surfaces and the Freundlich model is valid for non-ideal multilayer adsorption. These two models can be expressed by the following equations (1, 2):

Freundlich

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

(1)

$$\frac{q_e}{C_e} = \frac{1}{K_F Q_{max}} + \frac{C_e}{Q_{max}}$$

(2)

Where $q_e$ (mg/g) is the amount of uptake at equilibrium time; $C_e$ is the equilibrium concentration (mg/L), $K_F$ and $n$ are constants related to adsorption. $Q_{max}$ (mg/g) is the maximum metal uptake of Langmuir isotherm; $K_L$ is the equilibrium coefficient.

Freundlich constant $K_F$ is related to temperature [38], value of $n$ is correlated with the favorability of adsorption $n > 1$ indicates favorable adsorption isotherm [40].

The Langmuir equation is also used to obtain $R_L$, the dimensionless equilibrium parameter or the separation factor [41, 42] from the expression (3):

$$R_L = 1 \left(1 + \frac{K_L C_0}{1}ight)$$

(3)

The values of $b$ in the Langmuir model suggested whether the isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [43].
The linear Freundlich and Langmuir plots are obtained by plotting (i) log $q_e$ vs. log $C_e$ and (ii) $C_e/q_e$ vs. $C_e$, respectively, from which the adsorption coefficients could be evaluated.

Experimental data are fitted with both Langmuir and Freundlich adsorption isotherm model. Based on the experimental results, presented in (Figs. not shown), the parameters in the Langmuir and Freundlich adsorption isotherm model were determined and along with the regression coefficient $R^2$ presented in Table 3.

From Table 3, the $R^2$ of the Langmuir isotherm model were higher than those of Freundlich isotherm model, which indicates the experimental data fitted to Langmuir isotherm model better for both RS and MRS, accordingly, the adsorbed metal ions were on the active sites in the form of mono-molecules.

### Table 3: Adsorption isotherm parameters for (6 mmol/L) of Cu (II) on RS and MRS in aqueous solution.

<table>
<thead>
<tr>
<th></th>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{\text{max}}$ (mg/g)</td>
<td>$K_L$ (L/mg)</td>
</tr>
<tr>
<td>RS</td>
<td>10.7</td>
<td>$10 \times 10^{-3}$</td>
</tr>
<tr>
<td>MRS</td>
<td>14.0</td>
<td>0.013</td>
</tr>
</tbody>
</table>

#### 3.8. Adsorption kinetic studies

The kinetics of Cu (II) adsorption was evaluated by applying three common models: the pseudo-first order [44], the pseudo-second order [45] and Weber Morris models [46]. The pseudo-first-order model was applied to depict the adsorption of liquid/solid system based on solid capacity [47]. The pseudo-second-order kinetic model was used for explaining the adsorption mechanism of rate-controlling steps [48] which can be expressed as follows (4, 5, 6, 7):

- Pseudo-first-order $\log (q_e - q_t) = \log q_{e,1} - k_1 t$  
- Pseudo-second-order $\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{t}{q_{e,2}}$

Where:

$h = k_2 q_{e,2}^2$

Weber Morris models $q_t = K_{\text{int}} t^{0.5}$

$h$ is the initial adsorption rate (mmol/g min)), $K_{\text{int}}$ is the intraparticle diffusion rate coefficient (g mg$^{-1}$ min$^{0.5}$).

The parameters of two models were summarized in (Table not shown). As shown in Figures (9, 10), the values of $R^2$ for both RS and MRS higher in pseudo-second-order (0.99938 and 0.99878) showed better fitting results to the adsorption than the pseudo-first-order kinetic model (0.95721 and 0.98984). For this, the pseudo-second-order gave an excellent adaption to the data, which could be explained that the adsorption process of Cu(II) were mostly controlled by chemisorption behavior [49, 50].

**Intra particle diffusion model (Weber Morris):**

The adsorbate transport from the solution phase surface of the adsorbent particles may be controlled either by one or more steps, e.g. film or external diffusion, pore diffusion, surface diffusion and the adsorption on the pore surface, or a combination of more than one steps. In a rapidly stirred batch adsorption, the diffusive mass transfer can be related by an apparent diffusion coefficient which will fit the experimental sorption rate data. Generally, a process is diffusion controlled if it is dependent upon the role at which components diffuse towards one another. If the Weber, Morris plot of $q_t$ versus $t^{0.5}$ gives a straight line passes through origin, then the adsorption process is controlled by intra particle diffusion only.
The mathematical dependence of fractional uptake of the adsorbate is obtained if the adsorption process is considered to be influenced by diffusion in the cylindrical and convective diffusion in the adsorbate solution. It is assumed that the external resistance to mass transfer surrounding the particles is significant only in the early stage of the adsorption. Our results indicated that, the straight line of the plots do not pass through origin, suggesting that adsorption proceeds from boundary layer mass transfer across the interface to the intra particle diffusion across the pores of adsorbent [51]. This indicates the mechanism of Cu (II) adsorption by rice straw and its modified are complex and both, the surface adsorption as well as intraparticle diffusion contribute to the rate determining step.

3.9. Effect of temperature and Calculation Thermodynamic parameters

The amount of adsorption as a function of temperature was (Fig. not shown). Results indicate that the amount of Cu(II) adsorption increase for RS from 39.4% to 57.9% and for MRS from 46.2% to 62.3% when the temperature are in the range of 301–323 K, which might be due to the accelerated diffusivity of metal ions from the external layer into the micro pores of the rice straw with the increasing temperature [52].

The thermodynamic parameters such as $\Delta G^0$, $\Delta H^0$and $\Delta S^0$ can better describe the adsorption mechanism. The relationship of them can be expressed as follows (8, 9):

$$\ln K_d = \frac{\Delta S}{RT} - \frac{\Delta H}{RT}$$ ...................................................... 8

$$\Delta G = \Delta H - T\Delta S$$ ...................................................... 9

Where $\Delta G^0$ (kJ/mol) is adsorption free energy, $\Delta H^0$ (kJ/mol) is adsorption enthalpy, $\Delta S^0$ (kJ mol$^{-1}$K$^{-1}$) is adsorption entropy; R(8.314J/(mol K)) is universal gas constant, T (K) is temperature, $K_d$ value is known as the distribution coefficient of the adsorbate, is equal to $(q_e/C_e)$. $\Delta H^0$ and $\Delta S^0$ were slope and intercept of the linear relationship of $K_d$ versus $1/T$. The results of the adsorption of Cu (II) onto RS and MRS were calculated according to Eqs. (8,9). Table 4 shows the parameters of thermodynamics for RS and MRS, results indicated that $\Delta G^0$ were all negative at different temperatures, its absolute values increased with the rise of temperature, which suggested that the adsorption of Cu (II) could happen spontaneously. $\Delta H^0$ stayed positive values all the time, indicating that the reaction was endothermic and $\Delta S^0$ also maintained positive values, which inferred that the adsorbent had good affinity for Cu (II) [53].
The values of the activation energy \( (E_a) \) and sticking probability \( (S^*) \) were estimated from the experimental data. They were calculated using a modified Arrhenius type equation related to surface coverage as expressed in equations (10, 11):

\[
0 = 1 - \frac{c_e}{c_0} \quad \text{equation 10}
\]

\[
S^* = (1 - \theta) \exp \left( -\frac{E_a}{RT} \right) \quad \text{equation 11}
\]

The sticking probability, \( S^* \), is a function of the adsorbate/adsorbent system under consideration and is dependent on the temperature of the system. The parameter \( S^* \) indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinitely.

Table 4 also indicated that the values of \( S^* \leq 1 \) for RS and MRS, hence the sticking probability of the Cu(II) ion onto the two adsorbent systems are very high.

The apparent activation energy \( E_a \) also indicated that the higher solution temperature favors the adsorption process and also the adsorption process is endothermic in nature [54].

**Table 4**: Thermodynamic parameters for \((6\text{mmol/L})\) of Cu(II) on RS and MRS in aqueous solutions

<table>
<thead>
<tr>
<th>Rice Straw</th>
<th>Temp.K</th>
<th>( \Delta G ) (kJ/mol)</th>
<th>( \Delta S ) (J/mol k)</th>
<th>( \Delta H ) (KJ/mol)</th>
<th>( S^* )</th>
<th>( E_a ) (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS</td>
<td>301</td>
<td>-25.2</td>
<td>83.67</td>
<td>31.59</td>
<td>1.48\times10^{-3}</td>
<td>15.13</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-26.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-27.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MRS</td>
<td>301</td>
<td>-21.8</td>
<td>72.63</td>
<td>27.76</td>
<td>1.54\times10^{-3}</td>
<td>14.84</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-22.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-23.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Cost of Adsorbents**

The production of rice straw in Egypt is about 4.7 million ton annually. The adsorbent material used in this study is generally available at a relatively cheap rate, 100 L.E. /ton for rice straw. The treatment of 1m\(^3\) of wastewater with RS would cost approximately 31.25 L.E [55].

**Conclusions**

The adsorption properties of Cu\(^{2+}\) by untreated rice straw and alkali treated rice straw were examined in this experiment. The results obtained from the present investigation reveal that:

- The rice straw which is abundantly available and can be easily converted into good adsorbent by using simple method of activation, such as activation with alkali.
- Rice straw is an environmentally friendly potential adsorbent for toxic metals. This work examined the efficiency of this adsorbent in removal of some metal ions from aqueous solution. The present investigation shows that the rice straw is an effective and inexpensive adsorbent for the removal of Cu (II).
  - As the material is a waste product, the use of activated rice straw as adsorbent would also solve their disposal problem.
  - The concentration of copper metal ions from 127.1 mg/L to 889.7 mg/L.
  - It was found that the percentage removal of toxic copper ions was dependent on the dose of low cost adsorbent and adsorbent concentration.
  - The contact time necessary for maximum adsorption was found to be 3.5 hours.
  - The optimum pH range for toxic copper ions adsorption was 1.8– 4.6.
References


