Cr(VI) ADSORPTION – MECHANISTIC APPROACH FOR BIOSORPTION FROM AQUEOUS SOLUTIONS

Biswajit Singha and Sudip Kumar Das

FTIR
Chromium (VI)
Coconut shell
Hyacinth roots
Neem leaves

Paper presented in International Conference on Environment, Energy and Development (from Stockholm to Copenhagen and beyond)
December 10 - 12, 2010, Sambalpur University
BISWAJIT SINGHA AND SUDIP KUMAR DAS*
Department of Chemical Engineering
University of Calcutta, 92, A. P. C. Road, Kolkata - 700 009, INDIA
E mail: drsudipkdas@vsnl.net

ABSTRACT

Cr(VI) containing waste water discharged from various industries, including mining, tanning, cement, production of steel and other metal alloys, electroplating operations, photographic material and corrosive painting industries [Bhattacharya et al., 2008 and Malkoc et al., 2006]. In the present study, three different biosorbent namely hyacinth root, neam leaves and coconut shell have been used for adsorption of Cr(VI) from its aqueous solution. Initially operating parameters, i.e. pH of the solution, initial metal ion concentration, adsorption dosages, contact time and equilibrium time are optimized in batch operation. Characterizations of the adsorbents are carried out using modern techniques. A detailed FTIR characterization of adsorbents and Cr(VI) loaded adsorbents were carried out. The results show that the different functional groups such as surface hydroxyl, alkene group, alkane group, sulphonic acid etc were responsible for the adsorption process.

*Corresponding author
INTRODUCTION

Cr(VI) is reported to be carcinogenic, mutagenic and toxic, thus, its presence in the environment poses a significant threat to aquatic life and as well as public health (Hsu et al., 2009). The maximum permissible limit of Cr(VI) for the discharge to inland surface water is 0.1 mg/L and in potable water is 0.05 mg/L (EPA, 1990 and IS, 1991). The Ministry of Environment and Forest (MOEF), Government of India has set minimal national standards (MINAS) of 0.1 mg/L for safe discharge of effluent containing Cr(VI) in surface water (MINAS, 2001). In order to comply with this limit, industries have to treat their effluents to reduce the Cr(VI) concentration in wastewater to acceptable levels. In waste water treatment various technologies are available such as chemical precipitation, ion exchange, electrochemical precipitation, solvent extraction, membrane separation, concentration, evaporation, reverse osmosis, emulsion per traction, adsorption etc. (Naiya et al., 2009). Among these technologies, adsorption is a user-friendly technique for the removal of heavy metal. This process includes the selective transfer of solute components in the fluid phase onto the surface or onto the bulk of solid adsorbent materials.

In recent years, several natural or agricultural wastes (Chatterjee et al., 2010, Miretzky and Cirelli, 2010) have been used for the removal of heavy metal from industrial waste water. In general natural or agricultural waste contains different functional groups like hydroxyl, aldehyde, aliphatic acid, alkene, amide, aromatic nitro, silicate, sulphonate etc. The present paper deals with the identification of functional groups which are responsible for Cr(VI) ion adsorption in the natural adsorbents.

MATERIALS AND METHODS

Preparation of adsorbents

Coconut shell, hyacinth roots and neem leaves were used as low cost natural adsorbent. All the adsorbents were collected from local area near Kolkota, West Bengal, India.

Hyacinth roots were boiled for 6hr. to remove color materials. Coconut shell was crashed in roll crusher and then grinded. Then neem leaves and coconut shell were treated with 0.1 N NaOH to remove lignin based color materials followed by 0.1 N H\textsubscript{2}SO\textsubscript{4}. Finally all the adsorbents were washed with distilled water several time and dried at 105ºC for 6 hr to remove the adherent moisture. After drying, all the adsorbents were sieved to obtain particle size of 250-350 μm prior to use for adsorption studies.

Reagents and equipments

All the necessary chemicals used in the study were of analytical grade and obtained from E. Merck Limited, Mumbai, India. The pH of the solution was measured with a EUTECH make digital microprocessor based pH meter previously calibrated with standard buffer solutions. UV-Spectrophotometer (U-4100 spectrophotometer, Hitachi, Japan) was used to determine the Cr(VI) content in standard and treated solutions after adsorption experiments. FT-IR (Jasco FT/IR-670 Plus) studies were carried out to determine the type of functional group responsible for Cr(VI) adsorption.

Preparation of standard Cr(VI) solution

The stock solution containing 1000 mg/L of Cr(VI) was prepared by dissolving 3.73 g of A. R. grade K\textsubscript{2}CrO\textsubscript{4}.2H\textsubscript{2}O in 1000 mL double distilled water. Required initial concentration of Cr(VI) standards were prepared by appropriate dilution of the above stock Cr(VI) solution.

Batch adsorption studies

Using the necessary adsorbents in a series of 250 mL stopper conical flask containing 100 mL of Cr(VI) solution batch adsorption were carried out. The pH of the solution adjusted by adding 0.1 N HCl or 0.1 N NaOH solution as required. Then the flasks were shaken for the desired contact time in an electrically thermostated reciprocating shaker with 120-125 strokes/minute at 30ºC. Cr(VI) concentration were estimated by drawing conical flask from shaker at regular intervals of time to find the equilibrium when the concentration
is constant against time. The contents of the flask were then filtered through filter paper (Whatman No.1). UV-visible spectrophotometer was employed to determine the remaining Cr(VI) concentration in the sample using 1,5-diphenylcarbazide method as laid down in standard methods for examination of water and wastewater (APHA, AWWA, WEF, 1998).

RESULTS AND DISCUSSION

Optimum pH and Cr(VI) adsorption mechanism

Metal sorption is depends on the solution pH. In general adsorption of anion is favored at pH < pH_{pzc} (Table 1). At very low pH, chromium ions exist in the form of HCrO$_4^-$, while in the increase in pH (up to pH = 6) different forms such as Cr$_2$O$_7^{2-}$, HCrO$_4^-$, and Cr$_3$O$_10^{2-}$, coexists, of which HCrO$_4^-$ predominates. As the pH increases equilibrium shifted from HCrO$_4^-$ to CrO$_4^{2-}$ and Cr$_2$O$_7^-$ (Bansal et al., 2009). At very low pH values, the surface of adsorbent would be surrounded by the hydronium ions which enhance the Cr(VI) interaction with binding sites of the biosorbent by greater attractive forces. As the pH increased, the overall surface charge on the biosorbents became negative and adsorption decreased [Malkoc et al., 2006]. The following equilibrium may be written for the Cr(VI) anions present in aqueous solutions [Miretzkya and Cirelli, 2010].

$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+ \quad k_1 = 1.21 \quad (1)$$

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \quad k_2 = 35.5 \quad (2)$$

$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+ \quad k_3 = 3 \times 10^{-7} \quad (3)$$

Adsorption of Cr(VI) was not significant at pH values more than 6 due to dual complexation of the anions (CrO$_4^{2-}$, Cr$_2$O$_7^-$ and OH$^-$) to be adsorbed on the surface of the adsorbents, of which OH$^-$ predominates (Mallick et al., 2006).

Optimum adsorbent dosage

The effect of dosage for the removal of Cr(VI) from aqueous solution using initial metal ion concentration at 25 mg/L are carried out. The efficiency of Cr(VI) removal was found to increase rapidly at adsorbent dosage from 1 g/L to 7.5 g/L for all the adsorbent. After the aforesaid adsorbent dosage, incremental metal ion removal became very low as the surface metal ion concentration and the solution metal ion concentration came to equilibrium with each other. Further increase in adsorbent dosage above 10 g/L, the removal efficiency become almost remained constant which may be considered as an optimum adsorbent dosage level.

Optimum contact time

The influence of contact time on the batch adsorption of Cr(VI) ion indicated that the increase in contact time the percent removal of Cr(VI) enhanced significantly. Initial rapid adsorption gives away a very slow approach to equilibrium. The nature of adsorbent and its available sorption sites affected the time needed to reach equilibrium. The equilibrium time were 4 hr for all the adsorbents.

Effect of initial Cr(VI) ion concentration variation

Percent removal of Cr(VI) ion decreases with the increase in initial Cr(VI) ion concentration. At the lower concentration, almost all the Cr(VI) ions in the solution would react with the binding sites and thus facilitated almost complete adsorption. At higher concentration more Cr(VI) ions left un-adsorbed in the solution due

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Initial pH</th>
<th>Initial Cr(VI) concentration (mg/L)</th>
<th>Contact Time (min)</th>
<th>Adsorbent dosage (g/L)</th>
<th>Point of zero charge pH$^{pzc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyacinth roots</td>
<td>2</td>
<td>25</td>
<td>240</td>
<td>10</td>
<td>6.59</td>
</tr>
<tr>
<td>Neem leaves</td>
<td>2</td>
<td>25</td>
<td>240</td>
<td>10</td>
<td>6.94</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>2</td>
<td>25</td>
<td>240</td>
<td>10</td>
<td>6.62</td>
</tr>
</tbody>
</table>

Table 1: Optimum operating condition obtaining in the batch process

BISWAJIT SINGHA AND SUDIP KUMAR DAS
Table 2: Wave number (cm$^{-1}$) for the dominant peak from FT-IR for Cr(VI) adsorption

<table>
<thead>
<tr>
<th>Functional Groups</th>
<th>Hyacinth roots</th>
<th>Cr(VI) loaded hyacinth roots</th>
<th>Neem leaves</th>
<th>Cr(VI) loaded neem leaves</th>
<th>Coconut shell</th>
<th>Cr(VI) loaded coconut shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface O-H stretching</td>
<td>3328.53</td>
<td>3305.39</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Aliphatic C-H stretching</td>
<td>2924.52</td>
<td>2923.88</td>
<td>2920.28</td>
<td>2910.16</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Phosphite ester group</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>2353.97</td>
<td>2358.78</td>
</tr>
<tr>
<td>Aliphatic acid C=O stretching</td>
<td>1713.44</td>
<td>1713.44</td>
<td>1715.83</td>
<td>1715.67</td>
<td>1717.73</td>
<td>1715.75</td>
</tr>
<tr>
<td>Unsaturated group like alkene</td>
<td>1644.02</td>
<td>1633.41</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Aromatic C-NO$_2$ stretching</td>
<td>1514.81</td>
<td>1505.17</td>
<td>1515.46</td>
<td>1515.80</td>
<td>1507.22</td>
<td>1507.19</td>
</tr>
<tr>
<td>Alkene group stretching</td>
<td>x</td>
<td>x</td>
<td>1455.88</td>
<td>1455.98</td>
<td>1472.91</td>
<td>1456.25</td>
</tr>
<tr>
<td>-SO$_3$ stretching</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Sulphonyl chlorides stretching</td>
<td>x</td>
<td>x</td>
<td>1163.39</td>
<td>1162.00</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Sulphonic acid S=O stretching</td>
<td>1055.84</td>
<td>1035.59</td>
<td>x</td>
<td>x</td>
<td>1031.37</td>
<td>1032.23</td>
</tr>
</tbody>
</table>

Figure 1: FTIR spectra of (a) hyacinth roots and (b) Cr(VI) loaded hyacinth roots

Figure 2: FTIR spectra of (a) neem leaves and (b) Cr(VI) loaded neem leaves

to the saturation of the binding sites of the adsorbent surface. This indicates that the energetically less favorable sites become involve with increasing Cr(VI) ion concentration in aqueous solution (Bhattacharya et al., 2006). All the optimum condition for the batch experiment was reported in Table 1.

**FTIR analysis for Cr(VI) adsorption**

Fourier transform infrared spectroscopy (FTIR) was used to investigate the changes in vibration frequency in the functional groups of the adsorbents due to Cr(VI) adsorption.

Table 2 represented the shift in the wave number of dominant peak associated with the Cr(VI) loaded in the FT-IR plots (Figs. 1-2) by comparing between the fresh adsorbents and Cr(VI) loaded adsorbents. These shifts in the wavelength showed that there was metal binding process taking place at the surface of the adsorbents (Srivastava et al., 2006 and Pravasnt et al., 2006). There was a clear shifts from wave number of 3328.53 cm$^{-1}$ (hyacinth roots) to 3305.39 cm$^{-1}$ (metal loaded hyacinth roots) which indicated surface -OH group was one of the functional group responsible for adsorption. Aliphatic C-H stretching may be responsible for Cr(VI) adsorption onto neem leaves as wave number shift from 2920.28 cm$^{-1}$ to 2910.16 cm$^{-1}$. Unsaturated group like alkene was also responsible for adsorption of Cr(VI) onto hyacinth roots which was inferred from the shift of the peak more than 10 cm$^{-1}$.

Alkane group was only responsible for Cr(VI) adsorption onto coconut shell as indicated in Table 2. Major shift of these band indicated that Si-OH group is responsible for adsorption. -SO$_3$ stretching and sulphonic acid S=O stretching were found be to responsible for Cr(VI) adsorption onto coconut shell.

Figure 3: FTIR spectra of (a) coconut shell and (b) Cr(VI) loaded coconut shell
and hyacinth roots respectively.

Table 2 also indicated that the minor shift for the other band (phosphate ester group, aliphatic carboxylic acids, aromatic nitro and sulphonyl chloride group) which showed that these groups were not involved in the adsorption process.

Crystal radius of Cr(VI) is 0.52Å. It is moderately large ion, fit into the binding site of the rice waste and bind to several group present in rice waste simultaneously.

ACKNOWLEDGEMENT

Biswajit Singha wishes to thanks the University of Calcutta for the Project Fellow (UPE / Science and Technology), Ref. No. UGC/489/Fellow UPE (SC/T), dated the 16/4/2009. The authors acknowledge to AICTE for financial support (Project no.- F. No.: 8023 /BOR /RID/RPS-72/2008-09).

REFERENCES


EPA. (Environmental Protection Agency), 1990. Environmental Pollution Control Alternatives. EPA/625/5-90/025, EPA/625/4-89/023, Cincinnati, US.


