ADSORPTION AND KINETICS STUDIES OF Cu (II) IONS REMOVAL FROM AQUEOUS SOLUTION BY UNTREATED AND TREATED SUGARCANE BAGASSE

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ABSTRACT

Adsorption of Cu (II) ions by untreated sugarcane bagasse (USCB) and treated sugarcane bagasse (TSCB) was investigated. Sugarcane bagasse was treated with 0.1M oxalic acid prior to TSCB adsorption studies. Dependence of Cu (II) adsorption on pH, contact time, temperature and initial concentration of adsorbate solution were also investigated. Optimum pH 2 and contact time of 100 minutes were observed for both USCB and TSCB, while Cu II sorption increased with temperature. Under optimum condition, TSCB adsorbed Cu (II) ions better than USCB (1.854mgg⁻¹ and 0.556mgg⁻¹ respectively). Thermodynamic investigations showed that Cu (II) adsorption was feasible, spontaneous and endothermic. Kinetic data was adequately described by Ho’s pseudo-second-order kinetic model while intra-particle diffusion model described a slow adsorption affinity. It was concluded that Cu (II) adsorption by sugarcane bagasse is a favourable chemisorption process and was well explained by both Langmuir and Freundlich isotherms.

Keywords: Copper(II), Sugarcane bagasse adsorbent, Isotherm models, Kinetics, Thermodynamics

1. Introduction

Toxic metals are a matter of concern to various forms of life and this makes it necessary for their removal, majorly from industrial and municipal wastewater. Accumulation of high intake of copper (over 1.0 mg l⁻¹ in drinking water) in the liver of human beings and animals results to hemochromatosis and gastrointestinal problems (Pankaj Pandey et al., 2009). Copper is also toxic to aquatic organisms even at very low
concentration. The tolerable limits for Cu\(^{2+}\) in effluents released onto land according to Indian Standard Institute ISI specification is 3.0mg l\(^{-1}\) (Archana et al., 2004); beyond this concentration, the effluents must be treated before disposal. Contamination of water and soil by industrial waste streams from metal cleaning, plating baths, mining, metallurgical, pulp and paper, fertilizers, wood preserving and excessive use of copper based agro-chemicals could release high load of copper into the environment where it is toxic and can act as a carcinogen (Meena et al., 2005).

A wide range of chemical methods are available for the removal of toxic metal ions from aqueous solutions. Recent chemisorptions approach has been carried out using the electrocoagulation technique. This technique has been used for the removal of toxic metals such as chromium, copper, manganese, nickel and zinc ions (Heidmann and Calmano, 2007; Bhatti et al., 2009; Vlachou et al., 2013; Gatsios et al., 2015). Other chemical methods include ion exchange, solvent extraction, reverse osmosis, precipitation, chemical oxidation and reduction, filtration, electrochemical treatment etc. However, these chemical methods are either inefficient or expensive, while some constitute more toxicity in the environment due to the generation of secondary wastes which could prove untreatable (Duygu et al., 2008; Ahamed and Begum, 2012).

The use of biological methods for removal of toxic metals from solution is encouraged over chemical methods, due to its economic advantage, availability of adsorbents and effectiveness. The widely accepted biological method of toxic metal clean up is adsorption. Adsorption is briefly explained as the retention and accumulation of metal ions unto the surface of solid materials in solution. A wide variety of adsorbents from different biological and agricultural sources such as sawdust, groundnut shell or fly ash, have been used for removal of copper ions from wastes and aqueous solutions (Teker et al., 1999; Shukla et al., 2005; Kaushir et al., 2007; Najua et al., 2008; Korrapati et al., 2009). Adsorbents have also been developed from organic and inorganic waste products including organic wastes of plants and animals with high carbon content (fruit waste, rice husks, bark, seaweed, algae, peat moss, hair and keratin) and inorganic materials such as mud soil, zeolites, ore materials and metal oxides with successful removal of toxic metals (Ali et al., 2012).

Sugarcane bagasse is a waste product from sugar refining industry. Bagasse is often considered as solid agro-waste material which is widely available and cause a significant disposal problem. Therefore, this cheap and unconventional biological material could be used as an adsorbent for the removal of ions of toxic metal from solution.

The use of both untreated and treated sugar cane bagasse as adsorbent for the removal of copper (II) ions from aqueous solutions was investigated and the adsorption process was explained using various models.

2. Experimental procedure

2.1. Materials

All chemicals used in the study were of analytical grade. Oxalic acid, Hydrochloric acid, Sodium hydroxide and anhydrous copper (II) sulphate were all purchased from Sigma-Aldrich. Stock solution (1000 mg l\(^{-1}\)) of adsorbate (Cu (II) ions) was prepared by dissolving 2.51 g of dehydrated copper (II) sulphate in 1000 ml deionized water in volumetric flask. Lower concentrations of adsorbate were prepared from stock solution by dilution. The biomaterial, sugarcane bagasse, was obtained from an indigenous sugar refinery.

2.2. Equipment

Pulverization of the bagasse was done using electric blender (Tamashi Model: TBG296-1), and the drying was in a hot-air oven (Uniscope SM9053). pH of solution was recorded using pH/ ion 510 meter (Eutech Instruments). Elemental analyses were carried out on an Atomic Adsorption Spectrophotometer, AAS (GBC model Analyst 400).
2.3. Preparation of adsorbent

Sugar cane bagasse was pulverized and dried at 60 °C for 12 h in a hot-air oven. Thereafter, it was sieved to uniform particle size of 100 µm using a sieve of 100 µm mesh size, kept in an air-tight container and labeled as untreated sugarcane bagasse (USCB). To prepare treated sugarcane bagasse (TSCB), USCB of uniform particle size (100 µm) was treated with 0.1M oxalic acid for 48hrs in a conical flask. After bleaching with oxalic acid, treated bagasse was dried to constant mass and kept in an air-tight container for further studies.

2.4. Batch Adsorption Experiments and Equilibrium Study

Batch experiment has been carried out to find the optimum pH, contact time, thermodynamic studies, equilibrium isotherms and kinetic studies.

Optimization of pH condition was carried out by adjusting the pH of adsorbate solution in the range 2.0-10.0. The pH adjustment of solution was done using 1.0 M HCl and 1.0 M NaOH and pH values confirmed using a pH/ ion 510 meter (Eutech Instruments). Appropriate contact time was determined by allowing interaction of adsorbate to adsorbent between 20-120 minutes at 20-minute intervals. At each interval, residual Cu (II) concentration was analyzed. Effect of initial Cu II ion concentration was determined by preparing metal solution at different concentrations between 100-500 mg/L. Thermodynamic effects were determined by carrying out sorption experiments at optimum conditions while varying temperature of the environment between 25-45 °C (298-318 K) at intervals of 5 °C (5 K).

Adsorption experiments were carried out by placing Erlenmeyer flasks on a Thermostat Orbital shaker, agitating the mixture at 150 rpm at appropriate temperature for specified contact time of 100 mins and constant temperature. Equilibrium studies were carried out by varying initial Cu (II) concentration (25-100 mg l⁻¹) with a working volume of 20 ml. Experiments were done in triplicates and average of data obtained was calculated. Control experiments were carried out by running adsorption of Cu (II) ions in appropriate concentrations in solutions without adsorbent. After contact period, the mixture was filtered using Whatmann’s filter paper and residual concentration of Cu (II) ions in the filtrate (5 mL) was determined using the AAS.

Amount of metal ions adsorbed per gram of adsorbent and the efficiency of adsorption were calculated according to Equations 1 and 2 below:

\[ q_e = \frac{(C_0 - C_e)V}{M} \]  \hspace{1cm} (1)

Adsorption Efficiency (%) = \( \frac{(C_0 - C_e)100}{C_0} \) \hspace{1cm} (2)

Where \( q_e \) is amount of metal ions adsorbed per gram of adsorbent (mg g⁻¹), \( C_0 \) and \( C_e \) is the initial and equilibrium concentration of the adsorbate (mg l⁻¹) respectively, \( V \) is the volume of solution (l) and \( M \) is the mass of adsorbents (g).

3. Results and discussion

3.1. Effect of pH on adsorption

One of the most important factors which control the potential activity of an adsorbent in the uptake of toxic metals from aqueous solution- and consequently wastewater- is the acidity or alkalinity of the solution. The percentage removal of Cu II ions from solution by treated and untreated sugarcane bagasse was described in Fig. 1 and it can be deduced that pH of solution highly affected Cu II uptake. Highest Cu II uptake was observed for both TSSB and USCB at solution pH 2. However, TSCB showed higher adsorption rate of 73.8% than USCB which removed Cu II at a rate of 52.22% over the same contact period. However, there was continuous
decrease in adsorption capacity for both USCB and TSCB with increase in pH of metal solution. A steady
decrease in adsorption capacity was observed for USCB while over 59% of copper ions were removed from
solution up to weak acidic pH 6 by TSCB. It was also observed that there was rapid decrease in adsorption
rate thereof for TSCB while both adsorbent types showed similar adsorption rate in alkaline pH range.
Optimum pH observed and continuous decrease beyond optimum pH could be due to the effect of a net
positive charge on the surface of sugar cane bagasse in untreated and treated state at low pH optimum of 2.
This indicates strong electrostatic force for attraction between Cu (II) ion and the adsorbents as a result of
anions formed from net positive charge on the surface of adsorbents.

![Figure 1: Effect of pH on adsorption of Copper (II) ions. Initial Cu (II) ions conc. = 100mg l⁻¹, Adsorbent
dosage=0.2g/20ml, Contact time=100 min., Agitation speed= 150 rpm.](image)

3.2. Effect of contact time

The effects of exposure period on the adsorption rate of Cu II by USCB and TSCB were illustrated in Fig. 2.
Optimum sorption time was observed at 100mins for both treated and untreated adsorbent. It was observed
that there was increase in adsorption rate with increased contact between both types of adsorbent and the
metal solution. Copper II ions removal increased from 35.68% and 45.28% after 10mins of exposure to 68.63%
and 84.58% removal rate at 100mins for USCB and TSCB respectively. No further increase in adsorption rate
was observed for both adsorbents beyond 100mins. Also, more than 60% was removed after 20mins contact
between Cu II ions and TSCB, result similar to the maximum sorption rate achievable by USCB.
Optimum sorption period for maximum Cu II ions sorption is comparable with reports of Julkapli et al., 2013
using chitosan-gel adsorbents for Cu II removal and Kareem et al., (2014) for use of fungi as biosorbent for
toxic metals’ uptake from solution.
Adsorption of over 60% in 20mins by TSCB compared to 40% by USCB over the same period indicates the
presence and availability of active binding sites at the initial sorption process with more binding activity
occurring in TSCB.
Continuous sorption activity beyond 100 mins optimum contact period yielding no further increase in
adsorption rate could be attributed to exhaustion of binding sites (Qaiser et al., 2009).
3.3. **Effect of initial concentration of Cu (II) ions**

Efficiency of adsorption of Cu (II) ions at various initial concentrations of Cu (II) ions described in Figure 3 showed that TSCB showed higher adsorption rate of 84.58% than USCB with 68.63% at an optimum initial metal concentration of 100 mg/L. This implies that there was decrease in adsorption rate with increase in adsorbate concentration. However, over 50% removal rate was maintained by both types of adsorbent for the metal concentration range studied.
This is as a result of bulk mass transfer of Cu (II) ions at the surface of the adsorbents. After the saturation of the Cu (II) ions on the surface of the adsorbents more Cu (II) ions in excess surrounding the adsorbents causes desorption of the excess adsorbate. Also, higher adsorption rate at higher concentrations by TSCB compared to USCB indicates the availability of more activity sites on adsorbent surface although this was not enough to react more Cu II ions due to the larger number of the ions at higher concentrations (Khalid et al., 2000).

3.4. Equilibrium Adsorption Isotherm Models

In this research work, Langmuir (Langmuir, 1918) and Freundlich isotherm (Freundlich and Hatfield, 1926) models were used to analyze adsorption data by fitting them into the models. The linear forms of these equations are expressed in equation (3) and (5) below respectively.

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m}$$  \hspace{1cm} (3)

Where, $q_e$ is the amount of adsorbate adsorbed per unit amount of adsorbent (mg g$^{-1}$), $C_e$ the equilibrium concentration (mg l$^{-1}$), $b$ Langmuir equilibrium or adsorption constant (l mg$^{-1}$) and $q_m$ Langmuir monolayer saturation capacity (mg g$^{-1}$).

Essential feature of the Langmuir isotherm can be expressed by means of $R_L$, a dimensionless constant referred to as a separation factor or equilibrium parameter. $R_L$ is calculated by

$$R_L = \frac{1}{1+bC_o}$$  \hspace{1cm} (4)

Where, $C_o$ is the initial concentration of Cu (II) ions (mg l$^{-1}$) and $b$ is obtained from slope of Langmuir plot. Favourable copper adsorption is confirmed by the value of $R_L$ in the range 0 to 1.

The Freundlich linearized equation can be described by

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (5)

Where, $k_f$ is constant that described the adsorption capacity of the adsorbent (mg g$^{-1}$), $n$ is empirical parameter that dictates the intensity of the adsorption. The value of $k_f$ and $n$ are determined by intercept and slope of the plot of log $q_e$ against log $C_e$ respectively.

The favourable uptake of Cu (II) ions confirm by the value of $R_L$ in the range of 0 to 1 at all initial Cu (II) ions concentration shown in Table 1.

Isotherm constants for adsorption of Cu II by USCB and TSCB are described in Table 1. Adsorption data by both adsorbents fitted into the adsorption models, indicated by $R^2$ values higher than 0.9. Dimensionless constant for both adsorbents was between 0-1, describing a favorable sorption process. Langmuir constant, $b$, was higher in TSCB than when USCB was used for Cu adsorption. This shows that TSCB has higher affinity to react with Cu ions in solution than USCB. Empirical parameter, $n$, determined from the slope was higher than 1 for both adsorbent types and this indicates a homogenous adsorbent surface. Higher $n$ value for Cu adsorption using TSCB describes a more favourable Cu II adsorption in comparison with USCB (Haghseresht and Lu, 1998; Adamson, 2001; Fytianos et al., 2003).

Table 1: Adsorption isotherms data for adsorption of Cu (II) ions

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$q_m$ (mg g$^{-1}$)</th>
<th>B (l mg$^{-1}$)</th>
<th>$R_L$</th>
<th>$R^2$</th>
<th>$n$</th>
<th>$K_f$ (mg g$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>USCB</td>
<td>55.56</td>
<td>0.0045</td>
<td>0.69</td>
<td>0.996</td>
<td>1.366</td>
<td>0.556</td>
<td>0.999</td>
</tr>
<tr>
<td>TSCB</td>
<td>43.48</td>
<td>0.0159</td>
<td>0.39</td>
<td>0.988</td>
<td>1.739</td>
<td>1.854</td>
<td>0.975</td>
</tr>
</tbody>
</table>
3.5. Thermodynamic studies

Temperature effects on Cu II adsorption by USCB and TSCB were described in Figure 4. It showed that adsorption of Cu by both adsorbents increased with increasing temperature of the reaction environment. Temperature had a higher effect on USCB, increasing Cu adsorption from 60 to 80%, while TSCB maintained an 80% adsorption rate at all temperatures investigated. These observations imply that the adsorption process is endothermic in nature with external heat needed to improve adsorbate-adsorbent interactions.

Thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were determined using equations 6–8 and values are summarized in Table 2.

\[
\Delta G = -RT \ln K_c
\]

\[
K_c = \frac{q_e}{C_e}
\]

\[
\Delta G = \Delta H - T \Delta S
\]

Where, \( \Delta G^0 \) is standard free energy change (Joules), \( R \) is universal gas constant (8.314 Jmol⁻¹K⁻¹), \( T \) (K) is the absolute temperature, \( K_c \) is the adsorption equilibrium, \( q_e \) is the adsorption capacity of adsorbent at equilibrium and \( C_e \) is the residual concentration of adsorbate.

![Figure 4: Effect of Temperature on adsorption of copper (II) ions. Initial Cu (II) ions conc. = 100 mg L⁻¹, Adsorbent dosage=0.2g/20mL, pH 2, Contact time=100 min., Agitation speed= 150 rpm.](image)

Table 2: Thermodynamic parameters for Cu (II) ions adsorption onto untreated and treated sugarcane bagasse.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>USCB</th>
<th></th>
<th></th>
<th>TSCB</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔG (kJ/mol)</td>
<td>ΔS (kJ/k/mol)</td>
<td>ΔH (kJ/mol)</td>
<td>R²</td>
<td>ΔG (kJ/mol)</td>
<td>ΔS (kJ/k/mol)</td>
<td>ΔH (kJ/mol)</td>
</tr>
<tr>
<td>298</td>
<td>-1.729</td>
<td>0.094</td>
<td>26.42</td>
<td>0.995</td>
<td>-4.122</td>
<td>0.072</td>
<td>17.45</td>
</tr>
<tr>
<td>303</td>
<td>-2.323</td>
<td>0.094</td>
<td>26.42</td>
<td>0.995</td>
<td>-4.376</td>
<td>0.072</td>
<td>17.45</td>
</tr>
<tr>
<td>308</td>
<td>-2.68</td>
<td>0.094</td>
<td>26.42</td>
<td>0.995</td>
<td>-5.071</td>
<td>0.072</td>
<td>17.45</td>
</tr>
<tr>
<td>313</td>
<td>-3.157</td>
<td>0.094</td>
<td>26.42</td>
<td>0.995</td>
<td>-5.173</td>
<td>0.072</td>
<td>17.45</td>
</tr>
<tr>
<td>318</td>
<td>-3.677</td>
<td>0.094</td>
<td>26.42</td>
<td>0.995</td>
<td>-5.534</td>
<td>0.072</td>
<td>17.45</td>
</tr>
</tbody>
</table>
Negative free energy change ($\Delta G$) values obtained confirm the feasibility and spontaneity of the adsorption process. Also, positive enthalpy and entropy changes were described for both USCB and TSCB were described changes for both adsorbents (Table 2) and this confirms an endothermic sorption process. Enthalpy value of USCB (26.42 kJ mol$^{-1}$) was higher than that of TSCB (17.45 kJ mol$^{-1}$), indicating that higher temperature would be required to achieve high Cu II sorption comparable with TSCB sorption.

Similarly, positive entropy change indicates an endothermic process with a high degree of randomness. There is a higher degree of randomness using USCB (0.094 kJ kmol$^{-1}$) than when TSCB (0.072 kJ kmol$^{-1}$) is used in Cu II removal from aqueous solution.

### 3.6. Kinetic studies

The rate constant of adsorption Cu (II) adsorption by USCB and TSCB were determined from the pseudo first-order equation (Equation 9; Langergrern and Svenska, 1998) and the second-order equation (Ho and McKay, 1998; Equation 10) respectively. The mechanism of adsorption process by mass transfer was analyzed by intra-particle model described in equation 11.

\[
\log(q_e-q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{9}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \tag{10}
\]

\[
q_e = k_w t^{0.5} \tag{11}
\]

Where $k_w$ is intra particle diffusion rate constant (mg g$^{-1}$ min$^{-0.5}$), $q_t$ is amount of adsorbate adsorbed on adsorbent at contact time $t$ (min), $k_1$ and $k_2$ are equilibrium rate constant of pseudo-first- and second-order adsorption (min$^{-1}$).

All the data obtained from these studies were expressed in Table 3. Using the pseudo-first order equation, the slope and intercept when log ($q_e - q_t$) was plotted against $t$ was used to determine the rate constant ($k_1$) and $q_e$ respectively. As shown in Figure 5, the correlation coefficients of both USCB and TSCB were lower than 0.9, indicating that adsorption data did not fit into the pseudo first order model. Data were fitted into the second-order model and a linear plot with high correlation co-efficient (>0.9) was determined (Figure 6). This suggests that the pseudo second-order is better applicable to explain the adsorption process.

![Figure 5. Lagergren pseudo-first-order model for adsorption of Cu (II) ions onto USCB and TSCB](image-url)
The intra-particle model was used to analyze experimental data and good fit plots were obtained. However, adsorption of USCB ($R^2 = 0.932$) fitted better than TSCB ($R^2 = 0.885$). Also, low $k_w$ less than one for both USCB and TSCB describes low bonding and slow rate of adsorption rate between adsorbent and sorbate (Erhan et al., 2004). It was also observed that the $k_w$ of Cu II adsorption on TSCB is higher than that of USCB and this could be as a result of treatment with oxalic acid which increased the surface area for interaction.

**Figure 6.** Ho’s pseudo-second-order model for adsorption of Cu (II) ions onto USCB and TSCB.

**Figure 7.** Intra particle model for the adsorption of Cu (II) ions onto USCB and TSCB.

**Table 3.** The kinetic studies parameters for the adsorption of Cd (II) ions onto untreated and treated sugar cane bagasse.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Intra particle model</th>
<th>Lagergren pseudo-first-order model</th>
<th>Ho’s pseudo-second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_w$</td>
<td>$R^2$</td>
<td>$k_1$</td>
</tr>
<tr>
<td>USCB</td>
<td>0.673</td>
<td>0.885</td>
<td>0.074</td>
</tr>
<tr>
<td>TSCB</td>
<td>0.926</td>
<td>0.932</td>
<td>0.060</td>
</tr>
</tbody>
</table>
4. Conclusion

Adsorption capacity is dependent on the pH of the solution, contact time, initial concentration of Cu (II) ions and temperature of the solution. The maximum amount of the Cu (II) ions removed from solution by USCB and TSCB at optimum pH =2 and contact time of 100 minutes. The adsorption capacity of TSCB is more than that of USCB due to more porous surface area in the TSCB. Thermodynamic studies of the adsorption of Cu (II) ions unto USCB and TSCB show that the process is endothermic in nature that improved with increased temperature. Sorption data also fitted better into the second-order model while data also had good-fit when analyzed with both Langmuir and Freundlich models, but intra-particle diffusion model described a porous adsorbent with low sorption affinity.

References


