Adsorption of cadmium(II) Ions from aqueous solution using different adsorbents

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A comparative study on the adsorption of cadmium from aqueous solutions on a few low cost and locally available untreated and chemically treated adsorbents is carried out. Mustard husk, carbon aerogel and treated GAC are found to be most effective adsorbents in addition to treated GAC for the removal of cadmium from the aqueous solution at varying process parameters such as, pH (2-12) adsorbent dose (0.5-1.2 g/100 ml.), contact time (24-72 h) and initial cadmium concentration (1-5 mg/L). Treated GAC, carbon aerogel, and mustard husk show 100, 87 and 72 per cent adsorptive removal of cadmium, respectively, under optimized conditions of pH 4 and dosage 1 g/l00 mL for 2 mg/L cadmium aqueous solutions in 48 h. The adsorption parameters are determined using both Langmuir and Freundlich isotherm models. Surface complexation and ion exchange are the major removal mechanisms involved. The adsorption isotherm studies indicate that the adsorption process is a monolayer coverage of cadmium on surface of treated GAC and fits into the Langmuir model. The adsorptive behaviour of cadmium on untreated mustard husk and carbon aerogel satisfies not only the Langmuir assumptions but also the Freundlich assumptions, i.e., multilayer formation on the surface of the adsorbent with an exponential distribution of site energy. The results of the experimental studies as well as the model parameters are presented.

Keywords: Adsorption, Cadmium(II) ions, Aqueous solution
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Introduction

Most of the heavy metals above trace quantities are harmful to humans, animals and plants. Federal and local agencies have therefore stipulated discharge limits on the levels of these heavy metals in the effluents being discharged into the environment. Cadmium, used in this study, is one of these metals. It is an irritant to the respiratory tract, and prolonged exposure to this pollutant can cause anemia and a yellow stain that gradually appears on the necks of the teeth. Acute toxicity is almost always caused by inhalation of cadmium fumes or dust, which are produced by heating this metal. The industrial uses of cadmium are wide spread and are progressively increasing in electroplating, paint pigments, plastics, silver cadmium batteries, smelting, cadmium nickel batteries, stabilizer, phosphor fertilizer, mining and alloy industries. One of the major sources of cadmium discharge into natural waters is from the electroplating industries, which accounts for about 50 per cent of the annual cadmium consumption.

Removal of cadmium from effluents before they are discharged into the environment can be accomplished by processes such as, chemical precipitation, cementation, solvent extraction, reverse osmosis, and ion exchange. These processes are sometimes, neither effective nor selective and some of them are very expensive. Adsorption is a process for the removal of heavy metals, which is quite selective and effective, and is able to remove very low levels of heavy metals from the aqueous solutions/wastewater. Ion exchange resin and activated carbon are well known materials that are used for this purpose. Recently, some agricultural and forestry products/wastes have been recognized as new adsorbents. In general the cost of these biomaterials is negligible, compared to the cost of ion exchange and chemically prepared adsorbents. Activated carbon produced from almond shell, sawdust based GAC, tree bark treated with formaldehyde and sulphuric acid, bone char, tea leaves, wood charcoal, coconut shell carbon, sulphurized activated carbon, ozonized activated carbon, rice hulls and rice bran, pine bark, treated sawdust and agricultural waste have been used with and without treatment for the removal of heavy metals. Adsorption of heavy metals by these materials might be attributed to their protein, carbohydrates and phenolic compounds which have
metal binding functional groups such as, carbonyl, hydroxyl, sulphate, phosphate, and amino groups. Moreover the removal of metal ions from their solutions in the presence of agricultural materials may be due to the adsorption on surface and pores, and also to complexation by these materials.

The work aims to study the possibility of the utilization of carbon aerogel, treated GAC, and mustard husk for the adsorption of cadmium from contaminated aqueous solution/wastewater. The adsorption process parameters such as, initial concentration, pH, contact time and adsorbent dose for the maximum removal of cadmium from its aqueous solutions/wastewater were optimized.

Materials and Methods

I) Test Solution

Synthetic stock solution of cadmium was prepared by dissolving required quantity of cadmium metal in 5 mL concentrated HCl and 20 mL distilled demineralised water. The stock solution was further diluted with distilled demineralised water to desired concentration for obtaining the test solutions.

II) Preparation of Adsorbent

(a) Preparation of Treated GAC

Untreated GAC has poor adsorptive removal efficiency for cadmium ion because it lacks the appropriate chemical functional group on its surface. Therefore, chemical treatment is required to introduce suitable functional group (-SNa, -SH) on its surface for improving the adsorption capacity.

9.5 g of GAC (coconut based) is immersed for 24 h in minimum 750 mL of distilled water containing 0.5 g of Na₂S. The mixture was heated almost to dryness and then dried in an oven for 4 h at 110°C. The dried sample was washed with distilled water several times till it gave negative test for sulphide. The washed sample was again dried at 110°C for 4 h and stored in a dessicator for use.

(b) Carbon Aerogel

Carbon aerogel (supplied by Marketech International, USA) was used as an adsorbent material without any pre-treatment. Carbon aerogels are composed of covalently bonded nanometer sized particles that are arranged in 3-D network and possess high porosity and high surface area. Carbon aerogels may be produced in solid shapes, powder, and sheet forms. These are new and emerging adsorbent materials. Carbon aerogels having high porosity and high surface area, provided excellent treatment efficiency in a cost-effective manner for the purification of effluents/waste waters.

(c) Mustard Husk

Mustard husk was collected during the harvest season from the nearby villages of Jaipur district, Rajasthan, India. The mustard husk was used as an adsorbent material without any pre-treatment.

Screening studies were conducted to enable comparative evaluation of the various adsorbents for the removal of cadmium from aqueous/wastewater solutions. The adsorbents studied were: untreated and treated granular activated carbon (GAC), untreated and treated sawdust, weathered coal, tree bark, carbon aerogel, and mustard husk. Experiments for screening studies were carried out using stoppered conical flasks containing 100mL of 5mg/L cadmium test solution and 1g adsorbent materials. The flasks containing the test solution and adsorbent were placed in a thermostatic mechanical shaker for 24h contact time at 35°C.

On the basis of the results of screening studies the most promising adsorbents selected were treated GAC, carbon aerogel, and mustard husk, which were used for further experiments to study the effect of other parameters.

The experiments were carried out in a phased manner as given below:

Phase 1—Effect of initial concentration
Phase 2—Effect of adsorbent dosage
Phase 3—Effect of contact time
Phase 4—Effect of pH

Experimental conditions for phase 1, 2, 3, and 4 are as follows:

| Volume of sample taken for each experiment (mL) | 100 |
| pH range | 2-12 |
| Initial Cd(II) concentration range (mg/L) | 1 to 5 |
| (Based on analysis of actual plant effluent samples) | |
| Contact time (h) | 24, 48, 72 |
| Adsorbent dose (mg/100mL) | 0.5, 0.8, 1, and 1.2 |

The results of these studies were used to obtain the optimum conditions for maximum cadmium removal from aqueous solution.
Table 1 — Results of screening studies for selection of adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Weathered</th>
<th>GAC</th>
<th>Sawdust bark</th>
<th>Tree bark</th>
<th>Treated GAC</th>
<th>Treated Husk</th>
<th>Mustard Husk</th>
<th>Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>per centage removal</td>
<td>30</td>
<td>50</td>
<td>52</td>
<td>57</td>
<td>59.1</td>
<td>86.4</td>
<td>39.8</td>
<td>60</td>
</tr>
</tbody>
</table>

**Batch Experiments**

Batch adsorption studies were carried out using stoppered conical flasks containing required amount of test solution and adsorbent material. The flasks containing the test solution and adsorbent were placed in a thermostatic mechanical shaker for the required time period at 35°C. The contents were centrifuged and filtered through Whatman filter paper No. 41. The unadsorbed cadmium in the filtrate was estimated by atomic absorption spectrophotometer (AAS) using flame method.

The per cent cadmium removal was calculated using Eq. (1).

\[
\text{Per cent Cd removal} = \left(1 - \frac{C_f}{C_i}\right) \times 100
\]

where \(C_i\) = Initial Cd concentration of test solution, mg/L; \(C_f\) = Final Cd concentration of test solution, mg/L.

**Results and Discussion**

The results of the experiments carried out for the removal of cadmium from the synthetic samples using low cost adsorbents are discussed subsequently.

**Effect of the Nature of Adsorbent**

Eight different adsorbents namely, untreated and treated granular activated carbon, untreated and treated sawdust, mustard husk, weathered coal, tree bark and carbon aerogel were used in the experiments. Table 1 gives the per centage removal of cadmium by various adsorbents. From Table 1, it can be seen that the per centage removal is appreciably better with treated GAC, carbon aerogel and mustard husk.

In view of the poor cadmium removal efficiencies with sawdust, untreated granular activated carbon, treated sawdust, weathered coal and tree bark, it was decided to continue the remaining sets of experiments with carbon aerogel, treated GAC, and mustard husk as adsorbents.

**Effect of Initial Cadmium Concentration**

Figure 1 compares the per cent removal of cadmium with increasing initial cadmium concentration in aqueous solutions, using treated GAC, carbon aerogel and mustard husk for 1 g adsorbent dose and 48 h contact time. Treated GAC gives the best results, i.e., nearly 100 per cent removal of cadmium upto 4 mg/L level after which it decreases slightly to about 98 per cent for higher concentrations. Carbon aerogel is highly effective up to 1 mg/L after which the per centage removal decreases gradually to about 70 per cent at 5 mg/L. Mustard husk shows the lowest per centage removal at all initial concentrations. The above results may be explained on the basis of following facts:

At lower initial concentrations, sufficient active sites/surface area are available for the adsorption of the cadmium molecules, therefore the fractional adsorption is independent of initial concentration. Whereas, at higher concentrations the number of cadmium molecules is relatively higher compared to the availability of adsorption sites/surface area, hence the per centage removal of cadmium depends on the initial concentration and decreases with increase in initial concentration.

Differences in the extent of adsorption on treated GAC, carbon aerogel, and mustard husk are associated with the two main factors: (i) The availability of total surface area, which is in the following order: treated GAC (1000-1200 m²/g) > carbon aerogel (425 m²/g) > mustard husk (0.27 m²/g), and (ii) The presence of chemical functional groups such as -SNa/-SH, on the surface of treated GAC, which has more chemical affinity for cadmium. The effectiveness of carbon aerogel in the removal of Cd(II) may be due to porosity as well as a moderate
capacity for ion-exchange because of the presence of carboxylic and lactonic groups. The mustard husk had shown least adsorptive potential for the removal of cadmium, which may be attributed to the lowest surface area because of minimal porosity. The adsorption in the case of mustard husk is due to the presence of sulphur and oxygen, containing chemical functional groups on its surface rather than the surface area and porosity.

Effect of Adsorbent Dose

Figure 2 shows the comparative behaviour of various adsorbents with increasing adsorbent dosage. It is observed that there is a sharp increase in percentage removal with adsorbent dose for carbon aerogel increasing from about 67 per cent for 0.5 g dose to 97.7 per cent for 1.2 g. Mustard husk does not show much variation for low adsorbent dosage but increases gradually to 82 per cent for 1.2 g dose. Treated GAC shows uniformly high percentage removal (86-100 per cent) during adsorbent dosage studies.

It is apparent that the percentage removal of cadmium increases with increase in the dose of adsorbent due to the increased availability of the active sites/surface area for the adsorption of the cadmium. Whereas, at lower adsorbent dosage the number of cadmium molecules is relatively higher, compared to availability of adsorption sites/surface area.

Effect of Contact Time

Figure 3 shows comparative per centage removal of Cd(II) by treated GAC, carbon aerogel, and mustard husk for 1.0 g dose/100 mL Cd(II) solution of 3 mg/L initial concentration at different contact times. It is observed that in cases of carbon aerogel, and mustard husk the per centage removal of cadmium is comparatively lower for 24 h contact time and increases gradually with increasing contact times. In the case of treated GAC, the per centage removal efficiencies over the entire range of contact time are almost comparatively constant and are higher than that for the other adsorbents. Carbon aerogel shows lower removal per centage than treated GAC but the rise in per centage removal with increasing contact time is steep, showing more than 80 per cent removal beyond 48 h. On the other hand, per centage removal with mustard husk increases gradually with contact time, reaching 96 per cent removal at 72 h.

As seen earlier the contact time required to attain equilibrium is dependent on the initial concentration of cadmium. For the same concentration, the per centage removal of cadmium increases with increase in contact time till equilibrium is attained. The optimal contact times to attain equilibrium with carbon aerogel, and mustard husk adsorbent were experimentally found to be about 48 h. In the case of treated GAC the optimal contact time was 24 h (Figure 3).

Effect of pH

pH of the adsorptive solution is one of the most important parameters controlling the uptake of cadmium from aqueous solutions/wastewater by adsorbent. Figure 4 shows the effect of pH on cadmium removal efficiencies of all the three adsorbents.

The per centage adsorption increases with pH to attain a maximum at pH 4 and thereafter, it decreases with further increase in pH. The maximum removal of cadmium at pH 4 was found to be nearly 100, 80.6 and 70 per cent for treated GAC, carbon aerogel and mustard husk, respectively.
Initial Cd(U) concentration = 3 ml/L; Adsorbent dose = 1 g/100 ml
Contact time = 48 h

Fig. 4 — Effect of pH on percentage removal of cadmium for different adsorbents

There results clearly indicate that the solution pH has a considerable influence on the adsorption of cadmium ions on the surface of the adsorbent, because both the surface charge density of the adsorbent and charge of the cadmium ions present, depend on the pH.

Moreover, differences in the extent of adsorption are also associated with the chemical state of the metals in the adsorptive solutions. As observed subsequently, it determines the adsorptive species relevant to the adsorption process. The Cd$^{2+}$ ions in aqueous solution may undergo hydration, hydrolysis and polymerization,

\[
\begin{align*}
\text{Cd}^{2+} + nH_2O & = \text{Cd}(H_2O)_n^{2+} \\
\text{Cd}(H_2O)_n^{2+} & = \text{Cd}^{2+}(H_2O)_{n-1}(OH)^+ + H^+ \\
n\text{Cd}^{2+} + mH_2O & = \text{Cd}_n(OH)_{2n-m}^{(2n-m)+} + mH^+
\end{align*}
\]

Cd$^{2+}$ can form several hydrolysis products, which exist under widely varying conditions. In dilute solutions, however the formation of Cd$^{2+}$ hydrolysis products occur at pH > 6. This shows that cadmium in the adsorptive solution is likely to be found as free ions in equilibrium with hydrated species. The hydration numbers for Cd$^{2+}$ have been determined by various physical techniques and the proposed value ranges between 12 and 4.6 (ref. 23).

Lower pH results in the protonation of the adsorbent surface, which leads to the extensive repulsion of Cd$^{2+}$ ions. This results in a decrease in cadmium adsorption. With increase in pH from 2 to 4.0 the Cd exists as Cd(OH)$_2$ in the medium and surface protonation of adsorbent is minimum, leading to the enhancement of Cd$^{2+}$ ions adsorption.

Adsorption Isotherms

The adsorption studies were conducted at fixed initial concentration of cadmium by varying adsorbent dosage. The equilibrium data obtained was analyzed in the light of Langmuir and Freundlich isotherms.

The Freundlich equation is given by:

\[\frac{x}{m} = K C_e^{1/n}.\]  (1)

Taking the logarithmic form of the equation

\[
\log \frac{x}{m} = \log K + \frac{1}{n} \log C_e.\]  (2)

Langmuir equation is given by:

\[\frac{x}{m} = \frac{a b C_e}{1 + b C_e},\]  (3)

or,

\[\frac{x}{m} = \frac{1}{a b} (\frac{1}{C_e} + \frac{1}{a}).\]  (4)

where, \(x/m\) is the amount of cadmium adsorbed per unit mass of adsorbent in mg/g, \(C_e\) is the equilibrium concentration of cadmium in mg/L, \(K_e\) and \(n\) are Freundlich constants, \('a'\) is a Langmuir constant which is a measure of adsorption capacity expressed in mg/g. \('b'\) is also Langmuir constant which is a measure of energy of adsorption expressed in L/mg.

The parameters \('a'\) and \('b'\) have been calculated from the slope and the intercept of the plots.

Figure 5 gives the Freundlich adsorption isotherm plot of log\(x/m\) vs log\(C_e\). The values of \(K_e\) and \(1/n\) obtained from intercept and slope of the plot are given in Table 2.

Figure 6 gives the Langmuir adsorption isotherm plot of \(m/x\) vs \(1/C_e\). The essential characteristics of Langmuir isotherm can be described by a separation factor or equilibrium constant \(R_L\), which is defined as:

\[R_L = 1/(1+b C_i),\]  (5)

where, \(C_i\) is the initial concentration of cadmium (mg/L) and \(b\) is Langmuir constant which indicates the nature of adsorption. The separation factor \(R_L\) indicates the isotherm shape and whether the adsorption is favourable or not, as per the criteria given subsequently.

\[\begin{align*}
R_L \text{ Values} & \quad \text{Adsorption} \\
R_L > 1 & \quad \text{Unfavourable} \\
R_L = 1 & \quad \text{Linear} \\
0 < R_L < 1 & \quad \text{Favourable} \\
R_L = 0 & \quad \text{Irreversible}
\end{align*}\]

The values of Langmuir constants \('a'\), \('b'\) and \(R_L\) are presented in Table 2. Since \(R_L\) values lie between...
MEENA et al.: ADSORPTION OF CADMIUM(II) IONS

Amount of adsorbent = 1.2 g; contact time = 48 h

Table 2 — Values of Langmuir and Freundlich isotherm constants for adsorption of cadmium

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>a (mg/g)</th>
<th>b</th>
<th>R²</th>
<th>R_L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated GAC</td>
<td>104.78</td>
<td>1.10</td>
<td>0.96</td>
<td>0.16</td>
</tr>
<tr>
<td>Mustard husk</td>
<td>43.85</td>
<td>0.28</td>
<td>0.93</td>
<td>0.26</td>
</tr>
<tr>
<td>Carbon aerogel</td>
<td>400.80</td>
<td>0.35</td>
<td>0.99</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Fig. 5 — Freundlich isotherms of cadmium for various adsorbents

Conclusions

Following conclusions are drawn from the study:

(i) Treated GAC, carbon aerogel and mustard husk showed 100, 87 and 72 per cent, respectively, adsorptive removal of cadmium under optimized conditions of pH 4 and dosage 1 g/100 mL for 2 mg/L cadmium aqueous solutions in 48 h.

(ii) The adsorption is pH dependent and maximum adsorption occurs at pH 4.

(iii) The Langmuir model is found to be in good agreement with experimental data on the adsorptive behaviour of cadmium on treated GAC, whereas the experimental data on adsorptive behaviour of cadmium on mustard husk and carbon aerogel follow both Freundlich model and Langmuir models.

(iv) These experimental studies on low cost adsorbents would be quite useful in developing an appropriate technology for the removal of cadmium from contaminated plant effluents.

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