Removal of Cadmium from Aqueous Solution using Bentonite Clay

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Abstract

Removal of heavy metals from polluted waste water is a challenge to engineers and environmentalists. Pollutants may be inorganic or organic. Since inorganic ones are non-biodegradable, therefore their removals are difficult. When waste water containing heavy metals released in environment, it affects the lives on earth. Moreover it is also disturbing the aquatic systems. Therefore removal of these becomes significant for the safety of environment. In this study cadmium is chosen as pollutant in water and bentonite clay from Bhavnagar is taken as an adsorbent material. The bentonite clay was tested at IITB (Earth Science Department) for its characterization with XRD technique. It was found that the mineral montmorillonite is dominant among the other minerals. The adsorption of cadmium using the bentonite clay was studied using batch process. The parameters like pH value, clay dose, mixing time, speed and metal ion concentration studied and analyzed to obtain optimized conditions for maximum adsorption of cadmium on bentonite clay. Experimental data were fitted to the Langmuir and Freundlich adsorption isotherm. The maximum adsorption capacity of bentonite clay was observed as 13.5 mg/g at a correlation coefficient of 0.95. It was found that Langmuir and Freundlich adsorption models were fit very close with experimental data. Study shows that bentonite clay from Bhavnagar area can be used effectively for removal of cadmium from aqueous solution.

Keywords: Adsorption; batch process; bentonite clay; cadmium removal; Freundlich adsorption isotherm; heavy metals; Langmuir adsorption isotherm.

1. INTRODUCTION

Pollutants such as lead, arsenic, copper, cadmium etc are entering the environment
either by the way of emission or disposal of domestic/industrial waste. The waste water containing pollutants when released in environment causing the soil and water pollution. The pollution of soil with heavy metals is a significant unease worldwide (Ahmed Marzoog et al., 2014) since all heavy metals are hazardous.

When plants grow in polluted soil, they collect the heavy metals and this way leads to increase of metals level in human and livings consuming these plants on earth beyond permissible limit (Kumar, P. S. et al., 2012).

The excess amount of metals causes the health problems like affects on kidney, development of brain cells, further nausea, diarrhea (AsliBaysal et al., 2013). Therefore engineers and environmentalist are very keen to prevent the fertile soil, natural water bodies and underground water from reach of hazardous metals.

As such cadmium has no function in the body. However, its toxicity is more dangerous than other metals like lead or mercury when it concentrate in kidney, liver and other organs. The cadmium toxicity increases due to zinc deficiency. Zinc is acting as a protective against cadmium toxicity. The increase in zinc deficiency is because of use of processed foods, food grains grown in soil contaminated by use of superphosphate fertilizer, sewage sludge, use of refined foods, exposure to cadmium at places such as coating of cadmium on iron and copper, burning of plastics. The workers in factory of battery electrodes, semiconductors are more at risk of cadmium toxicity. Therefore, its removal from polluted soil and waste water is essential.

In past there were many processes being used for removing the toxic metals from soil and waste water e.g. ion exchange, coagulation, precipitation, cementation but each one has its disadvantage (Ming Qin J., et al., 2009), and hence they are not sustainable. Further these processes are not suitable in removing the heavy metals at low concentration. Therefore the output of conventional processes still not on safer side for life on earth (Caroline B., et al., 2011).

A physiochemical process which is more efficient, safer and economic in removing the heavy metals widely adopted (Kurniawan T. A. et al., 2006). This process is known as adsorption. It is a process in which accumulation of heavy metals occurs on the surface of adsorbent material via physical and chemical reaction.

Literature shows, varieties of adsorbent materials used for removing the heavy metals from polluted waste water (Kurniawan T. A. et al., 2006). Most frequently adopted adsorbent material for removal of heavy metal is the activated carbon (Shim et al., 1996; Ouki et al., 1997; Leyva-Ramos et al., 1997; Monser and Adhoum, 2002 and Leyva-Ramos et al., 2002) but it proves to be uneconomical. Therefore, researchers are trying to study the feasibility of other adsorbent materials for purifying the polluted water. Naturally available materials like fly ash, kaolinite and bentonite clay are some of the example of low cost adsorbent materials. Considering the availability and efficiency in removing the heavy metals, bentonite clay proves to be a low cost adsorbent material (Khan M. R. et al., 2017, Boyd et al., 1998; Brigatti et al., 1995; Gutierrez and Fuents, 1996; Lo et al., 1997).
2. METHODOLOGY AND MATERIALS

In this section, the detail of materials and methodology used for the study of adsorption of cadmium on bentonite clay is presented.

2.1 Material used for adsorption

The adsorbent material used for study of adsorption is received from the district Bhavnagar, of Gujarat, India. The mineralogical composition of which was determined by conducting the XRD test at Earth Science Department, IITB. The XRD pattern of bentonite was obtained by a Rigaku D-MaxIC X-Ray diffractometer. The X-ray generator operated at 45 kV 40 mA. Figure 1 shows that main mineral present in it is the Montmorillonite. The images of SEM (Scanning Electron Microscope) of bentonite clay at different magnifications are shown in Figure 2 (A and B). SEM images indicate that bentonite clay composed of irregular shapes which give rise to large surface area for adsorption. SEM images also indicate the surface texture and porosity of the material under study. Cadmium chloride (CdCl₂H₂O) is used as metal solution. The pH adjustment was carried out using 0.1 N hydrochloric acid (HCl) and sodium hydroxide (NaOH). Chemicals supplied from Merck of analytical regent were used.

![Figure 1. XRD pattern of bentonite clay.](image1)

![Figure 2. (A)](image2)
2. (B)

Figure. 2: (A and B). SEM photographs of bentonite clay at varying magnification.

2.2 Instrumentation

Cadmium analysis is carried out using the Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), make Spectro Analytical Instruments GmbH, Germany (Model ARCOS) at Sophisticated Analytical Instrument Facility (SAIF) Department of IITB, Mumbai. pH adjustments were carried out using digital pH hydrotester (Model: PH-80). Magnetic stirrer (Model-1 ML) supplied from REMI Laboratory Instrument, Goregaon, Mumbai was used for agitating the mixture of metal solution and bentonite.

2.3 Procedure

A batch process is adapted to study the adsorption of cadmium using the bentonite clay. For this a stock solution (1Litre) of cadmium metal of concentration of 1000 mg/l is prepared by dissolving 179 mg of (CdCl₂H₂O) in de-ionized water and final volume made equal to one litre. The metal solution of variable concentration is required for parametric study. Therefore, metal solution of required lower concentration is prepared by diluting the stock solution using the serial dilution method. The volume of sample is determined to be 50 ml (Ahmed Marzoog et al., 2014).

In brief, procedure is explained in following steps:

- pH adjustment : 0.1 N HCl and 0.1 N NaOH
- Amount of clay : 0.1 g to 1 g
- Agitation time : 2 Hour
- Agitation speed : 200 rpm.
- Clay separation : With Whatman filter paper 40
Cadmium concentration after adsorption: By ICP-AES

2.4 Adsorption model

Here the amount of cadmium metal adsorbed per gram of bentonite clay is modelled by mixing a known amount of clay in an aqueous solution of cadmium of known initial concentration. The final concentration of cadmium remains in solution after adsorption is determined using ICP-AES.

The adsorption capacity $q_e$ (mg/g) was calculated using the following adsorption model:

$$q_e = \frac{(C_o - C_e) \times V}{m}$$  \hspace{1cm} (1)

Where $C_o$ is the initial cadmium metal concentration, $C_e$ is the equilibrium concentration at equilibrium stage of adsorption (mg/l), $m$ is the clay mass (g), and $V$ is the volume of solution (l).

3. RESULTS AND DISCUSSION

To determine the efficiency of bentonite clay obtained from Bhavnagar in India for removing the cadmium metal from aqueous solution, an experimental parametric study is carried out. The outcome of the study is presented in this section.

3.1 Effect of metal concentration

To determine the optimum value of cadmium metal concentration, an experimental study is carried out in which metal concentrations varied from 1 mg/l to 100 mg/l. 1g of bentonite clay is mixed with 50 ml of metal solution at pH of 5.1. This mixture is agitated at 200 rpm for 2 hours. It is clear from Figure 3, the maximum adsorption occurs upto 20 mg/l after which it starts decreasing. At this level adsorbent becomes saturated and no more adsorption can occur. The maximum value of concentration is at which adsorption is maximum determined as 20 mg/l.

3.2 Effect of pH

The effect of pH on adsorption of cadmium on bentonite clay is studied experimentally by varying the pH value from 2 to 10 and keeping the other parameteric values similar to previous section.

It is clear from Figure 4, that adsorption increases with increase in pH value and remains constant after pH value of 6. This optimum pH value of 6 is used for further study to observe the effect of other parameters like clay dose, mixing time and speed.
3.3 Effect of Clay Dosage

An experimental study is conducted to determine the dose of clay giving the maximum adsorption. Clay dose is varied from 0.1 g to 1 g at optimum pH value. Figure 5 showing the effect of clay dose on adsorption. It is observed, that with increase in dose of clay the adsorption efficiency increases and this is because of increase in surface area of adsorbent. A maximum value of clay dose for removal of cadmium is 0.5 g per 50 ml of solution. The experimental maximum adsorption capacity is found as 6.95 mg per gram of adsorbent material.
3.4 Effect of Agitation Time

A study is carried out to determine the time required to complete the physiochemical process of adsorption. Therefore, the efficiency of adsorption is governed by the time required for mixing the adsorbate and adsorbent. To determine the optimum value of mixing time for removal of cadmium using bentonite clay, a batch process was used in which time was varied from 5 minutes to 60 minutes along with other parameters similar to previous studies. The results are presented in Figure 6. It is apparent from Figure 6 that maximum adsorption occurs within 5 minutes only and then remain almost constant.

3.5 Adsorption Isotherms

To study the adsorption process, a graph is plotted between amount of adsorbate (x)
adsorbed on (m) mass of adsorbent at equilibrium and constant temperature. This graph is known as adsorption isotherm. Langmuir represents the monolayer adsorption. The validity of Langmuir model is explained by different parameters such as uniform distribution of adsorption sites, saturation level of monolayer adsorbent surface and affinity of adsorbed molecules on the adsorbent surface sites. Freundlich model represents multilayer adsorption on adsorbent.

3.5.1 Langmuir isotherm

Irvin Langmuir in 1916 presented an adsorption model based on two basic assumptions. There are fixed number of accessible sites on the adsorbent surface and all of them have the same energy. Further adsorption is reversible and adsorption is monolayer. On the basis of this background he derived one mathematical equation and same is known as Langmuir equation as shown in equation 2.

\[
\frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{C_e}{q_m} \tag{2}
\]

Where \(C_e\) is the equilibrium concentration of the adsorbate, \(q_e\) is the adsorption capacity adsorbed at equilibrium, \(q_m\) is the maximum adsorption capacity and \(K_L\) is the Langmuir adsorption constant.

The linearized form of Langmuir equation (2) is represented by equation (3).

\[
\frac{1}{q_e} = \frac{1}{q_mK_LC_e} + \frac{1}{q_m} \tag{3}
\]

The Langmuir constants \(q_m\) and \(K_L\) can be determined from a plot of \(1/q_e\) versus \(1/C_e\). The linear plot of \(1/q_e\) vs \(1/C_e\) is shown in Figure 7.

The linear form of Langmuir equation for cadmium adsorption is represented by equation 4.

\[
\frac{1}{q_e} = \frac{2.96}{C_e} + 0.0738, \quad R^2 = 0.95 \tag{4}
\]

From this equation the cadmium maximum adsorption capacity \((q_m)\) is the 13.5 mg/g and \(K_L\) is the 0.025.
The separation factor or equilibrium parameter $R_L$ is given by equation (5).

$$ R_L = \frac{1}{1 + K_L C_0} \quad (5) $$

Here, $C_i$ is the highest initial cadmium concentration (mg/l). The adsorption characteristic of separation factor related with adsorption system is shown as below:

<table>
<thead>
<tr>
<th>$R_L$ value</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favourable</td>
</tr>
<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavourable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear</td>
</tr>
</tbody>
</table>

The value of $R_L$ obtained for experimental result is 0.44, indicating the adsorption of cadmium on bentonite clay is favourable.

### 3.5.2 Freundlich isotherm

The linearized form of Freundlich equation is shown below

$$ \log(q_e) = \log K + \left(\frac{1}{n}\right) \log(C_e) \quad (6) $$

The meaning of $q_e$ and $C_e$ is similar to those defined in previous section under Langmuir isotherm. $K$ and $n$ are known as Freundlich constants, constant $K$ relates to the degree of adsorption, and $n$ provides the rough estimation of the intensity of adsorption (Hema & Arivoli, 2008). Values of these constants, can be determined from a plot of $\log(q_e)$ vs $\log(C_e)$. This plot is known as Freundlich adsorption plot.
The Freundlich plot is shown by Figure 8. The linear form of Freundlich equation for cadmium adsorption is represented by equation 7.

$$ \log(q_e) = 0.246 + 0.61 \log(C_e), \quad R^2 = 0.92 $$

(7)

The constant K and 1/n were found to be 1.76 and 0.61 respectively. It is clear from Figure 8, that Freundlich isotherm curve is linear in adsorption of cadmium.

![Figure 8](image)

**Figure. 8.** Freundlich adsorption plot for adsorption of cadmium on bentonite.

**CONCLUSION**

The bentonite clay collected from district Bhavnagar of Gujarat, India can be efficiently used for cadmium removal from aqueous solution. The dose of clay of 10 g/l at pH of 6 is observed giving the maximum removal of cadmium. It is also observed that maximum adsorption occurs within 5 minutes. The maximum adsorption capacity obtained from Langmuir adsorption model is 13.5 mg/g and constant $K_L$ is 0.025 with regression coefficient of 0.95. It was found that Langmuir and Freundlich adsorption models were fit very close with experimental data. From this study it is concluded that bentonite clay from district Bhavnagar of Gujarat of India is very useful & efficient in removing the heavy metal like cadmium from aqueous solution. The bentonite clay is naturally occurring and cheapest among the adsorbent materials, therefore it can be effectively used by the industries for removing heavy metals like cadmium from their effluents.

**REFERENCES**

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