Removal of Cr(VI) from aqueous solution using Nirmali seed as biosorbent

PANDIAN Lakshmipathiraj*, SUBRAMANIAN Umamaheswari**, GUNDAMADUGU Bhaskar Raju***, SWARNA Prabhaskar***, GANDHIRAJ Caroling**, KATO Shigeru* and KOJIMA Toshinori†

* Department of Materials and Life Sciences, SeiKei University, Kichijoji, Musashino, Tokyo 180-8633, Japan
** Ethiraj college for women, Chennai, India.
*** National Metallurgical Laboratory, Madras centre, CSIR Madras complex, Taramani, Chennai 600 113, India

(Received November 9, 2010, Accepted February 15, 2012)

The removal of Cr(VI) from aqueous solutions was studied using the seeds of the plant species Strychnos potatorum L. The plant is grown in India and is called as Nirmali tree or clearing nut tree. The dried Nirmali seeds were powdered and used as adsorbent for the removal of Cr(VI) from aqueous solution. The zeta potential measurements have indicated negative surface charge similar to that of natural anionic polyelectrolyte. Batch experiments were conducted to study the adsorption of Cr(VI) onto Nirmali seed powder. The influence of pH, initial Cr(VI) concentration and the effect of anions on the removal of Cr(VI) was investigated. The removal of Cr(VI) was better in the acidic medium. The influence of anions such as Cl−, NO3− and SO4−2 on Cr(VI) removal was investigated and found that the removal was adversely affected in the presence of NO3− and SO4−2. The results obtained from equilibrium adsorption studies were found to fit in to Langmuir adsorption isotherm and the maximum uptake of Cr(VI) was found to be 59 mg g−1. The rate of removal of Cr(VI) was found to follow the pseudo second order rate equation.

Key Words: Eco-friendly, removal of Cr(VI), Nirmali seeds, Strychnos Potatorum L., Chromium, Adsorption kinetics, chemical equilibrium

1. Introduction

Chromium compounds are widely used in steel, alloys, metal plating, leather tanning, paints, pigments, inks, textile dyeing and also in wood preservation. Due to the widespread use of chromium in different industries, huge quantity of the chromium containing wastewater is being discharged into the environment1. The most of the chromium is released into the aqueous environment as Cr(III) and Cr(VI). The Cr(VI) compounds are known to be toxic and mutagenic for most living organism. Inhalation and ingestion of Cr(VI) over the period can cause cancer in digestive track and lungs, nausea, vomiting and diarrhea2). Considering the toxic nature of Cr(VI), the USEPA has set the Maximum Contamination Limit (MCL) as 100 μg L−1 for Cr in drinking water. The Ministry of Environment and Forests (MOEF), Government of India has set the Minimal National Standards (MINAS) for Cr as 2.0 mg L−1 for safe discharge of the effluents containing Cr ions into surface waters.

Several treatment methods have been reported for the removal of Cr(VI) from aqueous solution. The conventional treatment processes include chemical reduction and precipitation, ion exchange, Liquid extraction, reverse osmosis and membrane filtration have several disadvantages such as high operational cost, incomplete metal removal and generation of toxic sludge as a secondary pollutant which is relatively difficult to handle and dispose. It is therefore, necessary to develop the alternative and low cost technologies for the abatement of the wastewater containing Cr(VI).

In the recent years, the biosorption is gaining considerable importance as an alternative treatment technology3). The advantageous of biosorbents are; easy availability, huge number of active sites, high magnitude of adsorption towards the metal ion and easy regeneration. The effectiveness of different low cost agro based materials such as Tamarindus indica seed, crushed coconut shell, almond shell, ground nut shell and walnut shell was investigated for the removal of Cr(VI) from aqueous solution4). The maximum adsorption capacity of wheat bran was reported to be 40.8 mg of Cr(VI) per gram at pH 1.05). The Agricultural wastes such as sugarcane
bagasse, maize, corncob and jatropha oil cake were tried as adsorbents for the removal of Cr(VI) from aqueous solution\(^9\). The adsorption capacity of jatropha oil cake was observed to be 11.75 mg g\(^{-1}\).

*Strychnos potatorum* L. (Nirmali) is a moderate sized tree grown in southern and central part of India, Sri lanka and Burma is called as Nirmali tree or clearing nut tree. The seeds and the leaves of the tree are predominantly recognized for its medicinal values. Apart from it, the seeds were extensively used as coagulant by the rural community. The purification of turbid surface water is reported to be accomplished by ancient civilization in India using *Strychnos potatorum* seeds\(^3,9\). The property was attributed to the presence of natural polyelectrolyte, proteins, lipids and other functional group such as –COOH, -OH etc.\(^3,7,9,10\). Very few researchers have reported the removal of metal ion such as lead and fluoride from aqueous solution using Nirmali seeds\(^10,11\). The present study was aimed to understand the adsorption behaviour of Cr(VI) on the Nirmali seed powder under different experimental conditions.

**2. Materials and Methods**

**2.1 Reagents and materials**

All the chemicals used in the present study were of analytical grade. Potassium dichromate (K\(_2\)Cr\(_2\)O\(_7\)) obtained from Merck Speciality chemicals, India was used as model contaminant of Cr(VI) in the synthetic wastewater. The pH of the aqueous solutions was adjusted using 1M NaOH and 1M HCl.

*Strychnos potatorum* L. (Nimali) seeds collected from India were dried at ambient room temperature. The dried seeds were powdered using hammer mill. The fine powder obtained was preserved for the adsorption experiments.

**2.2 Adsorption experiment**

Batch adsorption experiments were conducted using 100 ml of Cr(VI) test solution of desired concentration in 200 ml high density polyethylene bottles. The pH was adjusted to the desired value by using NaOH or HCl. An accurately weighed quantity of adsorbent of 2.0 g was added to each of the test solution and equilibrated for 5 h with the help of laboratory shaker at room temperature. After the equilibration time of 5 h, the solutions were filtered through 0.2 µm membrane syringe filter and filtrates were analyzed for Cr(VI). Based on preliminary experiments, the concentrations of Cr(VI) chosen for kinetic studies were 10, 20, 40, 60, 100, 150, 200, 250 mg L\(^{-1}\). Aliquots of samples were taken at different time intervals and subjected to Cr(VI) analysis.

**2.3 Analysis**

Cr (VI) was estimated using 1,5-diphenylcarbazide [CO(NH-NHC6H5)2] as a complexing agent. The diphenylcarbazide reagent was prepared by dissolving 0.25 g in 100mL of acetone. The intensity of Cr(VI) diphenylcarbazide complex was measured at 540 nm using UV–vis spectrophotometer (SHIMADZU make model UV-160A).

**2.4 Zeta potential measurements**

Zeta potential measurements were carried out using zetameter (Zetameter 3.0+ Inc., USA). to understand the adsorption behavior of Cr(VI) on nirmali seed powder. The adsorbent sample (2.0 g) was suspended in a 0.1 N KCl solution (electrolyte) and the aqueous suspension was equilibrated at different pH values for 30 min. The equilibrated slurry was injected into the microelectrophoresis cell using disposable syringes. For each value a minimum of 10 readings were taken and the mean value was reported. prior to each measurement, the electrophoresis cell was thoroughly washed and rinsed with deionized water.

**3. Results and Discussion**

**3.1 Influence of pH on the adsorption of Cr(VI)**

Adsorption experiments were conducted to examine the adsorption efficiency of Cr(VI) on Nirmali seed powder at different pH values. The pH of the experimental solution varied from pH 1.0 to 8.0 with an initial Cr(VI) concentration of 20 mg L\(^{-1}\) and adsorbent dose of 2.0 g. The adsorption efficiency of Cr(VI) on to the adsorbent at different pH values is given in Fig. 1.

The removal of Cr(VI) was more than 99% at pH 1.0, however it decreased with increase of pH value. The removal was poor when pH value was more than 6.0. At pH 1.0, the surface of the adsorbent would be protonated to the greater extent which in turn, facilitate the adsorption of negatively charged Cr(VI) anions by electrostatic force of interaction. Conversely, the extent of the protonation at the surface of the adsorbent is decreased exponentially while increasing the pH.

![Fig. 1](image.png) Effect of initial pH on the adsorption of Cr(VI) onto Nirmali seeds surface.
The poor adsorption efficiency may be attributed to the electrostatic repulsion. The adsorption behavior was further supported by the zeta potential study of the Nirmali seed powder (Table 1). The zeta potential study reveals that the isoelectric point (iep) of Nirmali seed powder would be around pH 1.3 or 1.4. Below this pH, the adsorbent surface is negatively charged and above it the surface is positive. The surface characteristic of the adsorbent supports the earlier statement on nirmali seed that has exhibited the property similar to that of natural anionic polyelectrolyte.

Table 1: Electrokinetic measurements of the Nirmali seeds powder

<table>
<thead>
<tr>
<th>pH</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>16</td>
</tr>
<tr>
<td>1.5</td>
<td>-4</td>
</tr>
<tr>
<td>2.0</td>
<td>-18.5</td>
</tr>
<tr>
<td>3.0</td>
<td>-24.8</td>
</tr>
<tr>
<td>4.0</td>
<td>-33.5</td>
</tr>
<tr>
<td>5.0</td>
<td>-42.5</td>
</tr>
<tr>
<td>6.0</td>
<td>-48</td>
</tr>
<tr>
<td>7.0</td>
<td>-57</td>
</tr>
<tr>
<td>8.0</td>
<td>-72</td>
</tr>
</tbody>
</table>

In the studied pH range (pH 1.0 to 9.0), the maximum adsorption of Cr(VI) on the Nirmali seed was observed at pH 1.0 that is close to the observed iep (around pH 1.3 or 1.4) value of the Nirmali seeds adsorbent. It is evident that the initial part of the adsorption process was controlled by electrostatic interaction between positively charge adsorbent surface and negatively charged adsorbate ions at the active sites of the adsorbent surface.

3.2. Effect of initial concentration

The adsorption equilibrium isotherm was studied at different Cr(VI) concentrations of 10, 20, 40, 60, 100, 150, 200 and 250 mg L\(^{-1}\). The adsorbent (Nirmali seed powder) dosage was maintained at 2.0 g and pH at 1.0. The effect of contact time and the initial Cr(VI) concentration on the removal of Cr(VI) is shown in Fig. 2. It is apparent that the curve obtained for different initial concentration of Cr(VI) has two distinct phases. The initial phase indicates high sorption uptake of Cr(VI) which could be attributed to electrostatic attraction. The slow up take of the Cr(VI) in the second phase indicates the utilization of all actives sites over the sorbent surface and attainment of the saturation or equilibrium phase. The high uptake of the Cr(VI) at relatively less contact time of 4 min may be attributed to the interaction between the specific functional group and active surface of the adsorbent by electrostatic attraction. The maximum adsorption capacity of Cr(VI) on to the Nirmali seed powder surface was estimated to be 59 mg g\(^{-1}\). The adsorption capacity of nirmali seed for the removal of Cr(VI) is relatively high compared with other bio adsorbents reported\(^ {12} \). Langmuir and Freundlich isotherm models are most commonly used to represent adsorption of component from a liquid phase to a solid phase. The Langmuir model assumes monolayer adsorption while the Freundlich is empirical in nature. The adsorption data were analyzed with respect to Freundlich (\(R^2 = 0.63\)) and Langmuir (\(R^2 = 0.99\)) isotherm models and it was observed that the best fit was obtained for a Langmuir isotherm. Similar trend was observed in the case of lead adsorption onto Nirmali seed adsorbents\(^ {10} \).

3.3. Effect of adsorbent dose

The removal Cr(VI) at different adsorbent dose (2.0, 4.0 and 6.0 g) was studied at pH 1.0 and 100 mg L\(^{-1}\) of Cr(VI) initial concentration. The results are presented in Fig. 3. It was observed that the percent removal of Cr(VI) increased from 81 to 99% by increasing the adsorbent dose from 2.0 to 6.0 g, respectively. The resulting effect can be easily explained by an increase in surface area with increase in the adsorbent mass.
3.4. Effect of different anions

The effect of chloride, sulfate and nitrate on the adsorption of Cr(VI) are shown in Fig. 4. It is apparent that 100% of Cr(VI) could be removed in the presence of Cl\(^{-}\) whereas the removal is 76% and 70% in the presence of SO\(_4^{2-}\) and NO\(_3^{-}\) respectively. This may be attributed to the anion competition for surface binding sites.

![Fig. 4](image)

**Fig. 4** Effect of different anions on the adsorption of Cr(VI).

3.5. Kinetics of adsorption

The kinetic of the adsorption determines the uptake rate of the adsorbate and the equilibrium time for the adsorption process. The adsorption data obtained for the different initial concentration of Cr(VI) was analysed using the pseudo first and pseudo second order kinetic model. It is observed from the R\(^2\) values (Fig. 5) that the removal rate of Cr(VI) was followed the pseudo second order model. Also, the calculated equilibrium values are in agreement with the experimental results. Therefore, It is suggested that the adsorption of Cr(VI) onto the nirmali seed powder follow pseudo second order kinetics model.

![Fig. 5](image)

**Fig. 5** Pseudo second order rate kinetics.

4. Conclusion

Nirmali seed powder was observed to be efficient adsorbent for the removal of Cr(VI) from aqueous solution. The adsorption Cr(VI) is strongly influenced by pH. Higher removal of Cr(VI) is observed at pH 1.0 and it gradually decreases by increasing the pH from 1.0 to 8.0. The unit adsorption capacity of Cr(VI) on to the nirmali seed surface is estimated to be 59 mg g\(^{-1}\) and the adsorption equilibrium of Cr(VI) is found to fit into the Langmuir monolayer isotherm model. The removal rate of Cr(VI) follows the pseudo second order equation, indicating that the adsorption is controlled by chemical interaction.

References

2) Mei, B., Puryear, J.D., Newton, R.J.; Assessment of Cr Tolerance and Accumulation in Selected Plant Species, Plant and Soil, 247, 223-231 (2002).