Chapter - VI
Sorption of trace metal using Glass grade spodumene shell powder

Summary

Biosorption is a potential method separation for recovery of heavy metals and trace metals from waste water and effluents from various sources. Studies carried out on many environmental biosorbants present in nature exhibited great potential in the removal of these metals. This chapter deals with the work carried out on the sorption of uranium from iron ore leachates using glass grade spodumene (GSS) powder. It was found that crushed GSS powder possess relatively high sorption capacity. The biosorption experiments were performed under various conditions such as different concentration of sorbent solution, pH, time of contact, biosorbent concentration, temperature and addition of materials like chitosan and ammonium phosphate in acidic medium. It was found that the equilibrium of the process was reached after one hour at room temperature. About 1 gm of GSS powder was found to be enough to adsorb 100 µg of metal from 10 ml solution. The optimum pH value for adsorption was found to be 5.5. The procedure was successfully applied to remove uranium, chromium ions from different effluent samples.

Part presented in International symposium SESTEC-2012, SVKM COLLEGE, BOMBAY
INTRODUCTION

The extraction of heavy metal ions, recovery of radioactive or valuable metal ions from mining effluents, soils and waste water have been important in economic and environmental viewpoints [1-4].

Over the last few decades, the huge increase in the use of heavy metals has resulted in an increased flux of metallic substances in aquatic environment. The most important characteristics of these metals are that they are non-degradable hence persistent. Furthermore, most of the metal ions are toxic to living organisms. Therefore, in order to have a pollution-free environment, the toxic materials should be removed from wastewater before its disposal [5-9].

Removal of toxic heavy and extraction of precious trace metals from industrial wastewater has been practiced for several decades, the conventional physico-chemical removal methods, such as chemical precipitation, electro plating, membrane separation, evaporation or ionic exchange, are usually expensive and sometimes, not effective [10-14]. Recently, heavy metal ions removal from industrial waste streams became mandatory due to implementation of more stringent laws regulations that control the concentration of pollutants in effluents discharged into water and soils on the level lower than 1 mg/µg [15-19]. The industrial discharge of toxic heavy metals into water’s courses is a serious pollution problem affecting water quality. Major sources of water pollution with metals such as cadmium, chromium, thallium, copper, mercury, nickel, lead, and zinc are plating plants, mining, metal finishing, batteries, welding, and alloys manufacture. Concentrations of these metals in water supplies exceeding the standards constitute a severe health hazard. Their harmful effects in aquatic environments include accumulation in living species and magnification throughout the food chain [20-23].

The commonly used procedures for the removal of low concentrations of heavy metals from wastewater include ion exchange, reverse osmosis and solvent extraction, adsorption, and membrane separation [24-29]. These techniques apart from being economically expensive have disadvantages like incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal. Efficient and environment friendly methods are thus needed to be developed to reduce heavy metal content. In this context, considerable attention has been focused in recent years upon the field of biosorption for the removal of heavy metal ions from aqueous effluents [30-34]. Growing public concern
about risks occasioned by water pollution has led to stricter international regulations, forcing the search of more efficient, economical solutions to reduce it.

The process of heavy metal removal by biological materials is known as biosorption. Biomass viability does not affect the metal uptake. Therefore any active metabolic uptake process is currently considered to be a negligible part of biosorption. Various biosorbents have been tried, which include seaweeds, moulds, yeast, bacteria, crab shells, agricultural products such as wool, rice, straw, coconut husks, peat moss, exhausted coffee, waste tea, walnut skin, coconut fiber, cork biomass, seeds of *Ocimum Basilicum*, defatted rice bran, rice hulls, soybean hulls and cotton seed hulls, wheat bran, hardwood (*Dalbergia sissoo*) sawdust, pea pod, cotton and mustard seed cakes [35-38]

A large number of microorganisms belonging to various groups, viz. bacteria, fungi, yeasts, cyanobacteria and algae have been reported to bind a range of heavy metals to different extents (Table 1). The role of various microorganisms by biosorption in the removal and mending of heavy metal(s) has been studied. Most of the biosorption studies reported in literatures have been carried out with living microorganisms. However due to certain inbuilt disadvantages, use of living microorganisms for metal elimination and recovery is not generally practical in all situations. For example, industrial effluents contain high concentrations of toxic metals under widely varying pH conditions. These conditions are not always favorable to the growth and upholding of an active microbial population.

Biosorption has distinct advantages over the conventional methods which include: reusability of biomaterial, low operating cost, selectivity for specific metal, short operation time and no chemical sludge. In the recent years many biosorbent materials of agricultural base have been utilized for heavy metal biosorption. These include: coconut husk and shell, sea weeds, bagasse ash, hazelnut shell, peanut hull, tree fern, black gram husk, maize leaf, maize, sunflower waste, coffee beans, *Ficus religiosa* leaves, wheat bran, almond shell, tea waste [39-43].

There are several advantages of biosorption of using non living biomass and they are as follows:

- The biomass from an existing fermentation industry, which essentially is a waste after fermentation, can be a cheap source of biomass.
- The process is not governed by physiological constraints of microbial cells.
- Because cells are non-living processing conditions are not restricted to those conducive for the growth of the cells. Hence, a wider range of operating conditions such as pH,
temperature and metal concentrations are possible. Also aseptic operating conditions are not essential.

- Growth independent nonliving biomass is not subject to toxicity limitation by cells.
- Metals can be desorbed readily and then recovered. If the value and the amount of metal recovered are insignificant and if the biomass is plentiful, the metal loaded biomass can be incinerated, eliminating further treatment.
- Because nonliving biomass behaves as an ion exchanger, the process is very rapid, requiring anywhere between few minutes to few hours. Metal loading is very high on the surface of the biomass leading to very efficient metal uptake.

In cation exchange chromatography positively charged molecules are attracted to a negatively charged solid support. To optimize binding of all charged molecules, the mobile phase is generally a low to medium conductivity (salt concentration) solution. The adsorption of the molecules to the solid support is driven by the ionic interaction between the two moieties and binding capacities are generally quite high. The strength of the interaction is determined by the number and location of the charges on the molecule and solid support.

Biosobent spodumene a lithium aluminosilicate mineral \([\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2]\) occur in pegmatite ore with quartz and minor impurities, such as feldspar. The mineral occurs naturally in just a few regions around the world. Spodumene in the most economic commercial mineral used as a source of Lithia \([\text{Li}_2\text{O}]\) or Lithium. Lithia acts as a highly effective flux and reduces vitreifications temperatures, increases chemical resistance; producing harder, smoother and more resistant low temperature glasses and produces bodies with low coefficients of thermal expansion. For these reasons, Spodumene is used in a number of applications such as glass, ceramics, refractories, cement, metallurgy, casting and foundry moulds [44].

Since acidified GSS also possesses an affinity for heavy metals, considerable attention has been focused on the use of biosorbent for the adsorption of trace metals like uranium, complexes cyanides and metals present in various other forms from wastewater. It is feasible to grind and increases the surface area thereby the sorption capacity can be increased for adsorption of uranium. Environmental parameters affecting the biosorption process such as pH, contact time, metal ion concentration, adsorbent concentration and adsorbent size were evaluated.
EXPERIMENTAL

Apparatus

Absorbance studies were performed in Varian uv-vis spectrophotometer. pH measurements were made with Systronics pH meter, model 331. Shaking was done in time-temperature controlled orbital shaker.

Reagents

All the chemicals used were of analytical reagent grade or the highest purity available. Deionized water was used throughout the experiments for preparation and dilution of reagents as well as samples. Acids; H₂SO₄, HCl, HNO₃ from Hi Media Laboratories Pvt. Ltd, Mumbai. uranium chitosan and ammonium phosphate from Merck, India. The pH of the solutions was adjusted with .1N HCl and NaOH.

Materials

Biosorbent

Glass grade spodumene in powder form was used as the biosorbent. The shell powder GSS has the chemical composition: SiO₂ - 78.70, MgO - 0.003, Al₂O₃ - 17.68, TiO₂- Nil, Li₂O - 3.43, MnO - 0.01, Fe₂O₃ - 0.12, P₂O₅ - 0.06, CaO - Nil, K₂O - Nil, ZnO- Nil (report of analytical chemistry division BARC, Bombay). Main toxic metal like Pb, Cu, As, Se Hg, Cr etc are absent in this sorbent samples GSS used in this study were obtained, free of charge.

Column Preparation

5g of GSS was taken in a column (size 8mm X 180mm) and packed. Packing of the column was done in the following way, weighed dry support material GSS is suspended in excess of distilled water and stirred until all the air bubbles disappear, holding the column vertically the sorbent is slowly transferred into the column the bottom of which has been plugged with glass wool. After plugging the upper end of the column, preconditioning was done by passing ten times volume of the mobile phase.
Procedure employed in extraction chromatography

Batch distribution experiments

Fixed quantity (0.5 g) of GSS were equilibrated with 5 ml U (VI) solutions at different acids and different acidities (taken a set of six), after filtration aliquots were analyzed spectrophotometrically and found that 1M HNO₃ gave better adoption with low acidity. For calibration, varying concentration of U (VI) metal ion is added in 0.05 g of GSS with 5ml of 1M HNO₃ and stirred in a temp. controlled orbital shaker for about 30 min. The GSS, U in 1M HNO₃ solution was allowed to settle and the supernatant analyzed spectrophotometrically at 301 nm.

The D values in the batch experiments were evaluated as using the formula:

\[ D = \frac{A_i - A_f}{A_f} \times \frac{V}{M} \]

Where \( A_i \) and \( A_f \) are the initial and final concentration of the solutions. \( V \) and \( M \) are solution volume and weight of GSS in gm.

Column extraction and elution of uranium(VI)

The solution containing 1:1 mixture of U (VI) metal ions (100 µg) in 1M HNO₃ was passed through the column, total 25 mL of the solution was passed for complete adsorption. GSS column loaded with U (VI) was eluted at the rate of ~2ml / hr, using 0.02M HNO₃. Aliquots were analyzed at 301 nm spectrophotometrically. The same procedure was followed for waste water samples.

RESULTS AND DISCUSSION

Uptake of U (VI)

The plot of D values versus concentration (Figure-1) at fixed Uranium and HNO₃ concentrations gave a straight line. Table 2 shows the adsorption studies of certain other elements which are found in the water samples containing uranium. It was observed that the other metal ions do not interfere with the uptake of uranium in the process. The time required for effective adsorption of U (VI) metal ion on GSS was almost between 30 min to 60
It can be seen that there was no further improvement in adsorption even if the time is increased.

**Effect of time and temperature on uptake of uranium (VI)**

It was observed that on extending the time, there was no further improvement in the absorbance values (Figure 2) and efficiency of adsorption was varied with wide range of temperature. Maximum adsorption was observed at 34°C. However, the kinetics of adsorption can better be utilized at temperatures between 26 to 36°C.

**Biosorption kinetics**

The kinetic studies were carried out by conducting batch biosorption experiments with same acidified metal ion concentration at room temperature. Samples were taken at different time intervals and analysed for uranium ion concentration (Table 2).

**Effect of pH**

pH of the system has great effect on the solubility of metal ions and the concentration. The optimum pH value was found to be 5.5. The procedure was successfully applied to separate uranium ions from leachate samples.

**CONCLUSION**

GSS powder was an effective biosorbent for the adsorption of uranium from iron ore leachates. The biosorption capacity of GSS powder was superior due to the higher content of calcium groups. The effects of process parameters like pH, metal ion concentration, adsorbent concentration on process equilibrium were studied. The uptake of uranium ions by GSS powder was increased by increasing the metal ion concentration and the adsorbent concentration and decreased by increasing the adsorbent size. It was found that the equilibrium of the process was reached at 60 min. The detection limit of the method is 10 μg/mL. The optimum acidity for biosorption was found to be to be 4M. The entire adsorbed U(VI) could be eluted out by 0.01 M HNO₃.
**Table 1. List of sorption of heavy metal by microbial mass/biomass/Industrial waste**

<table>
<thead>
<tr>
<th>Biomass class</th>
<th>Biomass type</th>
<th>Metal</th>
<th>Metal uptake</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacterium</td>
<td>Bacillus biomass</td>
<td>Cr</td>
<td>118Cr3+ 60 Cr 6+</td>
<td>Brierley and Brierly, 1993</td>
</tr>
<tr>
<td>Yeast</td>
<td>Candida tropicalis</td>
<td>Cr</td>
<td>4.6</td>
<td>Mattuschka et al., 1993</td>
</tr>
<tr>
<td>Brown marine algae</td>
<td>Ascophyllum nodosum</td>
<td>Co</td>
<td>100</td>
<td>Kuyucak and Volesky, 1989</td>
</tr>
<tr>
<td>Brown marine algae</td>
<td>Ascophyllum nodosum</td>
<td>Cd</td>
<td>215</td>
<td>Holan et al.,</td>
</tr>
<tr>
<td>Biosorbent</td>
<td>Bacillus subtilis</td>
<td>Cu</td>
<td>152</td>
<td>Beveridge, 1986, Brierley et al, 1993</td>
</tr>
<tr>
<td>Bacterium</td>
<td>Bacillus biomass</td>
<td>Fe</td>
<td>107</td>
<td>Brierley and Brierley, 1993</td>
</tr>
<tr>
<td>Fungus</td>
<td>Rhizopus arrhizus</td>
<td>Hg</td>
<td>54</td>
<td>Tobin et al., 1984</td>
</tr>
<tr>
<td>Brown marine algae</td>
<td>Fucus vesiculosus</td>
<td>Ni</td>
<td>40</td>
<td>Holan an Volesky, 1994</td>
</tr>
<tr>
<td>Biosorbent</td>
<td>Bacillus subtilis</td>
<td>Pb</td>
<td>601</td>
<td>Brierley et al.,</td>
</tr>
<tr>
<td>Brown algae</td>
<td>Sargassum fluitans</td>
<td>U</td>
<td>520</td>
<td>Yang and Volesky, 1999</td>
</tr>
<tr>
<td>Biosorbent</td>
<td>Irish sphagnum moss peat</td>
<td>Cr(VI)</td>
<td>119.0</td>
<td>Sharma and Froster, 1993</td>
</tr>
<tr>
<td>Biosorbent</td>
<td>Sphagnum peat</td>
<td>Cu</td>
<td>40</td>
<td>Fattahpour Sedeh, 1996</td>
</tr>
<tr>
<td>Industrial waste</td>
<td>Activated red mud</td>
<td>Ni</td>
<td>160</td>
<td>Zouboulis and Kydros, 1993</td>
</tr>
<tr>
<td>Industrial waste</td>
<td>Bagasse fly ash</td>
<td>Cr(VI)</td>
<td>260</td>
<td>Gupta et al., 1999</td>
</tr>
</tbody>
</table>
Table 2. Study of different concentration of Uranium (VI) in µg/mL GSS added ~ 0.50 g

<table>
<thead>
<tr>
<th>Concentration µg/mL</th>
<th>Absorbance Before adsorption</th>
<th>Absorbance After adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.095</td>
<td>0.053</td>
</tr>
<tr>
<td>20</td>
<td>0.105</td>
<td>0.078</td>
</tr>
<tr>
<td>40</td>
<td>0.140</td>
<td>0.062</td>
</tr>
<tr>
<td>60</td>
<td>0.250</td>
<td>0.154</td>
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<tr>
<td>80</td>
<td>0.451</td>
<td>0.169</td>
</tr>
<tr>
<td>100</td>
<td>0.502</td>
<td>0.243</td>
</tr>
<tr>
<td>200</td>
<td>0.511</td>
<td>0.373</td>
</tr>
</tbody>
</table>

Table 3. Effect of pH on U(IV) biosorption by GSS

<table>
<thead>
<tr>
<th>pH</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of biosorption</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>45</td>
<td>85</td>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>
Figure 1. Experimental arrangement of column chromatography
Figure 2. Absorbance Vs Concentration of U (VI) μg/mL

Figure 3. Relative amount of uranium in samples ILA 1-8
References