Role of sawdust in adsorption of Zn\(^{2+}\) and Cd\(^{2+}\) ions from aqueous system

Qasimullah\(^1\), Anees Ahmad\(^2\), Mohd Rafatullah\(^3\),* Othman Sulaiman\(^3\) and Rokiah Hashim\(^3\)

\(^1\)Applied Science Section, University Polytechnic, Aligarh Muslim University, Aligarh, 202 002 UP, India
\(^2\)Department of Chemistry, Aligarh Muslim University, Aligarh, 202 002 UP, India
\(^3\)School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia

*Corresponding author, Phone: +604-653-4302, Fax: +604-657-3678, E-mail: mohd_rafatullah@yahoo.co.in; mrafatullah@usm.my

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ABSTRACT
Sawdust, an inexpensive material, has been utilized as an adsorbent for the removal of Zn\(^{2+}\) and Cd\(^{2+}\) ions from aqueous solution. The effects of contact time, pH, concentration, and dosage of the adsorbent on the removal of Zn\(^{2+}\) and Cd\(^{2+}\) ions have been studied. The equilibrium nature of Zn\(^{2+}\) and Cd\(^{2+}\) ions adsorption at different temperatures was also studied. Two model viz.; Freundlich and Langmuir were tried to fit the observed data. Both the metal ions show a very interesting trend of adsorption where minima are seen in the adsorption isotherms. The thermodynamic parameters like free energy, entropy and enthalpy changes for the adsorption of Zn\(^{2+}\) and Cd\(^{2+}\) ions have also been computed and discussed. It is seen that the overall process of adsorption of Zn\(^{2+}\) ions is a multilayer endothermic process whereas the Cd\(^{2+}\) ions shows composite adsorption behaviour.

1. Introduction
The increasing concentration of heavy metals in waters is mainly due to effluent discharges from industries. Pollution of natural waters by metal ions has become a major issue all over the world because metal concentrations in waters often exceed the admissible values. Consequently, industries are required to diminish the contents of heavy metals in their effluents to acceptable levels (Areco and Afonso 2010). Zinc is introduced into the streams by many industries such as steel works with galvanizing lines, zinc and brass metal works, electroplating, viscous rayon, yarn and fiber production, ground wood pulp production and news print paper production (Ramos et al. 2002). The zinc salts are also used in the pigment industries. Thus our aqueous environment has a high negative effect due to excessive addition of zinc beyond its permissible limit (5mg/L) for aquatic life (Moser and Adhaum 2002). Cadmium is introduced into the water from smelting, metal plating, cadmium-nickel batteries, phosphate fertilizers, mining, pigments, pigments, stabilizers, alloy industries and sewage sludge (Zhu et al. 2007). Maximum contaminant level for cadmium in drinking water is 0.005 mg/L determined by environmental protection agency. The harmful effects of Cd(II) include acute and chronic metabolic disorders, such as itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy.

At present, a number of technologies, such as chemical precipitation, evaporation, electroplating,
adsorption and ion-exchange processes, are used for the treatment of heavy metal-containing wastewater streams (Kaewsarn and Yu 1999). Activated carbon has been popular choice as an adsorbent for the removal of the pollutants from waste water (Hasar et al. 2003), but its high cost poses an economical problem. Therefore, there is a need for the development of low cost and easily available material which can be used more economically on large scale. Several contributions have made in this area utilizing number of materials like olive stone carbon (Ferro-Garcia et al. 1988 ), sunflower stalks (Sun and Shi 1998), sugarcane baggase (Basso et al. 2002), oak saw dust (Sciblan et al. 2006), black locust (Sciblan et al. 2006), meranti sawdust (Ahmad et al. 2009; Rafatullah et al. 2010), sisoo sawdust (Ahmad et al. 2007; Rafatullah et al. 2010), cassava waste (Abia et al. 2003), wheat bran (Farajzadeh et al. 2004), bone char (Ko et al. 2003), olive pomace (Pegnanelli et al. 2003), and carrot residues (Eslamzadeh et al. 2004).

Most of these materials contain functional groups associated with proteins, polysaccharide, lignin and cellulose as major constituents, with metal uptake believed to occur through sorption processes involving such functional groups. Sawdust is a cheap, widely available and abundant natural material. It has been reported to exhibit ion exchange and complexation properties for the heavy metals (Rafatullah et al. 2009).

This paper reports the systematic adsorption studies of Zn\(^{2+}\) and Cd\(^{2+}\) ions on saw dust. The effect of equilibrium time, pH, temperature, concentration, dose and salinity on adsorption of these metal ions has been described. The adsorption isotherm and probable mechanism have been explained.

2. Material and methods

1.1. Adsorbent

The sawdust of Mango tree (Mangefera indica) was used in this study. It was collected from timber workshop near the Aligarh Muslim University campus. It was sieved (50-60 mesh), treated with dilute HCl and washed several times with distilled water until no chloride was released. It was then used throughout the adsorption studies.

Adsorbate solution

The stock solution (0.005 M) of metal ions was prepared by dissolving their corresponding salt in distilled water and standardized complexometrically with EDTA (disodium salt) using EBT (Eriochrom Black-T). All the chemicals used were analytical reagent grade and were obtained from Loba, E. Merk and BDH Bombay (India).

1.2. Batch Adsorption Studies

Adsorption studies were carried out at different temperatures (22-60° C). 50 ml of the solution containing the desired quantity of the metal ion was treated with 0.5 g of sawdust in stoppard conical flasks for the different times using a temperature controlled shaker. After the predetermined time interval the reaction mixture was filtered and the filtrate was analyzed for the final concentration of the metal ions by titrating with EDTA. The amount of adsorbed metal ions was determined by subtracting the final concentration. Blanks were also prepared to find out the adsorption onto the internal surface of the containers, if any. The effect of pH of the solution was adjusted by either 0.1 M NaOH or 0.1 M HCl solutions.

To study the effect of salinity of the removal of Zn\(^{2+}\) and Cd\(^{2+}\) ions, the experiment was also conducted in presence of NaCl at 40 °C only. The concentration of the NaCl was maintained at 0.1 M by adding 5ml of 1 M NaCl stock solution.

Adsorption Models

To quantify, the adsorption capacity of sawdust for the removal of metal ions from water solutions, the Langmuir and Freundlich equations were applied.

Langmuir Model: According to this model (Langmuir 1918)-

\[
\frac{Ce}{Am} = \frac{1}{K} + \frac{1}{b} \cdot Ce
\]

where ‘Ce’ is the equilibrium concentration (mole/L), ‘Am’ is the amount adsorbed per specified amount of adsorbent, ‘K’ is the equilibrium constant and ‘b’ is the amount of adsorbate required to form monolayer.

Freundlich Model: According to this model (Freundlich 1907)-

\[
Am = K Ce^{1/n} \quad \text{or} \quad \ln (Am) = \ln K + \frac{1}{n} \ln(Ce)
\]

where all the terms have the usual significance and ‘n’ is an empirical constant. This model deals with the multilayer adsorption of metal ions on the adsorbate. The points in the figures indicate the observed data and the line corresponds to the fitted data.
A computer simulation technique has been applied to fit the Freundlich and Langmuir equations for the adsorption data. The coefficients of least squares fitting to straight line (R) were computed for these two models.

3. Results and discussion
3.1 Time of Equilibrium
The adsorption of \( \text{Zn}^{2+} \) and \( \text{Cd}^{2+} \) ions was studied with time and results are shown in Fig 1. It is observed that the adsorption of \( \text{Zn}^{2+} \) ions is multi step process and reaches to a final plateau after 70 minutes. The maximum uptake after this time is constant at a value of 61.5% adsorption. On the other hand, the adsorption of \( \text{Cd}^{2+} \) ions reaches to a value of 60% after 30 min onwards. Thus the adsorption of \( \text{Cd}^{2+} \) ions on sawdust is faster in comparison to that of \( \text{Zn}^{2+} \) ions. However, the time of equilibrium used in all the following studies was set to 1.5 hour for the sake of simplicity as well as to ensure the complete process of adsorption in both cases.

3.2 Effect of dose of sawdust
The effect of the dose of sawdust on the adsorption of \( \text{Zn}^{2+} \) and \( \text{Cd}^{2+} \) ions has been depicted in Fig 2. The percent adsorption increases with increase in the dose of adsorbent probably due to its high surface area. But the adsorption increases in a steeper fashion. In case of \( \text{Zn}^{2+} \) ions, the final plateau is attained at 62% adsorption for a dose of > 0.7 g of sawdust. On the other hand \( \text{Cd}^{2+} \) ions show three steps adsorption process which is initially very fast compared to \( \text{Zn}^{2+} \) ions and reaches to final plateau equivalent to 70% adsorption. This plateau was constant at dose of > 0.8 g of sawdust.

3.2 Effect of pH
The effect of pH on the adsorption of \( \text{Zn}^{2+} \) and \( \text{Cd}^{2+} \) ions are shown in Fig 3. Both the ions show almost similar trends but different extents of adsorption at different pH values on sawdust. The adsorption of \( \text{Cd}^{2+} \) ions starts at pH 2. It reaches up to 10% at pH 2.8, 55% at pH 6 and finally to a maximum value of 60% adsorption at pH 6.7 and remains constant at this level even at higher pH values. On the other hand the adsorption of \( \text{Zn}^{2+} \) ions starts only after pH 6. About 55% adsorption of \( \text{Zn}^{2+} \) ions is observed around pH 8 which reaches to a maximum value of 70% at pH 9 and remains constant thereafter. The adsorption behaviour of \( \text{Zn}^{2+} \) and \( \text{Cd}^{2+} \) ions on sawdust at different pH values may be explained through the ion exchange and complexation mechanisms.

Sawdust basically contains lignin and cellulose. The polar functional groups of lignin e.g., aldehydes, ketones, alcohols, acids and phenolic hydroxides are involved in these processes. They are affected by pH and may undergo protonation and/or deprotonation resulting thereby the variation in surface charge of the adsorbent (Huang and Rhoads 1989). This results the uptake of the metal ions from the solution via complexation and/or ions exchange processes. These ions show similar trends of adsorption probably because they belong to the same group of the periodic table. Their different extents of adsorption may be attributed to their different effective ionic radii. The ionic radius of \( \text{Cd}^{2+} \) ions is 5 \( \text{Å} \) while that of \( \text{Zn}^{2+} \) ions is 6 \( \text{Å} \). The smaller ionic size of \( \text{Cd}^{2+} \) ions helps in its easy approach to the less approachable sites of the adsorbent as compared to that of \( \text{Zn}^{2+} \) ions. Further the more hydration energy of \( \text{Cd}^{2+} \) ions in comparison of \( \text{Zn}^{2+} \) ions restricts its maximum uptake by the adsorbent.
3.3 Effect of concentration

The effect of concentration of Zn$^{2+}$ and Cd$^{2+}$ ions on their adsorption is shown in Fig. 4. The adsorption starts from concentration of 0.001 M and its shows that the change in concentration does affect the % adsorption of the two metal ions. However, the maximum adsorption in case of Zn$^{2+}$ ions is only 23% while in case of Cd$^{2+}$ ions it is up to 60%. The difference in the extent of adsorption is actually the effect of pH (as explained above) which is maintained between 6-7 to make an ideal situation.

3.4 Adsorption isotherm study

The related parameters for the fitting of Freundlich and Langmuir equation at different temperatures are summarized in Table 1 & 2.

Adsorption of Zn$^{2+}$ ions: The adsorption of Zn$^{2+}$ ions between pH 6-7 follows both Freundlich as well as Langmuir type isotherm. However, the Langmuir equation is better obeyed by the system than the Freundlich one as is evident from the values of regression coefficients (shown in Table 1) which are very close unity at 40 and 60 °C where as they are far from unity in both the cases at 22 °C.

The overall adsorption increases with the increase in temperature. Further, at each temperature, a minimum is seen corresponding to different values of Ce and Am as shown in Fig 5. The overall behaviour of the system indicates that it is probably a multilayer endothermic adsorption process. This statement contradicts to the earlier statement that Langmuir adsorption isotherm is better obeyed. It can be justified as follows:

(1) The multilayer adsorption process is not possible in case of Langmuir model. It is only possible in Freundlich adsorption model where the surface of the saw dust is assumed to be made up of heterogeneous patches which are homogenous in themselves (as explained above).

(2) The application of Von’t Hoff type equation for the calculation of thermodynamic parameters shows that the enthalpy of adsorption is positive in case of Freundlich adsorption model whereas it is negative for the Langmuir one. The positive $\Delta$H value of the former model corresponds to endothermic process which we have observed. Thus it indicates that Freundlich adsorption is obeyed in the adsorption of Zn$^{2+}$ ions on the saw dust.

To find out the reason of appearance of the minima in the adsorption isotherm, the pH of the system is noted and it is found to be 5.8, which is less than 6.5, a value to which system was preset by adding NaOH. The ion exchange seems to be the possible mechanism of these minima. With the increase in concentration, the aggregation of the metal ions at the surface of the saw dust increases which results to the exchange reactions with the already protonated sites, resulting thereby an increase in H$^+$ concentration and hence a decrease in pH. The latter effect decreases the adsorption of the metal ions leading to a minimum in the adsorption isotherm. With the rise in temperature, this minima shifts to a lower concentration of metal ions. The increase in temperature increases the aggregation of ionic species and hence brings about the ion exchange process at lower equilibrium concentration.

Adsortion of Cd$^{2+}$ ions: The adsorption of Cd$^{2+}$ ions at different temperatures is shown in Table 2. It is clear from the values of regression coefficients that neither it
Table 1: Parameters Related to the Adsorption of Zn\textsuperscript{2+} Ions on Sawdust at Different Temperatures

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Reg. Coeff. (R)</th>
<th>Freundlich Constant (K)</th>
<th>1/n</th>
<th>Langmuir Constant (K)</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>0.53</td>
<td>0.16</td>
<td>0.28</td>
<td>0.69</td>
<td>0.91</td>
</tr>
<tr>
<td>40</td>
<td>0.93</td>
<td>0.18</td>
<td>0.22</td>
<td>0.98</td>
<td>0.74</td>
</tr>
<tr>
<td>60</td>
<td>0.95</td>
<td>0.23</td>
<td>0.23</td>
<td>0.98</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Table 2: Parameters Related to the Adsorption of Cd\textsuperscript{2+} Ions on Sawdust at Different Temperatures

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Reg. Coeff. (R)</th>
<th>Freundlich Constant (K)</th>
<th>1/n</th>
<th>Langmuir Constant (K)</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>0.43</td>
<td>0.44</td>
<td>0.36</td>
<td>0.11</td>
<td>0.46</td>
</tr>
<tr>
<td>40</td>
<td>0.59</td>
<td>0.34</td>
<td>0.29</td>
<td>0.63</td>
<td>0.61</td>
</tr>
<tr>
<td>60</td>
<td>0.45</td>
<td>0.26</td>
<td>0.27</td>
<td>0.38</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Table 3: Thermodynamic Parameters for the Adsorption of Zn\textsuperscript{2+} Ions on Sawdust at Different Temperatures

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Freundlich Adsorption Isotherm</th>
<th>Langmuir Adsorption Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>lnK</td>
<td>(\Delta G)</td>
</tr>
<tr>
<td>22</td>
<td>-1.843</td>
<td>1.080</td>
</tr>
<tr>
<td>40</td>
<td>-1.733</td>
<td>1.077</td>
</tr>
<tr>
<td>60</td>
<td>-1.479</td>
<td>0.979</td>
</tr>
</tbody>
</table>

\(\Delta G = \text{Kcal/mole}^\circ\), \(\Delta S = \text{Kcal/mole}^\circ/\text{K}\), and \(\Delta H = \text{Kcal/mole}^\circ\)

3.4 Thermodynamic study

The thermodynamics, parameters \(\Delta G\), \(\Delta H\) and \(\Delta S\) were computed from the equation given below and listed in Table 3 & 4. The free energy change was calculated from the relations.

\[\Delta G = -RT \ln K\]  (3)

Similarly, the enthalpy change (\(\Delta H\)) between 22 to 66\°C was computed from the following equations.

\[\ln K = -\Delta H/RT + C\]  (4)

The entropy change (\(\Delta S\)) was calculated from the equation

\[\Delta G = \Delta H - T\Delta S\]  (5)

The various thermodynamic parameters, i.e., free energy (\(\Delta G\)), enthalpy (\(\Delta H\)) and entropy (\(\Delta S\)), associated with the sorption of Zn\textsuperscript{2+} and Cd\textsuperscript{2+} ions on to the treated sawdust were determined by using the equations 3, 4, and 5 and the values are listed in Table 3 and Table 4, where R is the universal gas constant, k and 22\°C become almost equal between Ce = 0.6 to 2M. With the increase in equilibrium concentration so many crossovers are observed among the three adsorption isotherms and finally the order of the extent of adsorption becomes 40\° > 22\° > 60\°. According to Giles classification (1960), the adsorption of Cd\textsuperscript{2+} ions on saw dust show 'S' type isotherm. This class of adsorption isotherm is indicative of the composite isotherm where there is a competition between the solute and solvent molecules for the adsorption on the absorbents. The following may be the possible mechanism of overall process of Cd\textsuperscript{2+} ions adsorption.

Initially the adsorption of Cd\textsuperscript{2+} ions at all the temperature occurs in the unhydrated form, i.e., the dehydration of both the ions and the adsorption site occurs first and the ions get adsorbed on the most easily accessible surface sites (exposed sites). However, the sites at the inner surface are still available. On increasing the concentration of the ions in solution, the aggregation of these ions increases on the surface leading to their access to the less accessible sites (i.e. the inner surface sites). This tends to an increase in the adsorption through the opening of the pores of adsorbent due to its swelling. The later effect facilitates the entry of water molecules too into the pores. On the entry of water, the adsorbed ions/sites get hydrates leading to a decrease/reversal in the extent of adsorption. Thus it causes a minimum in the adsorption process.

\(\Delta G = \text{Kcal/mole}^\circ\), \(\Delta S = \text{Kcal/mole}^\circ/\text{K}\), and \(\Delta H = \text{Kcal/mole}^\circ\)

Conclusion

Thus it is clear that sawdust is potential adsorbent for the removal of Zn\textsuperscript{2+} and Cd\textsuperscript{2+} ions from aqueous system. The adsorption of Zn\textsuperscript{2+} ions on saw dust shows a multilayer endothermic adsorption process. However, the adsorption of Cd\textsuperscript{2+} ions follow a composite isotherm which results in the reversal of order of selectivity of Cd\textsuperscript{2+} ions with the change in equilibrium concentration and temperature of the system leading to the minima in the adsorption isotherms.

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References