Chapter – 3

Adsorption studies on Parthenium hysterophorous weed: Removal and recovery of Cd (II) from wastewater

For the first time in the history of the world, every human being is now subjected to contact with dangerous chemicals, from the moment of conception until death.

Rachel Carson (1907-1964)
3.1. Introduction:

Heavy metals are essential in small amounts for the normal development of animals and plants but most of them are toxic at higher concentrations. Heavy metals are generally introduced into the environment through natural phenomena and human activities (Abollino et al., 2003). The contamination of the existing water resources is increasing day by day with increasing industrialisation. The disposal of wastewater containing heavy metals is always a challenging task for environmentalists. Various methods available for the removal of heavy metals from industrial wastewater are precipitation, ion-exchange, electrochemical reduction, evaporation and reverse osmosis but these methods involve large liquid surface area and long detention period (Rao et al., 2002). Adsorption on activated carbon is the promising process considered during the past few decades for the removal of trace pollutants but it is costly and requires high cost to regenerate. Therefore, there is a need for the development of low cost and easily available materials, which can adsorb heavy metals.

Cd (II) has been classified as a toxic heavy metal that can cause serious damage to kidney and bones. It also causes high blood pressure, skeletal deformity and muscular cramps (Banat et al., 2003). The World Health Organisation has recommended a maximum permissible limit of 0.005mg/l Cd (II) in drinking water. Numerous low cost adsorbents (Ho and Wang, 2004; Hashim and Chu, 2004; Lackovic et al., 2004; Ramiro et al., 2004) have already been explored for the removal of Cd (II) from aqueous solutions.

In the present study, the sorption behavior of Cd (II) ions on parthenium was examined. *Parthenium hysterophorous*, popularly known as congress weed, star weed, carrot weed, gajar ghas or ramphool, is the most feared weed species (Rao, 1956). It is one of the ten worst weeds in the world. Parthenium is herbaceous annual or ephemeral plant, reaching a height of 2 meter and flowering within 4-6 weeks of germination. The adverse effects of Parthenium on humans as well as on animals have been well
documented. It is known to cause asthma, bronchitis, dermatitis and hay fever in man and livestock. The chemical analysis has indicated that all the plant parts including pollen contain toxins. The major component of these toxins being parthenin and other phenolic acids such as caffeic acid, vanillic acid, anisic acid, chlorogenic acid, parahydroxy benzoic acid, and para anisic acid which are lethal to humans and animals. This weed is generally uprooted and destroyed by burning in air without any use.

The adsorption properties of this natural material have been explored, which can be utilised for the removal of Cd (II) ions from water. The dead biomass of parthenium in powder form may also be utilised to sequester Cd (II) ions in the soil. This technique may help to some extent in reducing the uptake of Cd (II) ions by agricultural crops.
3.2. Material and methods:

3.2.1. Preparation of Adsorbent:
Parthenium plants were collected from the university campus. They were washed with DDW to remove dust and dirt etc, dried in an open-air oven at 60 -70°C. The dried biomass was then crushed and sieved. The particles of 50 -100 (BSS) mesh size were collected and kept in sealed bottles for study.

3.2.2. Adsorbate solution:
Stock solution of Cd (II) was prepared (1000 mg/l) by dissolving the desired quantity of Cd (NO₃)₂·H₂O (AR grade) in DDW.

3.2.3. Adsorption studies:
Batch process was employed for adsorption studies. 0.5g adsorbent was placed in a conical flask having 50 ml Cd (II) solution and the mixture was shaken in a shaker incubator at 100 rpm. The mixture was then filtered at predetermined time interval and the final concentration of metal ions was determined in the filtrate by AAS (GBC 902). The instrument was calibrated with standard Cd (II) solutions under the following specifications.

- Wavelength  – 228.6 nm
- Slit width  – 0.5 nm
- Lamp current – 3 mA
- Flame  – Air – acetylene (Oxidising)
- Mode  – Double beam

Amount of Cd (II) adsorbed was then calculated by subtracting final concentration from initial concentration. Adsorption studies were carried out by varying the adsorbate concentration (10 to 100 mg/l), the agitation time (5 to 60 mints.), adsorbent amount (0.1 to 1.0 g) and adsorption temperature (20, 30 and 40°C). A series of experiments
with pH of the initial Cd (II) solution varying between 2 and 10 (by adding 0.1M HCl and 0.1 M NaOH solutions) were also carried out using 0.5 g adsorbent at 20°C. Adsorption isotherms were studied by varying the initial Cd (II) concentration from 10 to 100 mg/l while weight of adsorbent in each experiment was kept constant at (0.5 g). Each experiment was repeated three times and results were reported as average of them.

3.2.4. Desorption studies:
Batch process was used for desorption studies with varying amount of adsorbent (0.25 –1.0 g). The desired amount of adsorbent was taken in a conical flask and treated with 50 ml of Cd (II) solution (50 mg/l). After adsorption, the solution was filtered and adsorbent was washed several times with DDW to remove any excess of Cd (II). It was then treated with 50 ml of 0.1M HCl solution. The amount of Cd (II) desorbed was then determined as usual. The same procedure was repeated with different adsorbent doses. Attempts were also made to desorb Cd (II) with 0.1M NaCl in the same way.

3.2.5. Breakthrough capacity:
A 0.5 g of adsorbent was taken in a glass column (0.6 cm internal diameter) with glass wool support. One litre of Cd (II) solution of 50 mg/l strength was then passed through the column with a flow rate of 1ml/min. The effluent was collected in 40 ml fractions and Cd (II) was then determined in each fraction by AAS.
3. 3. Results and Discussion:

3.3.1. Effect of concentration:

Parthenium is an effective adsorbent over a wide range of Cd (II) concentration. When the initial Cd (II) concentration is increased from 10 mg/l to 100 mg/l, the adsorption remains maximum (99.5%) and decreases to 97% only when initial concentration is further increased to 150 mg/l (Figure 3.1). The adsorbent can be utilised effectively for the removal of Cd (II) from water at lower as well as higher initial concentration of Cd (II).

3.3.2. Effect of contact time:

The effect of contact time on the adsorption of Cd (II) at 50 mg/l initial Cd (II) concentration is shown in Figure 3.2. The rate of adsorption is very fast initially and maximum removal of Cd (II) occurs within 20 mins. The adsorption rate then decreases during the next 40 mins. The initial fast sorption may be due to the transfer of metal ions from bulk to the adsorbent surface. The active sites in the system is a fixed number and each active site can adsorb only one ion in a monolayer therefore metal uptake by the sorbent surface is rapid initially and then decreases as the availability of active sites decreases thus slowing down the transfer of metal ion from bulk solution to adsorbent surface. The rate of metal removal is of great significance for developing adsorbent based water technology (Saeed et al., 2005). The ability of parthenium to adsorb maximum amount of Cd (II) within 20 mins indicates that parthenium is an effective adsorbent for the removal of Cd (II) from wastewater.

3.3.3. Effect of pH:

Adsorption of Cd (II) at pH 2 is 66% and increases with increase in pH attaining maximum value in the pH range 3 - 4 (Figure 3.3). In acidic medium (pH 2) hydrogen ions compete with metal ions (Saeed et al., 2005) as a result, active sites (negatively charged) become protonated resulting the prevention of metal ions adsorption on the
surface of adsorbent. However, with increase in pH, more and more negatively charged surface of the adsorbent becomes available and hence uptake of metal ions increases. Adsorption of Cd (II) thus increases significantly as pH is increased (99.16% at pH 4). It is known that with the increase in pH, the solubility of metals decreases resulting in their precipitation as hydroxides. The precipitation of Cd (II) as hydroxide was found to occur at pH 9.2 (Namasivayam and Ranganathan, 1995) therefore all adsorption studies were carried out at or below pH 5, which is much below the precipitation pH of Cd (II).

3.3,4. Effect of adsorbent doses:

The adsorption density and percentage adsorption of Cd (II) on parthenium at pH 4.5 is shown in Figure. 3.4. The initial Cd (II) concentration was taken as 50 mg/l and the adsorbent dose was varied from 0.1 to 1.0 g at constant temperature (20°C). The percentage adsorption increases from 92.2 to 99% but adsorption density decreases from 23.05 to 3.53 mg/g when adsorbent dose is increased. The decrease in the adsorption density is due to the fact that some of the adsorption sites remain unsaturated when adsorbent dose is increased. On the other hand, more and more Cd (II) is adsorbed as the number of available adsorption sites are increased (Foster and Sharma, 1993) resulting in the overall increase in the removal efficiency.

3.3,5. Adsorption kinetics:

The rate constants were calculated by using pseudo-first order and pseudo-second order kinetic models (Banat et al., 2003). The first order expression is given as

\[
\log (q_e - q) = \log q_e - \frac{K_1}{2.303} \cdot t \quad (1)
\]

The values of \(K_1\) were calculated from slope of the linear plot of \(\log (q_e - q)\) vs \(t\) at various concentrations (Figure. 3.5). The values of regression coefficient \((R^2)\) and rate constants at various concentrations are reported in Table. 3.1.
The pseudo-second order kinetic rate equation is given as

\[
t / q = 1 / h + 1 / q_e \cdot t \quad \text{(2)}
\]

The values of h were calculated from the intercept of the linear plots of t/q vs t at various initial Cd (II) concentrations (Figure 3.6). Table 3.1 provides the values of k_1 and k_2, h = k_2 q_e^2 calculated equilibrium sorption capacity, q_e (theo) and experimental equilibrium sorption capacity q_e (exp) at various initial Cd (II) concentrations. The q_e (theo) values calculated from pseudo-first order kinetic model differed appreciably (not reported in the table) from the experimental values. However, in pseudo-second order kinetic model the calculated q_e (theo) are very close to experimental q_e (exp) values at various initial Cd (II) concentrations. Further, the values of correlation coefficients (R^2) of pseudo-first order model were slightly lower than pseudo-second order model indicating that pseudo-second order model is better obeyed than pseudo-first order model.

3.3,6. Effect of temperature:

The temperature range used in this study was from 20°C to 40°C. Thermodynamics parameters such as ΔG°, ΔH° and ΔS° were calculated from the following equation (Namasivayam and Ranganathan, 1995)

\[
K_c = C_Ac / C_e \quad \text{(3)}
\]

\[
ΔG° = -RT \ln K_c \quad \text{(4)}
\]

\[
\log K_c = ΔS°/ 2.303R - ΔH°/2.303RT \quad \text{(5)}
\]

ΔH° and ΔS° were calculated from the slope and intercept of Van’t Hoff plot of log K_c vs 1 / T (Figure 3.7). Table 3.2 shows the values of ΔH°, ΔS° and ΔG°. Positive value of ΔH° indicates the endothermic nature of adsorption. ΔG° is negative and decreases further with increase in temperature indicating that adsorption of Cd (II) on parthenium is spontaneous and spontaneity increases with increase in temperature. Positive value of
ΔS° suggests randomness at the solid/solution interface during adsorption (Namasivayam and Ranganathan, 1995).

3.3.7. Adsorption isotherms:

Langmuir and Freundlich adsorption models were used to analyse the adsorption data at various temperatures. Langmuir model may be described as

\[
\frac{1}{q_e} = \frac{1}{\theta^\circ} \cdot b \cdot \frac{1}{C_e} + \frac{1}{\theta^\circ}
\]

The plot of \( \frac{1}{q_e} \) vs \( \frac{1}{C_e} \) is linear showing that adsorption of Cd (II) follows Langmuir isotherm (Figure. 3.8). The experimental value of \( \theta^\circ \) is 27 mg/g that is very close to the calculated value (\( \theta^\circ = 23 \) mg/g). The value of \( b \) is 0.898 l/mg. The correlation coefficient (\( R^2 \)) is 0.9973. The value of \( \theta^\circ \) and \( b \) for various non-conventional adsorbents used for the removal of Cd (II) ions from water are listed in Table. 3.3. The higher value of \( b \) (0.898) for parthenium indicates that it has higher affinity to adsorb Cd (II) ions.

The essential feature of Langmuir model can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (\( R_L \)) given by relation

\[
R_L = \frac{1}{1 + b \cdot C_0}
\]

The values of \( R_L \) lie between 0.1 and 0.01 for the initial Cd (II) concentration range from 10 to 100 mg/l indicating the favourable adsorption (for favourable adsorption the value of \( R_L \) should lie between 0 and 1 (Poots et al., 1978)).

The Freundlich adsorption isotherm was also applied for the adsorption of Cd (II). The Freundlich equation is given as
\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  \hspace{1cm} (8)

Linear plot of log q_e vs log C_e follows Freundlich isotherm (Figure. 3.9). Value of K_f and n calculated from the slope and intercept is 10.275 and 3.8 respectively. The \( R^2 \) value in this case is 0.9841 showing that Langmuir model is better obeyed than Freundlich model. The higher value of K_f (10.275) indicates the higher adsorption efficiency of parthenium for Cd (II) ions.

3.3.8. Desorption studies:

Desorption studies shows that appreciable amount of Cd (II) could be recovered with 0.1M HCl solution (Table. 3.4). The percent recovery increases with increase in adsorbent dose and reaches to maximum (82 %) when 0.75 g of adsorbent is used. However, the desorption is negligible with 0.1M NaCl (Table. 3.5).

3.3.9. Breakthrough capacity:

The breakthrough curve (Figure. 3.10) indicates that 280 ml of the Cd (II) solution containing 50 mg/l could be passed through the column without detecting Cd (II) in the effluent. The breakthrough and exhaustive capacities were determined as 28 and 60 mg/g, respectively.
3.4. Conclusions:

*Parthenium hysterophorous* is a problem-creating weed. These plants are uprooted and burnt in order to prevent various diseases. Instead of burning, these plants may be dried and the dried mass of parthenium in the form of powder may be added in soil to sequester Cd (II) ions since it can remove up to 99.7% Cd (II) ions over a wide range of Cd (II) concentration (10 -150 mg/l).

The kinetic data shows that pseudo-second order kinetic model is better obeyed than pseudo-first order model since second order model provide high degree of correlation with the experimental data at various initial concentrations. The Langmuir and Freundlich isotherms indicate favourable adsorption and these data would be useful for designing of water treatment plants.

The breakthrough capacity reveals that 280 ml solution containing 50 mg/l Cd (II) can be treated without detecting it in the effluent.

The recovery of Cd (II) ions in the solution by 0.1M HCl is much higher (82 %) as compared to 0.1M NaCl (2 %) showing that adsorption occurs most probably via ion exchange. The material can be utilised to recover Cd (II) ions from wastewater.
Table. 3.1. Pseudo-first order and Pseudo-second order kinetics constants for adsorption of Cd (II) on Parthenium

<table>
<thead>
<tr>
<th>Concentration (mg /l)</th>
<th>Pseudo-first order kinetics</th>
<th>Pseudo-second order kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_1$ (1/min)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>25</td>
<td>0.2195</td>
<td>0.9804</td>
</tr>
<tr>
<td>50</td>
<td>0.1592</td>
<td>0.9836</td>
</tr>
<tr>
<td>75</td>
<td>0.0526</td>
<td>0.9883</td>
</tr>
<tr>
<td>100</td>
<td>0.0862</td>
<td>0.9975</td>
</tr>
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</table>

Table. 3.2. Thermodynamics parameters at different temperature for the adsorption of Cd (II) on Parthenium

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\Delta S^\circ$ (KJ/ mol-K)</th>
<th>$\Delta H^\circ$ (KJ/mol)</th>
<th>$\Delta G^\circ$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td></td>
<td></td>
<td>-6.0103</td>
</tr>
<tr>
<td>30</td>
<td>0.0961</td>
<td>22.147</td>
<td>-6.9713</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td></td>
<td>-7.9323</td>
</tr>
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</table>
Table 3.3. Uptake capacities for Cd (II) of various adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>θ (mg/g)</th>
<th>b (l/mg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>2.56</td>
<td>0.3600</td>
<td>Johnson, 1990</td>
</tr>
<tr>
<td>Waste Fe (III)/Cr(III)</td>
<td>39.00</td>
<td>0.1790</td>
<td>Namasivayam et al, 1995</td>
</tr>
<tr>
<td>Hydroxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pretreated fungal Biomass</td>
<td>62.90</td>
<td>0.1070</td>
<td>Qiming et al, 1999</td>
</tr>
<tr>
<td>Date pits</td>
<td>6.50</td>
<td>0.0396</td>
<td>Banat et al, 2003</td>
</tr>
<tr>
<td>Date pits (carbonized At 500°C)</td>
<td>3.00</td>
<td>0.0847</td>
<td>Banat et al, 2003</td>
</tr>
<tr>
<td>Date pits (carbonized At 900°C)</td>
<td>1.80</td>
<td>0.0905</td>
<td>Banat et al, 2003</td>
</tr>
<tr>
<td>Rice Husk</td>
<td>103.09</td>
<td>0.0060</td>
<td>Ajmal et al, 2003</td>
</tr>
<tr>
<td>Untreated Juniper Fiber</td>
<td>9.180</td>
<td>0.03</td>
<td>Han et al, 2004</td>
</tr>
<tr>
<td>Black gram husk</td>
<td>39.99</td>
<td>0.3730</td>
<td>Iqbal et al, 2005</td>
</tr>
<tr>
<td>Parthenium</td>
<td>27.00</td>
<td>0.8980</td>
<td>present study</td>
</tr>
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</table>

Table 3.4. Desorption of Cd (II) by 0.1 M HCl

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of adsorbent (g)</th>
<th>Cd (II) adsorbed (mg/l)</th>
<th>Cd (II) recovered (mg/l)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25</td>
<td>49.1</td>
<td>33</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>49.6</td>
<td>38</td>
<td>76</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>49.6</td>
<td>41</td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>49.6</td>
<td>41</td>
<td>82</td>
</tr>
</tbody>
</table>
Table 3.5. Desorption of Cd (II) by 0.1 M NaCl

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of adsorbent (g)</th>
<th>Cd (II) adsorbed (mg/l)</th>
<th>Cd (II) recovered (mg/l)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50</td>
<td>49.64</td>
<td>1.00</td>
<td>2.01</td>
</tr>
<tr>
<td>2</td>
<td>0.75</td>
<td>49.80</td>
<td>0.76</td>
<td>1.52</td>
</tr>
</tbody>
</table>
Figure 3.1. Effect of initial Cd (II) concentration on the adsorption on Parthenium.
Conditions: Adsorbent = 0.5g, temp = 20 °C, pH = 4.5

Figure 3.2. Effect of time on the adsorption of Cd(II) on Parthenium
**Figure 3.3.** Effect of pH on the adsorption of Cd (II) on Parthenium

**Figure 3.4.** Effect of adsorbent dose on the adsorption of Cd(II) on Parthenium
**Figure 3.5.** Pseudo-first-order kinetics for the adsorption of Cd (II) on Parthenium

**Figure 3.6.** Pseudo-second-order kinetics for the adsorption of Cd (II) on Parthenium
Figure 3.7. Van't Hoff plot for the adsorption of Cd (II) on Parthenium

\[ y = -1156.7x + 5.0206 \]
\[ R^2 = 0.9938 \]

Figure 3.8. Langmuir plot for the adsorption of Cd (II) on Parthenium

\[ y = 0.0482x + 0.0433 \]
\[ R^2 = 0.9975 \]
Figure 3.9. Freundlich plot for the adsorption of Cd (II) on Parthenium

Figure 3.10. Breakthrough curve for the adsorption of Cd (II) on Parthenium

\[ y = 0.2634x + 1.0118 \]

\[ R^2 = 0.9841 \]
References:


Banat, F., Al-Asheh, S.; Makhadmeh, L., Adsorption Science and Technology. 2003; 21(3) 245-260.


