APPLICATION STUDIES OF BIOSORPTION FOR MONAZITE PROCESSING INDUSTRY EFFLUENTS

T. R. Muraleedharan*
Indira Gandhi Institute of Development Research, Bombay - 400 065, India

Ligy Philip
Environmental Engineering Laboratory, Department of Civil Engineering, Indian Institute of Technology, Kanpur - 208 016, India

Leela Iyengar
Department of Chemistry, Indian Institute of Technology, Kanpur - 208 016, India

&

C. Venkobachar
Department of Civil Engineering, Indian Institute of Technology, Kanpur - 208 016, India

(Received 7 March 1994; revised version received 3 June 1994; accepted 7 June 1994)

Abstract

While studies on the potential of many biosorbents for heavy metal uptake have been reported, the results on scale-up are relatively scanty. Even in those papers where there is a report of reactor performance, more emphasis is given to the metal uptake part and the critical issue of headloss development in columns is not touched upon. This paper presents the results of a scale-up study conducted with an established biosorbent, Ganoderma lucidum, for uptake of rare earth elements. The uptake as well as the reactor characteristics are discussed.

Key words: Biosorption, rare earths, packed-bed reactor, head loss development.

INTRODUCTION

Biosorption, in which microbes are directed to accumulate metals from aqueous solutions, has emerged as a promising alternative technology in the last decade. From just a novel idea in the early eighties, biosorption has evolved into a commercial process in a short time. The undeniable fact that biosorption has become popular is exemplified by the fact that the Society of Chemical Industry (UK) considered it appropriate to organize a special conference for a realistic assessment of the commercial feasibility of this process (Eccles, 1990).

Rare earths is the name given to the following elements: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. For these elements, as the charge of the nucleus increases the balancing electron will fill in the inner incomplete 4f subshell. Since 4f electrons are well shielded by the 5s5p subshells, they play almost no role in the valency forces. All rare earths have three electrons in their valency shells, and, since these electrons are responsible for most physical and chemical properties, the rare earths closely resemble each other (Jorgerson, 1987).

All rare earths are metals; the misnomer 'earths' came out of a historical accident. The first observation concerning their existence was made by Arrhenius in 1794 (Szymanski, 1987), who reported the discovery of the earth yttrium, present in certain Swedish ores. During the eighteenth century, a number of oxides were isolated which were believed to be elements (Gschneidner, 1984). They had alkaline properties, and the scientists at that time were unable to melt them or observe any changes occurring in them when heated. Since yttrium resembled the common earths such as lime and alumina, it was referred to as a rare earth.

The three major minerals of rare earths are bastnasite, monazite and xenotime, of which the first two account for 95% of the rare earths being produced (Gschneidner, 1981). Bastnasites are fluorocarbonates; monazite and xenotime are rare earth phosphates. Monazite accounts for about 40% of the world...
utilization. India has significant deposits of rare earths in the form of beach sand. In the present study, the monazite processing industry is identified as an ideal site to verify the practical potential of the biosorption process, and hence a detailed description of the processing of monazite is warranted.

Monazite is a rare earth phosphate containing 5-10% of ThO₂, which presents some interesting problems associated with its processing and utilization. Since thorium is a fissionable material, it is removed and stockpiled before exporting rare earths. Because of the natural radioactivity of thorium, there are stringent environmental regulations for its processing.

The process effluent from rare earth processing contains heavy metals (Zn and Pb), phosphates, and fluorides, in addition to traces of the processed rare earth elements. In the Indian scenario particularly, since monazite contains thorium in addition to the rare earth elements, the process effluent will also contain traces of this radioactive nuclide. Because the concentration of the target elements are very low, conventional processes like chemical precipitation, etc., can not be economically or efficiently employed for the effluent treatment.

TOXICOLOGICAL INFORMATION

Rare earths belong to the category of heavy metals, whether taken from the electronic configuration point of view or the toxicity angle. However, not much information is available on the adverse environmental impacts of rare earths. This reflects the confined production and application of rare earths, rather than lack of detrimental effects. Rare earths can degrade DNA molecules (Eichborn, 1965) and have been reported to produce tumors at the site of interaction (Ball et al., 1970). Rare earths also bond with plasma proteins and accumulate in bones (Ando & Hisada, 1972). Lanthanum levels are consistently high in the blood of cancer patients, though a convincing direct cause-effect relationship is yet to be proved (Flessel et al., 1980).

BIOSORPTION IN RARE EARTH PROCESSING

Rare earth industry appears to be an ideal candidate for testing the biosorption process. First, the effluent consists of a mixture of elements, each of which is a pollutant and hence needs to be removed. Biosorbent is versatile, so a single adsorption bed can be employed for all the metals. Secondly, the effluent concentration of the elements is relatively small; thus, the traditional methods may not be cost-effective. Thirdly, the input to the industry is concentrated metallic solution, so the elements, if concentrated, can be directly pumped back into the process stream and no separate recovery unit is necessary. Most importantly, the rare earth industry is familiar with the ion-exchange process. As a result, the technology shock of introducing this new method will be minimal, unlike the case of metal processing or plating industries.

METHODS

Chemicals
All chemicals used were of analytical reagent grade. Rare earths used for the present study were of triple-nine (99.9%) purity grade, and were obtained from Indian Rare Earths Ltd (Udyogamandal, India).

Fungal fruiting bodies (mushrooms) for biosorption
Wood-rotting fungi grow prolifically in humid, temperate climates, and the maximum growth of fruiting bodies has been reported to be during the post-monsoon period (Smith, 1963). The mushrooms were therefore collected during the post-monsoon period (September–October) from forests in Kerala (India). The fruiting bodies were detached from the rotting wood, washed in water and sun-dried for two days before transporting to the laboratory.

Sample preparation for identification
Representative specimens from visibly different groups of mushrooms were soaked in 1% formaldehyde solution for 24 h to prevent biodegradation. These samples were then dried at 40°C for 24 h, packed in polyethylene bags and were despatched to the Royal Botanical Garden (Kew, UK) for identification.

Adsorbent preparation
Biosorbents were prepared from the mushrooms by pulverizing the fruiting bodies. Only particles between 1200 µm and 600 µm (geometrical mean size, 848 µm) were collected for adsorption study, as they facilitated easy handling.

Analysis of rare earth elements
Individual and mixed rare earth elements were analyzed using the colorimetric method developed by Onishi and Sekine (1972). A 15-ml sample of the rare earth was mixed with 50% ammonium acetate solution of 4 M hydrochloric acid to bring the pH to 3-0-3-5. Aqueous (0.1% w/v) Arsenazo III (1 ml) was added, and the volume made up to 25 ml. The absorbance was measured at 660 nm using a Systronics 106 (M/s Systronics, Ahmedabad) spectrophotometer. The calibration range was 0–20 mg/L. Qualitative analysis of the rare earths praseodymium and neodymium was done using a recording of UV-Vis spectrophotometer (Shimadzu, Japan) as suggested by Stewart and Kato (1958).

Head loss studies
Experiments to evaluate the head loss in a fixed-bed reactor were conducted using a 600-mm high bed. The column had five ports, connected to manometers, details of which are presented in Fig. 1. The flow rates were varied from 3 m³/m²/s to 17 m³/m²/s, and a constant head of 750 mm was maintained throughout.

Attrition studies
The physical breakdown of adsorbents in a packed bed adsorption reactor by both static and dynamic head is
to be evaluated. In case of excessive rupture of the adsorbent, head loss increases, and the advantage of bed reuse may not be available. To find out the degree of attrition in a dynamic condition, the column described previously was filled with a pre-weighed amount of biosorbent, which was retained in a 600-μm sieve. After allowing flow through the bed at a rate of 36 m³/m²/s (maximum flow possible at a head of 750 mm) for 24 h, the material was taken out, dried in an oven at 40°C and was sieved through a 600-μm sieve. The amount of adsorbent passed through the sieve was a measure of attrition and was reported as a percentage of the original.

**Bench scale columns for scaling-up**

Adsorption experiments were conducted in a number of fixed-bed reactors (down flow mode) employing mixed rare earth chloride as the adsorbate. Three 50-mm diameter columns, 300, 600 and 1200 mm long, respectively, were used to generate data for the bed-depth service time (BDST) model. The experimental setup with the flow arrangement is presented in Fig. 2. The influent concentration was maintained at 250 mg/l (as RCl₃) and buffered at a pH of 4.0 using acetate buffer at a flow rate of 1.018 m³/m²/h. The columns were run till exhaustion of the biosorbent capacity.

**Desorption studies**

Desorption experiments were conducted using a column of 50 mm diameter and 600 mm length. The influent consisted of 250 mg/l (as RCl₃) rare earth chloride, buffered at pH 4.0 with acetate buffer. After its exhaustion, the column was desorbed using 0.1 n HCl. After the adsorbed elements had been leached out, the column was thoroughly washed, using two bed volumes of distilled water, and the cycle was restarted.

**Studies with simulated effluent from monazite processing**

Effluent generated from the rare earth processing industry consists of traces of thorium and heavy metals (Cd and Zn), in addition to the rare earth elements. A typical effluent from a rare earth processing plant was simulated, composed as shown in Table 1. The effluent was passed through a column 1750 mm long with a 25-mm diameter at a rate of 1.018 m³/m²/h. The concentration of thorium and rare earths was monitored in the effluent and the column run was terminated upon exhaustion.

**RESULTS**

Adsorbents generally come into contact with adsorbates in packed-bed reactors. The same is true of ion exchange resins, where down-flow packed-bed reactors are the most common configuration. In view of the promising nature of G. lucidum, it was considered appropriate to conduct bench scale studies with packed-bed reactors in the down flow mode to evolve design criteria for the development of a prototype.

**Hydraulic loading and head loss**

In addition to the information on uptake potential, the possibility of metal recovery and the reuse of adsorbent bed, data regarding the operation of the fixed-bed reactor in terms of its hydraulic loading rate and development of head loss is also essential. Many biosorbents which gave excellent uptake potential in batch reactors were not amenable to fixed-bed operation and had to be immobilized, or complicated reactor configurations like pulse-bed reactors had to be employed (Volesky, 1987). In order to evaluate the behavior of G. lucidum for continuous flow operation, studies were conducted using a fixed-bed reactor.

The optimum flow rate necessary for best performance of the adsorption bed depends on the rate of uptake of the adsorbate from wastewater by the biosorbent. Both theoretical and experimental data support the contention that there are critical velocities for liquids passing through the porous bed which change.
Fig. 2. Column arrangement for the BDST model.

Table 1. Composition of mixed rare earths

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>23</td>
</tr>
<tr>
<td>Ce</td>
<td>46</td>
</tr>
<tr>
<td>Nd</td>
<td>05</td>
</tr>
<tr>
<td>Pr</td>
<td>20</td>
</tr>
<tr>
<td>Sm</td>
<td>04</td>
</tr>
<tr>
<td>Eu</td>
<td>02</td>
</tr>
<tr>
<td>Gd</td>
<td>02</td>
</tr>
<tr>
<td>Tb</td>
<td>02</td>
</tr>
<tr>
<td>Dy</td>
<td>02</td>
</tr>
<tr>
<td>Ho</td>
<td>02</td>
</tr>
<tr>
<td>Er</td>
<td>02</td>
</tr>
<tr>
<td>Tm</td>
<td>02</td>
</tr>
<tr>
<td>Yb</td>
<td>02</td>
</tr>
<tr>
<td>Lu</td>
<td>02</td>
</tr>
</tbody>
</table>

Fig. 3. Head loss in a downflow packed-bed adsorption reactor.

the nature of the resistance to diffusion. At low velocities, the solute content of the stagnant film surrounding the adsorbent will be depleted more rapidly than can be replaced by diffusion from the main body of the liquid. As the velocity is increased, a stage will be reached where the controlling rate will be the ability of the adsorbent to take up the adsorbate as rapidly as it is transported to the surface from the bulk liquid.

Column studies were conducted using the experimental setup presented in Fig. 1, with varying bed depths and flow rates to evaluate the head loss profile within the biosorbent bed. Tap water at flow rates varying from 3 m$^3$/m$^2$/h to 17 m$^3$/m$^2$/h was passed through the column at a fixed static head of 150 mm above the top of the column. Head loss values were measured at bed depths of 150, 300, 450 and 600 mm. The head loss profile determined by experimentation is presented in Fig. 3. At a flow rate suggested by the United States Environmental Protection Agency design manual for activated carbon absorption (EPA, 1973), <3-5 m$^3$/m$^2$/h, the head loss developed is only nominal. The head loss increased with the hydraulic loading rate. The experimental results indicate that within normal hydraulic flow rates the development of head loss is very gradual in columns packed with *G. lucidum*.

Attrition of biosorbents in packed-bed reactors

During the fixed bed operation, the biosorbent is subjected to extensive static and dynamic pressures. It is, therefore important to evaluate how effectively the biosorbent withstands this pressure. The physical breakdown of the biosorbent as a percentage of initial weight was found to be only 0.85% at a very high hydraulic flow rate of 36 m$^3$/m$^2$/h, indicating that the biosorbent was highly suitable for use in a packed-bed reactor.

Recovery of rare earths and reuse of column

Preliminary studies were conducted using a column with a 25-mm diameter and a length of 600 mm. The
column was packed with biosorbent and was challenged with a mixed rare earth chloride solution, buffered at pH 4.0 by 0.1 M acetate buffer. The column run was continued until complete exhaustion, at which time it was regenerated by 0.1 N HCl requiring a volume of 1/40th of the throughput (volume of effluent treated).

After desorption, the column was washed with tap water (2 bed volumes) and the adsorption cycle was restarted.

Figure 4 represents the results of two cycles of adsorption and desorption of mixed rare earths. While in the first cycle the column was run till \( C_e = C_o \) before desorption, the second cycle was terminated at breakthrough \( (C_e = 0.05C_o) \). It could be observed that there was no loss of capacity in the second cycle. The results clearly indicate the excellent potential of \( G. lucidum \) for deployment in a packed bed reactor for uptake and concentration of rare earths.

**Application of the BDST model**

Though the rational design of adsorption columns based on batch adsorption data and mass transfer coefficient is not impossible, it is desirable to carry out column studies to obtain empirical relationships for the design. One of the most widely used modes is the bed-depth service time (BDST) formulation (Benefield et al., 1982), which is a simplified form of the Bohart-Adams model based on surface reaction theory. Since the process of biosorption is chemical in nature, the use of this model may be appropriate.

According to the Bohart-Adams model, which is based on the surface reaction theory, the equation to find out the service time of a column is given as:

\[
t = \frac{N_o X}{C_o V} \ln \left[ \frac{C_o}{C_b} - 1 \right] \times \frac{K}{1/C_o} \tag{1}
\]

where,

- \( C_o \) = initial concentration of sorbate
- \( C_b \) = desired concentration of sorbate at breakthrough
- \( K \) = rate constant
- \( N_o \) = adsorptive capacity of sorbent
- \( X \) = depth of column bed
- \( V \) = linear flow velocity of feed
- \( t \) = service time of column.

The theoretical depth of adsorbent that is sufficient to prevent the effluent solute concentration from exceeding \( C_b \) at zero time is called the critical bed depth (length of mass transfer zone) and can be calculated by equating \( t = 0 \)

\[
X = \frac{V}{K N_o} \ln \left[ \frac{C_o}{C_b} - 1 \right] \tag{2}
\]

A series of three columns, each with an internal diameter of 50 mm and a varying height of 300, 600, and 1200 mm, respectively, was used for continuous flow studies. The influent was a mixed RC13 solution (composition as given in Table 2) and buffered to a pH of 4.0. Since no effluent standards have been fixed for rare earths, the occurrence of breakthrough was taken when \( C_e = 0.05C_o \). The flow rate maintained was 1.018 m³/m²/h, which falls within the flow rates in adsorption columns.

The time period for reaching breakthrough point for beds of different depths is plotted and presented in Fig. 5. The service time at breakthrough should be a linear function of bed depth if the flow rate and influent concentration are kept constant throughout the test. It can be observed from Fig. 5 that the linearity is maintained between the bed depth and the service time.

![Fig. 4. Regeneration and rescue of biosorbent for mixed rare earths.](image-url)
Table 2. Simulated effluent of monazite processing industries

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th⁴⁺</td>
<td>5</td>
</tr>
<tr>
<td>RCl₃</td>
<td>50</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>2</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>2</td>
</tr>
<tr>
<td>F⁻</td>
<td>40</td>
</tr>
<tr>
<td>PO₄⁻⁴</td>
<td>400</td>
</tr>
</tbody>
</table>

**For one concentration can be modified to be applicable for another concentration:**

\[ a' = (C_0/C_1) \times a \]  \( (7) \)

and

\[ b' = b + \frac{\ln\left(C_0/C_F - 1\right)}{\ln\left(C_0/C_F - \frac{C_0 K}{C_F}\right)} \]  \( (8) \)

where \( C_o \) and \( C_1 \) are the old and new influent concentrations and \( C_b \) and \( C_F \) the old and new effluent concentrations.

The curve developed and the constants evaluated can thus be employed for the design of adsorption columns over a range of feasible flow rates and concentrations.

**BIOSORPTION FOR TREATMENT OF MONAZITE PROCESSING EFFLUENTS**

Effluents emanating from rare earth processing industries represent one of the major sources of rare earth pollution. Because they are confined geographically to a few locations all over the world, in a small number of countries, and mostly under the direct control of the respective governments, pollution control from these industries has not yet been accorded the urgency it demands, despite the recorded evidence of the toxicity of these effluents to human beings.

India is one of the major rare earth producing countries, and deposits of rare earths are found on long stretches of beach along the western coast. The ore of rare earths in India is Monazite, a mixture of rare earths and thorium phosphate. The presence of thorium makes processing of this ore even more hazardous and the disposal of resulting effluents more difficult (Sarat, 1992). It is therefore appropriate to apply the process of biosorption to remove the rare earths from the liquid effluents and recover it as a resource.

Monazite processing wastewater was simulated in the laboratory composed as shown in Table 1. The waste consisted of significant amount of anions (fluoride and phosphate), traces of heavy metals (Zn and Pb), in addition to rare earths and thorium. The pH was maintained at 4.0 using acetate buffer. The simulated wastewater was passed through the column (50 mm ID) at a flow rate of 1.018 m³/m²/s.

As can be seen in the breakthrough curve presented in Fig. 6, the biosorbent \( G. \) lucidum could bring the concentration of both rare earths and thorium down to levels undetectable by the analytical methods employed (0.1 mg/l for thorium and 0.15 mg/l for RCl₃). The breakthrough curves for columns run only with thorium are presented in Fig. 7. Independent analysis of thorium and rare earths in the monazite processing effluent was not possible, as one interfered with the analysis of the other. The results highlight the potential of employing
the biosorption by *G. lucidum* as a plausible alternative effluent treatment strategy in rare earth processing. The advantages of biosorption over conventional techniques of the monazite industry effluent treatments are:

1. A single unit is necessary for removal of both thorium and rare earths. In the case of precipitation, a two-step process for removal of Th and rare earths, in two separate reactors, is needed, followed by processing in a solid-liquid separation facility.

2. The elements taken up could be desorbed using HCl and recycled back to the process stream. Alternatively, the biosorbent loaded with the toxic elements could be immobilized onto a cement concrete matrix for containment (similar to those employed in nuclear power plant effluents).

**CONCLUSIONS**

The study presented in the paper establishes the potential of the use of the biosorbent *Ganoderma lucidum* for the uptake of rare earth elements. The material was tested for its physical strength as well as its head loss behavior in a packed bed reactor and performed well in both cases. It was possible to desorb the elements adsorbed and reuse the material. Most interestingly, it was possible to use a single reactor for uptake of both rare earth elements and thorium emanating from the processing of monazite.

![Fig. 6. Breakthrough curve for monazite processing effluent.](image)

![Fig. 7. Breakthrough curve for thorium.](image)
REFERENCES


