REMOVAL OF COPPER (II) FROM AQUEOUS SOLUTION BY AGRICULTURAL BY-PRODUCTS-SAWDUST.

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Abstract

The present work deals with the use of chemically activated sawdust as an adsorbent for the retention of copper (II) ions from synthetized aqueous solutions. Experimental measurements were carried out batchwise in order to investigate the effects of various parameters such as contact time, pH of the solution, initial concentration of the metallic ion and adsorbent dose.

The Langmuir and Freundlich models were tested in order to determine the adsorption isotherms and it was found that the experimental data fitted reasonably well Langmuir adsorption isotherm, indicating mono layer coverage by the copper (II) ions.

A kinetic study was also included testing pseudo-first and second order kinetics as well as the intraparticle diffusion model, for a good understanding of the reaction mechanism.

Finally the use of sawdust presents an interesting option for both tertiary wastewater treatment (as a possible non-conventional sorbent for the removal of copper), and a recycled waste as a fertilizer and compost, for instance.

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Key words: Sawdust; activated sawdust; heavy metal; copper; adsorption; retention; ion exchange; adsorption isotherm; kinetics model.
1. Introduction

The industrial activities and technology development lead to a significant release of important quantities of heavy metal ions, to the environment. As examples of industries releasing wastewaters charged of heavy metal ions, one can cite mining, electroplating, electronic equipment, battery manufacturing processes, etc. The wastewater commonly contains Cu, Ni, Cd, Cr, and Pb which are not biodegradable and their accumulation in ecological system can cause harmful effects to human, animals and plants [1]. Copper is a widely used metal in industries such as plating, mining and smelting, brass manufacture, electroplating industries, petroleum refining, etc. [2], which produce much wastewater and sludge containing Cu(II) ions with various concentrations, which may have negative effects on the environment. High doses of copper can cause serious toxicological concerns since it can be deposited in the brain, skin, liver and pancreas. It will then lead to nausea, vomiting, headache, diarrhea, respiratory difficulties, liver and kidney failure, and death [3]. The world Health Organization recommended a maximum acceptable concentration of Cu(II) in drinking water less than 1.5mg/l [4]. In a recent past, a number of non-conventional strategies have been followed to remove Cu (II) from domestic waters. These included use of lignocellulosic materials [5-6], inorganic clay materials [7-8], biopolymers [9] and synthetic polymeric hydrogels [10-11]. However agricultural wastes like sawdust, rice husk, peanut husk, coconut shell etc. are often preferred due to their low cost, great availability and their susceptibility to chemical modification for better performance. In this perspective the present work is focusing on chemical modifications of sawdust to yield a cation exchange material for effective removal of Cu(II) from aqueous solutions.

2. Experimental

2.1. Adsorbent

Sawdust obtained from locally used wood was used after treatment and with a mean size of 0.315mm, for the removal of copper (II) from synthetisized aqueous solutions. It was washed with hot distilled water, sun dried and then dried in oven at 80ºC to a constant dry weight. Then it was activated with 1N H₂SO₄ used in the ratio 1/10(sawdust: H₂SO₄, w/w) at 150 0C for 24 h. The treated material was washed with distilled water and soaked in 1% sodium bicarbonate solution overnight to remove residual acid. Then the material was kept in oven for 24h, to be dried at 105 0C.

2.2. Chemicals

- All the chemicals used were of analytical grade and were supplied by PRS Panreac and PRS Chiminova;
- Copper sulphate was also obtained from PRS Panreac and hydrated with a molecular weight of 249.68. Synthetic aqueous solutions containing copper was prepared by dissolution of copper sulphate in distilled water;
- Water was distilled locally using a GFL 2001/4 distillation.

2.3. Adsorption studies

Batch mode adsorption studies were carried out to determine the adsorption of copper (II) on sawdust. Tests were performed by agitating 0.5g of adsorbent with 50ml of the copper solution of 20 mg/l.
Continuous mixing was ensured during the experiment with an agitation speed of 500 rpm for predetermined time intervals ranging from 5-120 min at 23°C. After equilibration the suspension was filtered through filter millipore 0.2μm - Sartorius MINISART SRP 15 and then analyzed with an atomic absorption AA spectrophotometer RAYLEIGH operating with an air-acetylene flame, where, calibration curves have been prepared from samples of 1 g/l aqueous copper solution.

The effect of several parameters such as contacting time, size pore, the solution pH, sorbate concentration was studied. The pH of the suspension in the experiments was adjusted with NaOH 0.1 M (1M) and HNO₃ 0.1 M (1M). Adsorption of copper in the walls of the batch was determined by running the blank experiments and was found negligible. All the experiments were performed at least twice to ensure repeatability and mean values were considered.

3. Results and discussion

3.1. Effect of contact time

The copper removal was studied as a function of contact time at conditions of adsorbent dose, pH, and agitation speed where maximum copper removal could take place. Results are presented in Figure 1 which shows an increase of the removal efficiency of chemically activated sawdust (CAS) as contact time increased, before remaining constant at saturation. The Cu removal efficiency increased from 46.22% (9.245 mg g⁻¹) to 97.37% (19.475 mg g⁻¹) when contact time increased from 5 to 60 min. This can be explained by the affinity of the support towards copper. Also as represented in Figure 1, the copper removal efficiencies for the adsorbent for 60 min and 120 min of contact time are 97.01 and 97.37%, respectively, and hence no much difference. Therefore, 120 min of contact time was adopted for the batch experiments.

![Fig. 1. Effect of the agitation time on the retention of Cu by sawdust C₀=20mg/l, V=500 rpm, T=23°C, d=0.315mm, pH=4.19, r=1g/l](image-url)
3.2. Effect of pH

Knowledge of the optimum pH is very important since it affects not only the surface charge of adsorbent, but also the degree of ionization and speciation of the adsorbate during reaction. To examine the effects of pH on the removal efficiency, experiments were carried out in the pH range 2.0 to 7.0. Since copper started to precipitate as Cu(OH)\(_2\) above pH 6 [12]. Adsorption increased with increasing pH from 2 to 6 up to certain value and then decreased slightly with further increase of pH. The maximum adsorption took place around pH 6.0. At very low pH values, copper adsorption was found to be very low due to the competition between H\(^+\) and Cu (II) ions for the adsorption sites where the adsorbent surface acquired a positive charges and hence inducing repulsive forces. A decreasing trend in adsorption was also observed at pH 7 and this may be due to the formation of the precipitate Cu(OH)\(_2\) and formation of soluble hydroxy complexes [13].

3.3. Effect of initial concentration of Cu (II)

Figure 3 shows the effects of the initial concentration of copper on the adsorption by the adsorbent. The adsorption capacity of Cu (II) increased with time and reached a maximum value at 60 min before remaining constant indicating that no more Cu (II) ions were further removed from the solution. Equilibration time of 120 min is sufficient to reach equilibrium. On changing the initial concentration of Cu (II) from 10 to 60mg/l, the amount adsorbed increased from 9.8652 to 37.3344 mg/g. This may be attributed to an increase in the driving force of the concentration gradient with the increase in the initial concentration of copper in order to overcome all mass transfer resistance of Cu (II) ions between the aqueous and solid phases, therefore, a higher initial concentration of Cu(II) ions may increase the adsorption capacity [14].
3.4. Effect of the adsorbent dose

The dependence of Cu sorption on adsorbent dose was studied by varying the amount of CAS from 0.5 to 2g/l while keeping the other parameters (pH, contact time, initial concentration, and agitation speed) constant. Figure 4 presents the Cu removal efficiency of CAS and shows that the absorbed amount of Cu (II) ions decreased from 28.418 to 9.95414mgg⁻¹ as the adsorbent dose increased from 0.5 to 2g/l. This may be due to adsorption sites remaining unsaturated during the adsorption process [15].
3.5. Adsorption isotherms

Two well known adsorption isotherm models were again tested in the present study namely Langmuir [17] and Freundlich [18]. The linear forms of the Langmuir and Freundlich isotherms are presented by the following equations:

\[
\frac{C_e}{q_e} = \frac{1}{Q_0b} + \frac{C_e}{Q_0} \tag{1}
\]

where \( C_e \) is the equilibrium concentration (mg L\(^{-1}\)), \( Q_0 \) is the monolayer adsorption capacity (mg g\(^{-1}\)) and \( b \) is the constant related to the free adsorption energy (Langmuir constant, L mg\(^{-1}\))

\[
\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{2}
\]

with \( k_F \) is a constant related to adsorption capacity of the adsorbent (mg g\(^{-1}\)) and \( n \) indicates the intensity of the adsorption.

![Graphs of adsorption isotherms](image)

Fig. 5. (a) Copper adsorption isotherms, (a) Langmuir; (b) Freundlich: V=500rpm, pH=4.17, r=1g/l, d=0.315mm, T=23°C

The constant and the correlation factor values are shown on Table 1 as follows:

<table>
<thead>
<tr>
<th>Models</th>
<th>Constant</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( a=37.664783 )</td>
<td>0.96689</td>
</tr>
<tr>
<td></td>
<td>( b=0.00027187 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( k_F=20.6117232 )</td>
<td>0.8072</td>
</tr>
<tr>
<td></td>
<td>( 1/n=0.19683 )</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It can be seen that the correlation factor \( R^2 \) is close to the unity for Langmuir model, indicating a good representation of the experimental results by this model as also shown in Figure 5 and table 1.
3. Adsorption Kinetics

A kinetic study is important to an adsorption process because it depicts the uptake of adsorbate, and controls the residual time on the whole adsorption process. The pseudo first and second orders [19-20] and the diffusion kinetic models were tested for the present adsorption process.

3.1. The pseudo first order equation

A pseudo first–order equation can be expressed in a linear form as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$$

where \( q_e \) and \( q_t \) are the amount of copper ions adsorbed (mg g\(^{-1}\)) on the adsorbent at the equilibrium and at time \( t \), respectively, and \( k_1 \) is the rate constant of pseudo first order (min\(^{-1}\)). Values of \( k_1 \) were calculated from the plots of \( \log(q_e - q_t) \) versus \( t \) for concentration of Cu (II) 20 mg/l. The values \( k_1 \) is given in Table 2.

3.2. The pseudo second order equation

The linear form of the pseudo second order is expressed as follows:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where \( k_2 \) is the rate constant of pseudo second-order adsorption (g mg\(^{-1}\) min\(^{-1}\)) the constants can be obtained from plotting \( (t/q_t) \) versus \( t \). The values \( k_2 \) is given in table 2.

![Experimental and Linear Fit plots for pseudo first and second order equations](image)

Fig. 6. Adsorption kinetics, (a) Pseudo first order kinetic ; (b) pseudo second order kinetic : V=500rpm, pH=4.17, r=1g/l, d=0.315mm, T=23°C
3.3. The Intraparticle diffusion equation

In order to identify the diffusion mechanism, the kinetic results were analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism, which is expressed as [21]:

\[ q = k_i t^{0.5} \]  

(5)

where \( q \) is the amount of copper adsorbed (mg g\(^{-1}\)) at time \( t \), \( k_i \) is intraparticle diffusion constant (mg/g min\(^{0.5}\)).

The constants were calculated and listed in Table 2. The adsorption rate for intraparticle diffusion of the system is calculated from the slope of the linear portion of the respective plot with unit mg/g min\(^{0.5}\). The plot passes through the origin, then limiting process is due to the intraparticle diffusion. The diffusivity value of copper into chemical activated sawdust was \( D \leq 2.10^{-7} \) cm\(^2\)s\(^{-1}\) and is consistent with the reported values.

![Fig. 7. Intraparticle diffusion kinetics of Cu(ii); a) the intraparticle model; (b) Linear regression test: V=500rpm, pH=4.17, r=1g/l, d=0.315mm, T=23°C](image)

From linear test regression presented in Fig. 6 and Fig. 7, it can be concluded that the retention of copper onto activated sawdust is better represented by second order kinetics and controlled by intraparticle diffusion. The values of the different constants are shown in Table 2:

Table 2: Kinetics constants for the adsorption of Cu (II) on activated sawdust

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Constants</th>
<th>Correlation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo first-order kinetic</td>
<td>( k_1 = 0.04774 )</td>
<td>-0.94777</td>
</tr>
<tr>
<td>Pseudo second-order kinetic</td>
<td>( k_2 = 0.00808634 )</td>
<td>0.99962</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>( k_i = 3.72918 )</td>
<td>0.99912</td>
</tr>
</tbody>
</table>

**Conclusion**

The results show that sawdust obtained as by-product from locally used could be used as an effective adsorbent for the removal of copper from aqueous solution. It is concluded that this material has a high
retention capacity after activation. The study considered the effect of different physico-chemical parameters on copper retention such as adsorbent dose, agitation time, pH, initial concentration of sorbate. The adsorption isotherms of copper onto sawdust follow Langmuir model even though the difference in correlation coefficients.

The kinetics study has shown that adsorption follows a second order model controlled by intraparticle diffusion.

References


[13] Aanoop Krishnan K and Anirudhan TS. Removal of Cadmium (II) from Aqueous Solutions by Steam-Activated Sulphurised Carbon prepared from Sugar-Cane Bagasse Pith: Kinetics and Equilibrium Studies, Water SA Vol. 29 No. 2 April 2003; ISSN 0378-4738Effect of different physico-chemical parameters on copper retention such as adsorbent dose,


