Removal of Cr(VI) from Spiked solutions by Natural adsorbent – a fixed bed study

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Abstract

Discharge of heavy metals from metal process industries is known to have adverse effects on the environment. Conventional treatment technologies for removal of heavy metals from aqueous solutions are non-economical and generate huge quantities of chemical sludge. Bio-sorption of heavy metals by chemically inactive non-living biomass of microbial of plant origin is an innovative and technology of these pollutants from aqueous solutions.

The operating conditions such as pH, dose required, initial metal concentrations and treatment performance are presented, recovery adsorbent was also discussed. The efficiency of fixed bed system depends on the initial concentration of influent rate and bed height. The effects of parameters on the adsorption of Cr(VI) on BFFD were examined. A simpler approach to fixed bed adsorption has been proposed by Hutchin which is called bed – depth - service time, (BDST) Model service time with parameters, initial concentrations, flow rate and bed heights. A bed height of 3.0 cm having 2.0 gm adsorbent was used, to study the effects of initial metal ion concentration. The metal ion concentration varied from 20 - 40 ppm and flow rate of 10 ml/min, at required pH. The effects of flow rate on adsorption of Cr(VI) was studied with 20 ppm of Cr(VI) solution was allowed to pass through the column of an adsorbent 3.0 cm at different flow rates. Effects of metal initial concentration of 20 ppm, flow rate of 10 ml/min, bed heights contains different weights were used to study.

Key words: Bagasse, Heavy metals. Wastewater treatment, Removal, Advanced techniques

Adsorbent: Bagasse power
The Bagasse were collected near village of Visakhapatnam, Andhra Pradesh, cleaned thoroughly with water and soaked in distilled water for 24 hours and again washed with double distilled water and dried under sun light. The dried drupes were pulverized and the pulverized material was screened for various particle sizes like 0.430, 0.600 and 0.800 mm.

Adsorbate: Chromium solution
AR grade potassium dichromate solution was used to prepare Cr(VI) solution. A stock solution of 1000 mg/l of Cr(VI) was prepared by dissolving 2.830 g of dried potassium dichromate in double distilled water and made up to 1000ml.

Introduction
Heavy metals can be found in industrial wastewater/effluents from many sources and are deemed undesirable by many researchers/environmentalists. It ranks 21st in abundance among all elements with an average concentration of 100 ppm (Manonmani 2002) and enters into the environment through natural and anthropogenic sources. It is also used in metal plating, tanneries and oil drillings. Most of the chromium is present in wastewaters, especially Cr(VI), is the result of emissions from industries such as electroplating, metal finishing, magnetic tape manufacturing, pigment production, fungicides, paint and primer pigments manufacturing. The concentration of Cr(VI) found in the typical wastewater (such as electroplating or leather tanning wastewater), ranges of between 50 lutants defined by United States Environmental protection agency (EPA 2003u). Chromium
exists in nature mainly in two stable oxidation states +3 and +6. In +3 state it acts as bio element, while in +6 state it causes mutagenicity. Therefore, the speciation of chromium in contaminated environments becomes critical for understanding its fate and exposure. The hydrolysis behavior of Cr(III) is complicated, and it produces mono nuclear species \( \text{CrOH}^{+2} \), \( \text{Cr(OH)}_2^{+1} \), \( \text{Cr(OH)}_4^{-1} \) and \( \text{Cr(OH)}_3^{+6} \), polynuclear species \( \text{Cr}_2\text{(OH)}_2 \) and neutral species \( \text{Cr}_3\text{(OH)}_4^{+6} \). The hydrolysis of Cr\(^{6+}\) produces only neutral and anionic species. The predominant species are \( \text{CrO}_4^{-2} \), \( \text{HCrO}_2^{-1} \) and \( \text{Cr}_3\text{O}_7^{+2} \).

The survey of literature shows that metal ion reduction and removal techniques have been mostly considered as possible solutions. Ion-exchange (Tiravanti et al., 1997) chemical reduction (Seaman et al., 1999), and chemical precipitation (Zhou et al., 1993), Polymer-based filtration & membrane separation (Chakravarti, 1995), adsorption (Dahbi et al., 1999), electrochemical precipitation (Kongsricharoern et al., 1996), solvent extraction (Pagilla et al., 1999), cementation (Lin et al., 1992), electro kinetic remediation (Sawada et al., 2004) and microbial adsorbents also using recently for the removal of heavy metals (Mousumisen et al., 2005) are among the available methods for effectively accomplishing metal concentration and reduction. Nevertheless, many of these approaches are marginally cost-effective or practically difficult to implement in developing countries. Hence, the need for a treatment strategy that is simple, robust cost effective and acceptable.

Adsorption can be an effective and versatile method for removing Cr(VI) particularly when combined with an appropriate regeneration steps. This addresses the problems of sludge disposal and renders the system more economically viable, especially if low-cost adsorbents are used. Many adsorbents were tried to remove Cr(VI) from aqueous solutions and wastewaters. Studies on Tamarind nut carbon (Srinivasan et al., 2004), mixture of flyash and papal bark (Vasanthy et al., 2003), soybean hull, corncob, rice husk and bituminous coal as adsorbents are available in the literature.

4.1.3.9 Column Study
The efficiency of a fixed bed system depends on the initial concentration of the influent, flow rate and the bed height. The effects of these parameters on the adsorption of Cr(VI) were examined. A simpler approach to fixed bed adsorber has been proposed by Hutchin (Equation-1) which is called Bed-Depth-Service- Time (BDST) model which correlates service time (t) with the parameters; initial concentration, flow rate and bed heights (Hutchin., 1973).

4.1.3.9.1 Effects of Metal ion Concentration on Cr(VI) Adsorption
A bed height of 3.0 cm having 2.0 g of the adsorbent was used to study the effects of initial metal ion concentration. The initial Cr(VI) concentrations were varied from 20 to 40 mg/l at constant bed height of 3.0 cm and flow rate of 10ml/ min and adjusted to pH 2.0. The efficiency of the fixed bed method depends on the shape of the breakthrough curves obtained by plotting \( \frac{C_t}{C_o} \) vs volume or time. Breakthrough volume is defined as the maximum volume of effluent required to reach \( \frac{C_t}{C_o} = 0 \) or \( \frac{C_t}{C_o} = 0.5 \) (ml) (50% breakthrough). The plots of \( \frac{C_t}{C_o} \) vs effluent volume for different Cr(VI) concentrations are shown in Fig-1. The plots are traditional “S” shape but the steepness of the curve varies with the concentrations of Cr(VI). The breakthrough volumes at \( \frac{C_t}{C_o} = 0 \) for Cr(VI) concentrations of 20, 30 and 40 mg/l were found to be 300, 200 and 100 ml respectively. The time for 50 present breakthrough (\( t_{0.5} \)) decreased from 52.5 to 22.5 min for Cr(VI) concentrations of 20 mg/l to 40 mg/l. The results are shown in Table-1.
Breakthrough volumes for Cr(VI) Adsorption for different concentrations

Particle size : 0.800 mm  
Initial pH : 2.0  
Bed height : 3.0 cm  
Flow rate : 10 ml/min

<table>
<thead>
<tr>
<th>Initial concentration (mg/l)</th>
<th>Breakthrough volume</th>
<th>Time for 50 % breakthrough to 0.5 (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_t/C_o = 0$ (ml)</td>
<td>$C_t/C_o = 0.5$ (ml)</td>
</tr>
<tr>
<td>20</td>
<td>300</td>
<td>525</td>
</tr>
<tr>
<td>30</td>
<td>200</td>
<td>350</td>
</tr>
<tr>
<td>40</td>
<td>100</td>
<td>225</td>
</tr>
</tbody>
</table>

4.1.3.9.2 Effects of Flow Rate on Cr(VI) Adsorption

The effects of flow rate on adsorption of Cr(VI) was studied with 20 mg/l concentration of Cr(VI) solution at pH 2.0 and solution was allowed to pass through a column of adsorbent (Bed height 3.0 cm) at different flow rates of 5, 10 and 15 ml/min. The plots of $C_t/C_o$ vs effluent volume for different flow rates are shown in Fig-2. The flow rate has been considered to study the Cr(VI) removal; when flow rate is low the breakthrough volume is high. The results indicate that breakthrough volume at ($C_t/C_o = 0$) was higher for 5 ml/min than for 10 and 15 ml/min. The results are shown in Table-2.
Table-2

Breakthrough volumes for Cr(VI) Adsorption for different flow rates

<table>
<thead>
<tr>
<th>Flow rate (ml/min)</th>
<th>Breakthrough volume</th>
<th>Time for 50 % break through t_{0.5} (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_t / C_o = 0 (ml)</td>
<td>C_t / C_o = 0.5(ml)</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
<td>600</td>
</tr>
<tr>
<td>10</td>
<td>300</td>
<td>525</td>
</tr>
<tr>
<td>15</td>
<td>250</td>
<td>475</td>
</tr>
</tbody>
</table>

Table-3

Breakthrough volumes for Cr(VI) adsorption for different Bed heights

<table>
<thead>
<tr>
<th>[Cr(VI)] : 20 mg/l</th>
<th>Flow rate : 10 ml/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH : 2.0</td>
<td></td>
</tr>
<tr>
<td>Particle size : 0.800 mm</td>
<td></td>
</tr>
</tbody>
</table>

Fig-2

Effects of Bed height on Cr(VI) removal

The experiment was carried out with an initial Cr(VI) conc. of 20 mg/l, flow rate of 10 ml/min at pH 2.0. The beds of different heights (3.0, 3.8 and 4.6 cm) containing adsorbent weights of 2.0, 2.6 and 3.2 g were used to study the effects of bed height on Cr(VI) removal. The plot of C_t/C_o vs effluent volume is shown in Fig-3. The breakthrough volumes at (C_t/C_o = 0) increased from 300 to 525 ml when bed height was increased from 3.0 to 4.6 cm. The results are shown in Table-3.
Application of BDST model

As predicted from Hutchin’s equation for BDST (Equation-1), the plot of $C_0 t$ vs $\ln\left((C_0/C_t) - 1\right)$ should be a straight line. The data for BDST equation are given in Tables-15, 16 and 17 for different Cr(VI) concentrations, different flow rates and different bed heights respectively. The plots of $C_0 t$ vs $\ln\left((C_0/C_t) - 1\right)$ are linear (Fig-4, 5 and 6) obeying Hutchin’s (1973) equation. The constants $K_a$ and $N_o$ namely the rate constants of adsorption and adsorption capacity respectively were obtained from the slope and intercepts of the plots (Fig-4, 5 and 6). From the data it is evident that increase in initial concentration of Cr(VI) solutions from 20 to 40 mg/l increased the adsorption capacity from 1040 to 1100 mg/l and decreased the rate constant from $8.0 \times 10^{-3}$ to $6.13 \times 10^{-3}$ l/min/mg. Similar behavior has been observed by Ranganathan and Namasivayam (1998).

At fixed influent concentration and bed heights, smaller flow rate of 5 ml/ min showed better adsorption capacity of 2400 mg/l than 10 and 15 ml/min. The $K_a$ values in Table-4 shows that higher flow rates saturate the bed more quickly than slower flow rates. The data obtained for different bed heights, reveals that increase in bed height form 3.0 to 4.6 cm increases the breakthrough volumes ($C_t/C_o = 0$) increased from 300 to 525 ml and $N_o$ from 1050 to 1550 mg/l. Increase in bed height increased the adsorption capacity. This is due to the fact that the number of adsorption sites increases with increase in adsorbent dosage (Kannan et al., 2003).

<table>
<thead>
<tr>
<th>Bed height (cm)</th>
<th>Breakthrough volume</th>
<th>Time for 50 % break through to 0.5 (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_t / C_o = 0$ (ml)</td>
<td>$C_t / C_o = 0.5$(ml)</td>
</tr>
<tr>
<td>3.0</td>
<td>300</td>
<td>525</td>
</tr>
<tr>
<td>3.8</td>
<td>400</td>
<td>650</td>
</tr>
<tr>
<td>4.6</td>
<td>525</td>
<td>825</td>
</tr>
</tbody>
</table>

Fig- 3
Fig 4

Effects of Cr (VI) Concentration on BDST model for Cr (VI) adsorption

- Bed Height: 3.0 cm
- Flow Rate: 100 ml/min
- [Cr (VI)]: 20 mg/l
- 20 mg/l: 0.9994
- 40 mg/l: 0.9992

Fig 5

Effects of flow rate on BDST model for Cr (VI) adsorption

- Bed Height: 3.0 cm
- [Cr (VI)]: 20 mg/l
- Flow Rate: 5 ml/min
- 5 ml/min: 0.9708
- 10 ml/min: 0.9884
- 15 ml/min: 0.9838
Table - 4

BDST Constants for Cr(VI) Adsorption

<table>
<thead>
<tr>
<th>BDST Constants</th>
<th>Concentration (mg/l)</th>
<th>Flow rate (ml/min)</th>
<th>Bed height (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>$K_a \times 10^{-3}$</td>
<td>8.00</td>
<td>6.45</td>
<td>6.13</td>
</tr>
<tr>
<td>$N_0$ (mg/l)</td>
<td>1040</td>
<td>1070</td>
<td>1100</td>
</tr>
</tbody>
</table>

Conclusion

Collection of adsorbent is cheap and easy to collect, which are agricultural wastes and non-toxic in nature. Flow methods good efficient for the purification of bulky waters like wastewater collected form industries and bulky wastewater collected from towns. Adsorbent was recollected form metal adsorbed adsorbent and reuse for further purification. From the data it is evident that increase in initial concentration of metal Cr(VI) solutions increased the absorption capacity and decreased in the rate constant. At fixed influent concentration and bed heights, smaller flow rates shows better adsorption capacity. Data shows that higher flow rates saturate the bed more quickly than slower flow rates. Increase in bed heights increased the adsorption capacity. This is due to the fact that the number of adsorption sites increased with increase in adsorbent dosage.

References


