Selective sorption of heavy metals using an iron-rich waste byproduct

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SELECTIVE SORPTION OF HEAVY METALS

USING AN

IRON–RICH WASTE BYPRODUCT

by

ANAND RAMESH

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Abstract

The decontamination of heavy metal laden wastewater is currently accomplished using processes like precipitation, coagulation/coprecipitation, activated carbon adsorption or ion exchange. Although these processes are very efficient as far as metal removal is concerned, there are many shortcomings which tend to diminish their overall cost–benefit. In this study, the viability of using an inexpensive iron–rich adsorbent to remove heavy metals is investigated. The adsorbent utilized in the study is a granular iron–rich material co–produced during the process of metal recovery from Electric Arc Furnace (EAF) dust. The co–product is primarily a mixture of iron oxide and calcium aluminosilicates. It is produced in large quantities in the U.S, and has been found to have metal removal capability, although the exact mechanism has not been identified. It has been given the trade name ECOSORB.

The primary objectives of this study were to identify the mechanism by which heavy metals are removed and to determine the metal uptake capacity of ECOSORB. An attempt was also made to regenerate the sorbent by desorbing heavy metals from the exhausted sorbent, enabling the sorbent to be disposed off as a non–hazardous or permitting possible re–use of the sorbent. Apart from this, experiments were concurrently conducted using a chelating ion–exchange resin, namely IRC–718, to compare metal uptake of the iron–rich sorbent with that of an exchanger.

The fixed bed column runs performed with ECOSORB indicate a metal removal capacity comparable to that of commercially available chelating exchangers. The experiments also proved that ECOSORB has high selectivity
towards the bivalent transition metal cations like cadmium, nickel, copper and lead. The study indicated that ion–exchange accompanied by Lewis acid–base interaction is the possible underlying mechanism responsible for the high metal–ion affinity of ECOSORB. The predominant removal mechanism depends on the type of metal ion, concentration of metal ions, pH of solution and other factors; at low metal ion concentration, adsorption/ion exchange is the primary removal mechanism. As metal concentration increases both adsorption and precipitation become important and, at very high concentrations, precipitation dominates the sorption process.

Regeneration of spent ECOSORB with chelating agents and acid resulted in about 50% recovery. Batch tests performed on regenerated ECOSORB showed that ECOSORB loses its metal sequestering property on regeneration.

The experimental results obtained in this study indicate that ECOSORB is a viable alternative to the more expensive chelating polymers and biosorbents for the selective removal of heavy metals.
1.1 HEAVY METALS AND THEIR ENVIRONMENTAL IMPACT

Greater awareness of the ecological effects of toxic metals released into the environment, together with increasing value of some of these metals, has resulted in a concerted effort to develop better technology for the recovery of these metals from industrial discharges. In particular, the removal from wastewater, of a group of trace elements which are known somewhat arbitrarily as "heavy metals", has received a lot of attention.

The term "heavy metals" is misleading because these elements are not all "heavy" in terms of atomic weight, density or atomic number, and they are not even entirely metallic in character. As a rough generalization, the "heavy metals" may be said to include all metals of the Periodic Table between Groups IVA and VIII, such as lead, copper, cadmium, zinc, nickel, mercury and many others [1]. Although there may be some equivocalness in the exact definition of heavy metals, there is certainly no equivocalness about its toxicity.

It has been well established that most heavy metals, even when present at trace levels, are extremely toxic. Previously, a toxicity limit called the "threshold toxicity" had been evaluated for many metals and was defined as the concentration...
above which a metal began to have a deleterious effect. Continued release of metal laden wastes into the environment was justified on the basis of dilution to undetectable levels or to levels below the “threshold toxicity” value in the receiving water body. Subsequent research has ascertained that some metals tend to accumulate to higher concentrations in the food chain, thus increasing its potency and ultimately endangering human health. This phenomenon is called bioaccumulation. Consequently, regulatory agencies have established extremely low allowable concentrations of these metals in effluent discharges to receiving waters. The ultimate aim of the regulatory agencies is to establish a zero pollutant discharge level for some of these metals. Although treatment technology does exist for achieving these increasingly stringent effluent quality criteria, it is the lack of an economically viable process, which has prevented any headway being made towards implementation of the ‘zero pollutant discharge rule’ [2]. At present the maximum allowable levels of heavy metals in treated wastewater ranges between 1.0 and 5.0 mg/l.

The main source of heavy metal wastes are the metal processing, finishing, and plating industries. Apart from these, the wastewater from the accumulator industry, industrial photographic laboratories and printing plants are also major sources of heavy metals in the environment.

Apart from the environmental threat posed by the presence of these heavy metals in the environment, the other major reason for increased demand for the removal of metals from industrial effluents, is the economic value of some of these heavy metals. Industries can substantially increase the efficiency of their production process by recovering these precious heavy metals from the wastewater and subsequently reusing the reclaimed heavy metals.
1.2 REMOVAL PROCESSES AND SHORTCOMINGS

Conventional physicochemical methods for removing heavy metals from wastewater include chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, membrane technologies, and evaporation recovery. Although most of these processes are efficient as far as metal removal is concerned, there are many shortcomings which tend to diminish their overall cost benefit [3].

Specifically, processes like precipitation and coagulation/coprecipitation produce unwieldy amounts of sludge, the cost of disposal of which has increased considerably in recent years. These processes may also be ineffective when the metals are in solutions containing in the order of 1 to 100 mg/l of dissolved metals.

The main drawback of the ion–exchange process is the high capital required to set up such units. The ion–exchange process also becomes uneconomical when the solution to be treated contains very high concentration of heavy metals. Another significant shortcoming of ion exchangers is that their utility is restricted to treating purely aqueous solutions. The process has not been applied successfully to slurry reactors because the extremely small size of the ion–exchange beads makes it difficult to recover the expensive ion–exchanger beads from the rest of the suspended solids. Although several modifications have been made to conventional reactor configurations in an attempt to circumvent this problem, none of them have been put to commercial use.

A direct result of the lack of a perfect treatment process has been the constant upgrading of existing technology and the development of new technology for treating heavy–metal laden wastewater. One area which has received
considerable attention in recent years has been that of metal-sequestering adsorbents. The adsorption of heavy metals by various substrates has been the subject of many studies over the years. Oxides of iron, aluminium and silicon have been shown to be strong adsorbents of a host of metal ions in laboratory studies, but these properties have not been properly exploited in practice to a significant extent. These hydrous oxides are dominant sorbents in nature because of their tendency to be finely dispersed and to coat other particles. This has been recognized and studied for at least 100 years, mostly by soil scientists. In the past quarter century there has been increasing interest in the sorptive properties and surface chemistry of hydrous oxides by researchers in other fields. This has resulted in significant advances in the understanding of the mechanisms involved in the sorption of chemicals, particularly inorganic species, on hydrous oxides. It has been well established that the interactions involved in the sorption of metal ions on hydrous oxide surfaces is a combination of physisorption, chemisorption, ion exchange, surface complexation and surface precipitation [4].

In the present research endeavor, the use of an inexpensive adsorbent which has the ability to remove metals from aqueous solutions is investigated. The adsorbent in question is an iron-rich material produced during the process of metal recovery from Electric Arc Furnace (EAF) dust. It has been given the trade-name ECOSORB and will be referred to by this name throughout this report. A description of the adsorbent and the process by which it is produced is delineated in the next chapter.
1.3 PREMISE OF THE STUDY

The toxic nature of heavy metals makes it imperative to remove them from wastewater to the maximum extent possible, before discharging the wastewater into the environment. Currently available treatment technology has limitations which this study attempts to overcome by proposing a cost-effective and reliable method of treatment.

All industrial wastewaters contain in addition to heavy metals, innocuous substances, which are present at concentrations several orders of magnitude greater than the toxic metals. The aim of any treatment process should be to selectively remove these target contaminants without necessarily altering the innocuous substance concentration.

The study envisages using the iron-rich adsorbent in a process arrangement identical to that used for conventional adsorbents, that is, in a fixed bed process. Commonly used sorbents such as ion exchange resins, activated carbon and activated alumina are either too expensive or not effective with respect to heavy metal removal.

The adsorbent used in this study, being the residue of the material from which cadmium, zinc and lead are recovered, does contain these metals in the solid phase, albeit at low levels. The standard leachability test (TCLP) was performed on ECOSORB and the results have proved the non-leachability of these heavy metals from ECOSORB. On this basis, virgin ECOSORB can be classified as a non-hazardous material [5].

ECOSORB has very high natural basicity. It imparts alkalinity to any solution with which it is equilibrated, resulting in an increase in pH. If this solution contains
a high concentration of heavy metals, immediate precipitation of heavy metals is triggered. Thus the adsorbent can act simultaneously as both a precipitator of heavy metals as well as a filter. The aforementioned scenario is applicable only when heavy metals are present at concentrations high enough for precipitation to occur. But, if heavy metals are present at concentrations below their solubility limits (as would be the case in groundwater contaminated with heavy metals), the high basicity of ECOSORB alone would not ensure complete heavy metal removal. Therefore, it is important to ascertain whether ECOSORB is capable of removing heavy metals when they are present at relatively low concentrations. For this reason, the primary aim of this study was to determine whether mechanisms other than precipitation were responsible for heavy metal removal.

1.4 OBJECTIVES OF THE STUDY

The primary objective of this study was to identify an inexpensive sorbent for the selective removal of heavy metals from aqueous solutions. With the proven carcinogenicity and toxicity of heavy metals, a need for a reliable and cost-effective treatment method has been well recognized.

The study had the following objectives:

1. Checking the ability of ECOSORB to remove heavy metals and ascertaining the mechanism or mechanisms by which this removal occurs.

2. Studying the effect of pH and competing ion concentration on the uptake capacity of ECOSORB.

3. Comparing the performance of ECOSORB with that of a commercially available chelating ion-exchanger.
4. Studying the possibility of desorbing heavy metals from the spent adsorbent and exploring the potential for multiple reuse of the adsorbent.

5. Quantifying uptake capacity of ECOSORB in terms of meq/gm of adsorbent.
Chapter 2

ECOSORB

2.1 BACKGROUND

The emergence of Electric Arc Furnaces (EAF) for the production of steel from recycled ferrous scrap has resulted in the global production of more than one million tons of metal-laden dust annually. In addition to ferrous-type metals, the electric arc furnace dust (EAF dust) contains significant quantities of zinc, lead and cadmium volatalized during the steel-making process. With increased use of galvanized steel in durable goods, automotive and construction industries, significant growth in the generation of high zinc EAF dusts has occurred, as scrap material from these sources is eventually recycled. Because many of the contained heavy metal oxides are water leachable, the U. S. Environmental Protection Agency (USEPA) has listed EAF dust as a hazardous waste after Congress amended the Resource Conservation and Recovery Act (RCRA) in 1980. Regulations developed by the EPA will ultimately prohibit landfilling of EAF dust unless the material is first processed using the Best Demonstrated Technology. As a result, it will become the norm to process EAF dust before disposal. The Waelz Kiln, a high-temperature, thermal processing technology, has been specifically recognized by the EPA as a Best Demonstrated Available Technology. Using this process, a substantial amount of zinc, cadmium and lead is recovered from the EAF dust [6]. A schematic of the
Waelzing process is shown in Fig. 2–1. The scanning electron micrograph of EAF dust shows a fairly porous structure with each particle appearing to be an agglomerate of smaller particles (Fig. 2–2).

A coproduct of the Waelzing of EAF dust is an iron–rich material (IRM) which is virtually free of lead, cadmium and zinc and which exhibits no hazardous characteristics. Horsehead Resource Development, Inc. (HRD), a subsidiary of Zinc Corporation of America, has been studying possible uses of this iron–rich material. This iron–rich material (IRM) has been given the trade name ECOSORB and will be referred to by this name in this report.

2.2 CHARACTERIZATION OF ECOSORB

ECOSORB is a granular product, consisting of a porous matrix of uniformly distributed lime, silica, carbon and iron and manganese oxides. Its physical characteristics are listed in Table 2–1 and its chemical composition is given in Table 2–2 [5]. Electron micrographs of granules of virgin ECOSORB at different
magnifications are shown in figure 2-3. The electron micrographs show a heterogeneous structure with large number of pores. Every particle appears to be an aggregate of many micro-particles. The unusual porous structure of ECOSORB, its high surface area and relatively high void volume provide unique properties to this material and make it amenable to treating aqueous solutions by simple column percolation [5].

Table 2–1: Physical Properties

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Area</td>
<td>9.7 m²/g</td>
</tr>
<tr>
<td>Pore Volume</td>
<td>25 %</td>
</tr>
<tr>
<td>Median Pore Distribution</td>
<td>4 µm</td>
</tr>
<tr>
<td>Void Volume</td>
<td>-41.2 %</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>1.49 g/cc</td>
</tr>
</tbody>
</table>

Table 2–2: Chemical Composition

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>28.2</td>
</tr>
<tr>
<td>Ca</td>
<td>10.7</td>
</tr>
<tr>
<td>Mg</td>
<td>2.6</td>
</tr>
<tr>
<td>Si</td>
<td>8.4</td>
</tr>
<tr>
<td>Zn</td>
<td>4.2</td>
</tr>
<tr>
<td>Mn</td>
<td>3.6</td>
</tr>
<tr>
<td>Al</td>
<td>3.6</td>
</tr>
<tr>
<td>Pb</td>
<td>0.18</td>
</tr>
<tr>
<td>Cu</td>
<td>0.62</td>
</tr>
<tr>
<td>Ni</td>
<td>0.12</td>
</tr>
<tr>
<td>Ti</td>
<td>0.17</td>
</tr>
<tr>
<td>Cr</td>
<td>0.31</td>
</tr>
<tr>
<td>Na</td>
<td>0.55</td>
</tr>
<tr>
<td>K</td>
<td>0.31</td>
</tr>
</tbody>
</table>
Figure 2-2: Scanning electron micrograph of EAF dust at (a) 1000x and (b) 10000x
Figure 2–3: Scanning electron micrographs of (a) virgin ECOSORB (1000x) and (b) the porous structure under larger magnification (20000x)
2.3 POTENTIAL USES OF ECOSORB

A number of uses have been found for this iron–rich material. Among the more conventional applications are as a road base and as an anti–skid material to control icy winter road conditions. Other uses under investigation are as a source of iron in the manufacture of Portland cement, as an aggregate in highway blacktop, and as a source of iron and manganese in steel production. The most innovative use developed is as an environmental scavenger of heavy metals from contaminated solutions. This invention, for which a patent has been obtained by Horsehead Resource Development Company, Inc., has already demonstrated, in initial testing, its efficacy in removing heavy metals from solutions [6].

2.4 INVESTIGATIONS BY HRD, INC.

Horsehead Resource Development, Inc., based in Palmerton, PA conducted preliminary tests on the by–product from the Waelzing process and discovered that this iron–rich material had an uncanny ability to remove heavy metals from solutions. The experiments involved passing a metal laden solution through a column containing ECOSORB and monitoring the effluent metal concentration. Although substantial metal removal was achieved no conclusions could be drawn about the removal mechanism because of the manner in which the experiment was conducted. The feed solution used in the experiments contained metals at concentrations of 1000 ppm. Since ECOSORB has very high inherent basicity, the effluent pH was always above 8 in all the experiments, resulting in precipitation of the metal hydroxides. ECOSORB's role could very well have been that of an alkalinity providing agent and a filtering aid. If this was indeed the case, its utility would be restricted to treating solutions high in heavy metal concentration, where
as, at present, the need is for inexpensive adsorbents capable of treating solutions containing heavy metals in the 1 to 50 parts per million (ppm) range. As mentioned earlier, one of the primary aims of this study was to determine whether ECOSORB was capable of scavenging metal ions present at levels below their solubility limits [5].
Chapter 3

EXPERIMENTAL PROCEDURE

3.1 MATERIALS: ADSORBENTS AND REAGENTS

The process by which the adsorbent used in this study (ECOSORB) is prepared has been described in the previous chapter. Before using the iron–rich material (ECOSORB) provided by HRD, Inc. in the experiments, it was sieved using ASTME–11 specification sieves. The material in the 0.6mm to 0.355mm particle size range (20–50 mesh) was used in all the experiments involving ECOSORB. This is generally the size range of conventional ion–exchange resins. All experiments involving ECOSORB were performed using this material.

A widely used chelating ion–exchanger, IRC–718, was used in this study to compare the performance of ECOSORB with that of a commercially available chelating ion–exchanger. The functional group of this resin is \(-\text{N}(\text{CH}_2\text{COOH})_2\); and is analogous to ethylene diamine tetra–acetic acid (EDTA). The idealized structure of this resin is shown in Figure 3–1. IRC–718 has iminodiacetate functionality, which makes it a very good sequesterer of bivalent and trivalent transition metals. The exchanger was used in the spherical bead form with an effective diameter of approximately 0.5 mm. The resin was conditioned by exhaustion with 2% sodium hydroxide. After conditioning, the resin was washed with distilled deionized water.
All metal-laden solutions used in the experiments were synthesized in the laboratory using analytical grade chemicals obtained from Fisher Chemical Co. pH adjustments were made using either aqueous NaOH (prepared from NaOH pellets) or H₂SO₄. Deionized water, obtained by passing distilled water through an ion exchange column (Barnstead ion-exchange column), was used in all experiments, starting from preparation of aqueous solutions to dilution of samples for analyses.

### 3.2 FIXED BED COLUMN RUNS

Fixed bed column runs were performed to determine ECOSORB's metal uptake mechanism(s) and to compare its metal uptake capacity with that of a commercially available chelating ion exchanger, namely IRC-718. The column runs with ECOSORB and IRC-718 were performed using glass columns of internal diameter 11 mm and 9mm respectively. The feed solution was pumped through the sorbent bed in an upflow manner using a positive displacement pump. The influent was pumped through the column in an upflow direction because of better gradation of the bed obtained by operating the column in an upflow manner. The experimental
Figure 3–2: Experimental Set-Up for Column Experiments
set-up is shown in figure 3–2. A flow rate of 2 cc/min was employed for both column runs. The hydrodynamic conditions for the column runs were not identical because of the different internal diameters of the two glass columns used in the experiments. The effluent from each column was passed through an on-line pH-meter before being collected in 25 ml test-tubes using an interval-stepping fraction collector (ISCO Cynget Fraction Collector). In the column run with ECOSORB, the bed was divided into an upper and lower layer using glass wool. Each layer consisted of 7 g of ECOSORB. This arrangement of adsorbent in the column was adopted in order to test for occurrence of elution of heavy metals from the spent ECOSORB. Deductions can be made about the occurrence or extent of elution from the bed by regenerating the upper and lower layers separately and comparing the mass of metal ions that was obtained from each layer. Partitioning of the bed was not done for the column run with IRC–718.

Apart from the aforementioned column runs, an experiment was also performed to compare ECOSORB’s acid neutralizing capacity with that of CaCO₃. Amorphous CaCO₃ was placed in a column in an arrangement similar to that described earlier for IRC–718, except that glass beads were interspersed with the amorphous CaCO₃ particles to reduce the high pressure drop that would normally occur if solution were to be pumped through a bed containing only amorphous CaCO₃ particles.

The spent ECOSORB was removed from the column, washed with distilled water, oven-dried and then divided into portions; each portion being regenerated with a different eluting agent. The eluting agents used were oxalate, ethylenediamine tetra-acetate (EDTA) and 2% nitric acid. The spent regenerant
was then analyzed for various metal ions to compare the recoverability of metals from spent ECOSORB and probable re-use of the regenerated ECOSORB.

Apart from these column runs, a fixed bed column run was also conducted with ECOSORB as the adsorbent and distilled water as the adsorbate. The process arrangement used was very similar to that used for the other column runs except that a glass column of 25mm internal diameter and distilled water was pumped through the bed at a rate of 50 cc/min.

3.3 BATCH EXPERIMENTS

A batch test was conducted to identify the cationic and anionic species which solubilize when ECOSORB is equilibrated in de-ionized (DI) water. This was done by equilibrating 50g of ECOSORB with 1 l of DI water in a beaker and analyzing the supernatant solution for various cations and anions.

A batch test was also conducted to determine whether the regenerated metal–loaded ECOSORB (regenerated by passing an acidic solution through a fixed–bed containing spent ECOSORB) could sustain its metal–sequestering capability. This was accomplished by equilibrating acid–regenerated ECOSORB with a spiked solution of 50ppm Ni(II). Once again, the admixture was allowed to equilibrate for 24 hours before extracting the supernatant solution for analysis.

In order to quantify ECOSORB’s acid neutralizing capacity, 50 g of ECOSORB equilibrated in 1 l DI water in a plastic container, was titrated with 2% nitric acid. Acid was added to the container in 10 ml steps, shaken vigorously and the pH measured. This process was repeated until the pH of the supernatant dropped to about 7.5.
The temperature during all the tests was the ambient room temperature of 25 ± 0.2°C.

3.4 ANALYTICAL METHODS

Metal and calcium concentrations were determined with an atomic absorption spectrophotometer (Perkin Elmer Model 2380) using either a flame or graphite furnace accessories. Sodium and anion analyses were done with the aid of a Dionex ion chromatograph (model 4000i). Aluminum and silica analyses were performed using a spectrophotometer (Perkin–Elmer Model Lambda 2) [7]. All pH measurements were taken using a standard polymer–body liquid filled combination electrode using a Fisher Accumet model 930 pH meter.
Chapter 4

RESULTS AND DISCUSSION

In this chapter, the results of experiments performed using ECOSORB, IRC-718 and CaCO₃ as adsorbents will be discussed.

4.1 BATCH EXPERIMENT USING ECOSORB

The elemental composition of ECOSORB in the solid phase has been given in Table 2-2; but the percentage distribution of elements in a solution equilibrated with ECOSORB will be different from the solid phase elemental composition. In order to identify the constituents of ECOSORB that solubilize on equilibration with water, a batch test was conducted in which 50 g of ECOSORB was equilibrated with deionized water for 48 hours. The supernatant was filtered and analyzed for various anionic and cationic species using ion chromatography and atomic absorption spectroscopy. The results are tabulated in table 4-1.

In any aqueous solution the total number of equivalents of anions should be equal to the total number of equivalents of cations for electroneutrality to be maintained. From table 4-1, it is evident some anionic species are unaccounted for. X-ray diffraction studies performed on ECOSORB revealed the presence of calcium aluminosilicates as one of its constituents [5]. Based on this fact, the supernatant was analyzed for silica. Analysis by spectrophotometry indicated the presence of substantial quantities of silica in the supernatant. Although the supernatant tested
positive for silica there was some uncertainty about whether silica desorbed from the glassware in which the experiment was conducted, especially since the pH of the supernatant was above 10 (dissolution of silica is substantial at alkaline pH). A similar batch test was performed using a plastic container. Analysis of the supernatant from this test also gave positive results for presence of silica, albeit at lower levels than previously detected. Analyses for heavy metals were not conducted because of the low solubility of heavy metals at alkaline pH.

Table 4–1: Ions present in solution after equilibration of ECOSORB with DI water

<table>
<thead>
<tr>
<th>CATIONS</th>
<th>mg/l</th>
<th>meq/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>46</td>
<td>46/20</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>1</td>
<td>1/14</td>
</tr>
<tr>
<td>K$^{+}$</td>
<td>44</td>
<td>44/39</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>Na$^{+}$</td>
<td>140</td>
<td>140/23</td>
</tr>
<tr>
<td>TOTAL:</td>
<td>9.6</td>
<td>meq/l</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ANIONS</th>
<th>mg/l</th>
<th>meq/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^{-}$</td>
<td>5</td>
<td>5/35.5</td>
</tr>
<tr>
<td>F$^{-}$</td>
<td>2.8</td>
<td>2.8/19</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>400</td>
<td>400/48</td>
</tr>
<tr>
<td>TOTAL:</td>
<td>8.62</td>
<td>meq/l</td>
</tr>
</tbody>
</table>
4.2 COLUMN RUN WITH ECOSORB

To determine the metal uptake capacity and the mechanism by which metal removal occurs, experiments were performed using the experimental set-up illustrated in figure 3–2. ECOSORB was placed in two layers separated by glass wool in a glass column of 11 mm internal diameter. The total bed depth was 10 cm. A synthetic solution with the composition given in Table 4.2 was passed through the column in an upflow direction at a rate of 2cc/min.

The feed solution was prepared from the nitrate salts of the respective metal ions to minimize the effect of complexation (nitrate is an extremely poor ligand). Sodium in the nitrate form was added to the feed solution at a relatively high concentration to study the specificity of metal ion uptake by ECOSORB in the presence of a competing ion (sodium in this case). The heavy metal concentration in the feed solution was kept low to avoid metal hydroxide precipitation (refer to Appendix A). Since ECOSORB has very high acid neutralizing capacity, a very high metal concentration in the feed solution would result in hydroxide precipitation dominating the sorption process and consequently obscuring the effect of other removal processes (In general, the carbonates of these metals are the governing solid phase but in this case it was assumed that solubility was controlled by the hydroxyl species. This assumption is based on the fact that the carbon content of ECOSORB is negligible (refer to table 2–2)). Besides, fixed-bed processes are most often utilized to treat wastewater containing metals at levels at which removal by precipitation would be ineffective. Therefore, it is imperative to ascertain whether ECOSORB's is able to sequester metals when these metals are present at low concentrations. Another advantage of maintaining low aqueous phase metal concentrations is that the metal ions can be treated as a trace species. Under this
condition, the competition among metal ions for the same active sites on the sorbent can be ignored. This would simplify modelling of the sorption process.

Table 4–2: Composition of Feed Solution for Column Runs with ECOSORB and IRC–718.

<table>
<thead>
<tr>
<th>Feed Solution Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
</tr>
<tr>
<td>Cd, Pb, Ni</td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>pH</td>
</tr>
</tbody>
</table>

Figure 4–1 shows the effluent history for the aforementioned column run.

The observations made from the column run are listed below:

- Almost complete metal ion removal is achieved up to 5000 bed volumes. This combined with the fact that Ni, Cd and Cu are present at levels below their hydroxide solubility limits in the influent, indicates that apart from precipitation, there are other mechanisms responsible for ECOSORB’s high metal uptake capacity.

- The high metal removal efficiency achieved with an EBCT of just under 4 minutes indicates that metal uptake by ECOSORB is an extremely rapid process.

- Based on the order in which breakthrough occurs, the selectivity sequence or binding strength of metals onto ECOSORB in increasing order is as follows:

  Lead > Copper > Nickel > Cadmium (at pH 4.0)
Figure 4-1: Sorption of Metal(II) Ions on ECOSORB.

SLV, superficial liquid velocity; EBCT, empty bed contact time

$C$, effluent concentration; $C_0$, influent concentration
Figure 4-1: Sorption of Metal(II) ions on ECOSORB.

- SLV, superficial liquid velocity
- EBCT, empty bed contact time
- C, effluent concentration
- C₀, influent concentration

<table>
<thead>
<tr>
<th>INFLUENT:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(II)    : 2.0 mg/l</td>
</tr>
<tr>
<td>Cd(II)    : 2.0 mg/l</td>
</tr>
<tr>
<td>Pb(II)    : 2.0 mg/l</td>
</tr>
<tr>
<td>Cu(II)    : 0.1 mg/l</td>
</tr>
<tr>
<td>Na        : 250 mg/l</td>
</tr>
<tr>
<td>pH        : 4.0</td>
</tr>
<tr>
<td>EBCT      : 3.9 min</td>
</tr>
<tr>
<td>SLV       : 1.26 m/hr</td>
</tr>
</tbody>
</table>
Figure 4-2: Scanning Electron Micrograph of (a) Virgin Ecosorb (10000x) and (b) Metal loaded Ecosorb (10000x)
This result is in agreement with the selectivity sequence obtained by other researchers for adsorption onto iron oxyhydroxides [8,9]. Thus, at pH 4.0, lead is the most preferred species and cadmium is the least preferred species.

Heavy metal removal is achieved in the presence of high background concentration of sodium ions. This shows that ECOSORB has the ability to selectively remove target contaminants (heavy metals) in the presence of high alkali earth metal concentration. This property of ECOSORB would make it a viable alternative to conventional adsorbents because most toxic wastes usually contain substantial amounts of innocuous dissolved solids which need not be removed during the treatment process. For this particular fixed bed column run, the metal uptake capacity of ECOSORB was determined to be 0.69 milliequivalents per gram of ECOSORB (Table 4–3). This value compares favorably with the uptake capacity of conventional cation–exchangers which is generally about 1.0 milliequivalent per gram of dry resin.

Table 4–3: Metal Uptake Capacity of ECOSORB

<table>
<thead>
<tr>
<th>Metal</th>
<th>Total Metal Uptake (mg)</th>
<th>Uptake Capacity (mg/gm of ECOSORB)</th>
<th>Uptake Capacity (meq/gm of ECOSORB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>98.6</td>
<td>7.05</td>
<td>0.125</td>
</tr>
<tr>
<td>Ni</td>
<td>123.2</td>
<td>8.80</td>
<td>0.300</td>
</tr>
<tr>
<td>Cu</td>
<td>12.65</td>
<td>0.90</td>
<td>0.030</td>
</tr>
<tr>
<td>Pb</td>
<td>338.8</td>
<td>24.2</td>
<td>0.235</td>
</tr>
</tbody>
</table>

\[ \text{Total uptake Capacity} = 0.69 \text{ meq/gm of Ecosorb} \]
The effluent history pattern for cadmium and copper show that for a short period of time these metals appear in the effluent at concentrations higher than that in the influent. This phenomenon of chromatographic elution occurs only when ion-exchange takes place. To be more specific, when two ions A & B partake in an ion-exchange reaction, the ions for which the exchanger has greater affinity occupy the active sites on the exchanger, taking the place of ions on the surface with lesser binding strength. The ions which are desorbed from the exchanger will eventually appear in the effluent. The relative affinity of an exchanger for specific ions is quantitatively expressed in terms of a separation factor $\alpha_{AB}$. This parameter is defined as:

$$\alpha_{AB} = \frac{\lambda_A}{\lambda_B}$$

where $\lambda_A$ and $\lambda_B$ are the distribution coefficients of the two species.

The distribution coefficient of each species is defined as the ratio of the concentration of the species in the solid and liquid phase. If $\alpha_{AB}$ is greater than unity, it indicates that solute A is preferred over solute B by the sorbent, which in this case is ECOSORB. Table 4–4 gives the separation factor of the metal ions investigated with respect to cadmium ($\alpha_{MCd}^Me$) at pH 4.0 (refer to Appendix B for detailed calculations). From the values obtained, it can be concluded that ECOSORB has greatest affinity for lead, and least affinity for cadmium.

**Table 4-4 : Separation factor of Metals with respect to Cadmium for ECOSORB (at pH 4.0).**

<table>
<thead>
<tr>
<th>Metal (Me)</th>
<th>Distribution Coefficient $\lambda_{Me}$</th>
<th>Separation Factor $\alpha_{Cd}^Me$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>3500</td>
<td>1.00</td>
</tr>
<tr>
<td>Ni</td>
<td>4400</td>
<td>1.25</td>
</tr>
<tr>
<td>Cu</td>
<td>9050</td>
<td>2.57</td>
</tr>
<tr>
<td>Pb</td>
<td>12100</td>
<td>3.44</td>
</tr>
</tbody>
</table>
Although the phenomenon of chromatographic elution is sufficient proof of the occurrence of ion-exchange in the metal sequestering process, it is difficult to pinpoint which specific ions on the ECOSORB surface are being exchanged for the metal ions. Based on the fact that a substantial amount of dolomitic limestone is added to condition EAF dust, one could surmise that the surface exchange ions are mainly alkaline or alkali earth metal ions like Na⁺, K⁺ or Ca²⁺. Additional experiments have to be conducted to identify specifically the exchangeable ions present at the active sites on ECOSORB.

Efﬂuent pH remains higher than the inﬂuent pH even after passing close to 24000 bed volumes of pH 4.0 feed solution (Figure 4–3). This proves that ECOSORB has immense acid neutralizing capacity and more importantly, is able to sustain this acid neutralizing capacity by the slow release of hydroxyl ions. X-ray diffraction studies of ECOSORB revealed the presence of calcium aluminosilicates. These aluminosilicates have been known to undergo incongruent dissolution reactions which result in the release of cations and silic acid. It involves transformation of a mineral to a secondary mineral (reaction product) with a corresponding increase in the alkalinity of the dissolved phase. This process may be represented as:

\[ \text{Cation Al silicate(s)} + \ H_2O \rightarrow \ H_4SiO_4 + \text{Cation + Al silicate(s)} + \text{OH}^- \]

As a result, alkalinity is imparted to the dissolved phase. The rate of this reaction is very slow. ECOSORB's ability to impart alkalinity to large volumes of wastewater can be attributed to the slow release of OH⁻ ions [10,11].

Even though the metal ion concentration in the feed solution was maintained at a low level to avoid hydroxide precipitation on the adsorbent, the formation of precipitates in the bed was discernible. Of the four metal ions used in
this study, lead was the least soluble. At a pH of 8 its solubility was only 0.01 mg/l (Appendix A). The yellowish–white precipitate deposited on the bed could be either Pb precipitates or the product of incongruent dissolution. Figure 4–2 compares Scanning Electron Micrographs (SEM) of virgin and exhausted ECOSORB. Compared to virgin ECOSORB, there is a clear reduction in the pore volume in the exhausted ECOSORB. This filling up of the voids could be due to the formation of precipitates.

Figures 4–4 & 4–5 show effluent pH and effluent metal ion concentration as functions of the number of bed volumes passed. It is observed that metal removal occurs even after the effluent pH has dropped to around 6.0. This is additional proof that precipitation alone is not responsible for heavy metal removal.
Figure 4-3: Effluent pH as a function of bed volumes passed for the ECOSORB column run
Figure 4-3: Effluent pH as a function of bed volumes passed for the ECOSORB column run
Figure 4-4: Effluent Pb concentration and effluent pH as functions of the number of bed volumes passed.
Figure 4-4: Effluent Pb concentration and effluent pH as functions of the number of bed volumes passed
Figure 4-5: Effluent Cu concentration and effluent pH as functions of the number of bed volumes

**INFLUENT:**
- Ni(II) : 2.0 mg/l
- Cd(II) : 2.0 mg/l
- Pb(II) : 2.0 mg/l
- Cu(II) : 0.1 mg/l
- Na+ : 250 mg/l
- pH : 4.0
- EBCT : 3.9 min
- SLV : 1.26 m/hr
number of bed volumes

Figure 4-5: Effluent Cu concentration and effluent pH as functions of the

Cu(II) conc. (mg/l)

0.00
0.05
0.10
0.15
0.20

0
5000
10000
15000
20000
25000

Bed Volume

Time (hrs)

0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000

pH

INFLUENT:

Cd(II) : 2.0 mg/l
Cu(II) : 0.1 mg/l
Pb(II) : 2.0 mg/l

Effluent:

Cu conc.

Bed Volume

SLV: 1.26 m/hr

NaHCO₃: 2.0 g/l
NaCl: 0.05 g/l
Concentration: 1.26 g/l
4.3 COLUMN RUN WITH IRC–718

A fixed bed column run with IRC–718, a weak base cation exchanger, was performed to compare ECOSORB's metal uptake capacity with that of a commercially available chelating ion exchanger. The functional group of this resin is $-\text{N(CH}_2\text{COOH)}_2$; and is analogous to ethylenediamine tetracetic acid (EDTA). IRC–718's affinity for metal ions follows the same pattern as the complex stability constants of EDTA in solution. This resin is used commercially as an agent for removing heavy metals from industrial effluent.

The experimental method used was essentially the same as that used to perform the fixed bed column run with ECOSORB, except that the preconditioned ion–exchange resin was placed in a glass column of smaller internal diameter (9mm). A synthetic solution with the same composition as that used for the ECOSORB column run was used as the feed solution. The solution was pumped through the column in an upflow direction at a flow rate of 2 cc/min. The hydrodynamic condition in the column varied slightly from that maintained for the ECOSORB column run (EBCT 2.6 min., SLV 2 m/hr). The effluent history for this column run is shown in Fig. 4–6. Based on the sequence in which breakthrough of the metal ions occur, the relative affinity of the exchanger for these metal ions is as follows:

Copper $\gg$ Lead $>$ Nickel $>$ Cadmium (pH 4.0)

IRC–718 has strong affinity for transition metals because these metals link covalently with oxygen atoms present in the iminodiacetate functionality and coordinatively with the nitrogen atoms. The strength of the bonding between metal ions and the donor atoms follow the same pattern as the stability constants of the complexes these metal ions form with EDTA in aqueous solution [12]. Based on
these stability constants, IRC–718 should have greatest affinity for Cu ions and least affinity for Cd ions. This affinity sequence is substantiated by the results obtained in this study.

A difference in the selectivity sequence between IRC–718 and ECOSORB is observed. ECOSORB has greater affinity for lead than copper where as IRC–718, because of its iminodiacetate functionality, has greatest affinity for copper. Except for this difference, there is a similarity in the breakthrough patterns observed for ECOSORB and IRC–718. The phenomenon of chromatographic elution which is exhibited by any ion–exchange resin, is observed in this case too. A comparison of the breakthrough of metal ions for both the ECOSORB and IRC–718 column runs will be presented in the next section.

Fig. 4–7 shows the variation in effluent pH with time and bed volumes passed. Even though initially the effluent pH is as high as 10.0, unlike ECOSORB, this pH is not sustained for a protracted period of time. In fact, after passing a few hundred bed volumes of feed solution the effluent pH drops to influent pH. The high effluent pH obtained initially was due to pre–conditioning of the resin with 5% NaOH solution.
Figure 4-6: Sorption of Metal(II) Ions on IRC-718.

- **Cd**
- **Ni**
- **Pb**
- **Cu**

**INFLUENT:**
- Ni(II) : 2.0 mg/l
- Cd(II) : 2.0 mg/l
- Pb(II) : 2.0 mg/l
- Cu(II) : 0.1 mg/l
- Na : 250 mg/l
- pH : 4.0
- EBCT : 2.63 min.
- SLV : 1.88 m/hr

**Graph Details:**
- **x-axis:** Time (hrs)
- **y-axis:** C / C₀
- **Bed Volume**
Figure 4-6: Sorption of Metal(II) Ions on IRC-718.
Figure 4-7: Effluent pH as a function of Bed Volumes Passed for IRC-718 Column Run.
Figure 4-7: Effluent pH as a function of Bed Volumes Passed for IRC-718 Column Run.
4.4 COMPARISON OF ECOSORB AND IRC-718 UPTAKE MECHANISMS

Figures 4-9 through 4-12 show the relative breakthrough of metal ions for the column runs performed using ECOSORB and IRC-718. The time at which breakthrough for the metals of interest occurs indicates that ECOSORB's metal uptake capacity is comparable to that of IRC-718 (at pH 4.0). In fact, fig. 4-8 indicates that ECOSORB performs better than IRC-718 with respect to Cd removal. Ni breakthrough occurs almost simultaneously in both the column runs. Since the IRC-718 column run was terminated before Pb and Cu breakthrough could occur, it would be difficult to compare the time of breakthrough of these metals, although one can surmise with some certainty that IRC-718 would be superior to ECOSORB with respect to Cu removal. Due to its high stability constant, copper undergoes coordinated complex formation with IRC-718 more easily than the other metals and hence its greatest affinity towards Cu.

It has been well established that cation exchange accompanied by chelation is responsible for metal uptake by chelating ion exchangers. For a metal ion having four coordinated water molecules in the aqueous phase, [Me(H2O)4]2+, the overall reaction involves the following [1]:

\[
\text{CH}_2\text{COO}^- \text{Na}^+ + \text{Me(H}_2\text{O)}_4^{2+} \leftrightarrow \text{R-CH}_2\text{N-CH}_2\text{COO}^- \text{Na}^+ + \text{Me(H}_2\text{O)}^2+ + 2\text{Na}^+ + 3\text{H}_2\text{O}
\]
Figure 4-8: Comparison of Cd breakthrough pattern for Column Runs using ECOSORB and IRC-718.

INFLUENT:
Ni(II) : 2.0 mg/l
Cd(II) : 2.0 mg/l
Pb(II) : 2.0 mg/l
Cu(II) : 0.1 mg/l
Na  : 250 mg/l
pH   : 4.0
Flow rate : 2 cc/min
Figure 4.8: Comparison of Cd breakthrough pattern for Column Runs using ECOSORB and IRC-718.

**Legend:**
- Ecosorb
- IRC-71B

**Influent:**
- Ni(II) : 2.0 mg/l
- Cd(II) : 2.0 mg/l
- Pb(II) : 2.0 mg/l
- Cu(II) : 0.1 mg/l
- Na : 250 mg/l
- pH : 4.0
- Flow rate : 2 cc/min

**Graph Details:**
- Cd(II) concentration (mg/l) vs. Bed Volume
- Scale: 0 to 4.0
- Data points for each condition are marked accordingly.
Figure 4-9: Comparison of Ni breakthrough pattern for Column Runs using ECOSORB and IRC-718.
Figure 4-9: Comparison of Ni breakthrough pattern for Column Runs using ECOSORB and IRC-718.
Figure 4-10: Comparison of Cu breakthrough pattern for Column Runs using ECOSORB and IRC-718.
Figure 4-10: Comparison of Cu breakthrough pattern for Column Runs using ECOSORB and IRC-718.
Figure 4–11: Comparison of Pb breakthrough pattern for Column Runs using ECOSORB and IRC–718.
Figure 4-11: Comparison of Pb breakthrough pattern for Column Runs using ECOSORB and IRC-718.
Figure 4-12: Comparison of Effluent pH for Column Runs using ECOSORB and IRC-718
Figure 4-12: Comparison of Effluent pH for Column Runs using ECOSORB and IRC-718

**INFLUENT:**
- Ni(II): 2.0 mg/l
- Cd(II): 2.0 mg/l
- Pb(II): 2.0 mg/l
- Cu(II): 0.1 mg/l
- Na: 250 mg/l
- pH: 4.0
- Flow rate: 2 cc/min.
The three water molecules (ligands) from the coordination sphere of the metal ion are replaced by one nitrogen and two oxygen donor atoms in the imino–diacetate functionality of IRC–718 [1]. The arrows indicate metal–ligand or Lewis acid–base (LAB) interaction. The high metal–ion selectivity is due to ion–exchange accompanied by Lewis acid–base interaction.

From a thermodynamic perspective, $\Delta G^\circ$, the overall free energy change for the reaction can be represented as the sum of two components,

$$\Delta G^\circ = \Delta G^\circ_{\text{IX}} + \Delta G^\circ_{\text{LAB}}$$

where $\Delta G^\circ_{\text{IX}} \rightarrow$ free energy change due to ion exchange reaction.

$\Delta G^\circ_{\text{LAB}} \rightarrow$ free energy change due to LAB interaction.

The above reaction can be rewritten as,

$$-RT\ln K_{\text{overall}} = RT\ln K_{\text{IX}} - RT\ln K_{\text{LAB}}$$

or

$$K_{\text{overall}} = K_{\text{IX}} \cdot K_{\text{LAB}}$$

Therefore, the overall equilibrium constant could be expressed as the product of two terms, $K_{\text{IX}}$ and $K_{\text{LAB}}$, where $K_{\text{IX}}$ refers to the interaction which is purely electrostatic and $K_{\text{LAB}}$ refers to the interaction which is primarily Lewis Acid–Base in character [1].

Conventional ion exchange involves uptake of ions through electrostatic interaction only. The equilibrium constant for such a reaction or exchange is given by $K_{\text{IX}}$. Therefore, the overall equilibrium constant will be represented by $K_{\text{IX}}$ only. The equilibrium constant for an interchange which involves both electrostatic as well as Lewis acid–base interaction is therefore much higher. The corresponding free energy change at equilibrium is therefore more negative. This means that the reaction or interchange is more spontaneous and the corresponding uptake of
species will therefore be much higher. This is the reason for IRC–718’s high metal uptake capacity.

The similarity in the breakthrough patterns of ECOSORB and IRC–718 indicate a generic similarity in the metal uptake mechanism. Based on the composition of ECOSORB and experimental results obtained, ion–exchange accompanied by Lewis acid–base interaction (coordinate bonds) appears to be the primary mechanism by which ECOSORB sequesters dissolved heavy metals. Figure 4–13 shows the general schematic for these binding mechanisms; the iminodiacetate exchanger (IRC–718) behaving as a tridentate ligand and the iron–rich adsorbent (ECOSORB) behaving as a bidentate ligand. In this case, the metal ion coordinates with two oxide sites simultaneously on the ECOSORB surface. The metal ion may also coordinate with a single oxide site on the ECOSORB surface. Studies on iron oxyhydroxides have shown that its surface consists of several distinct types of sites with varying affinities for adsorbate ions, depending on the nature of the bonding, which may be monodentate or bidentate [8]. Since ECOSORB contains iron oxyhydroxides, it may also have multiple active sites with varying affinities for the adsorbate ions.

The aluminosilicates present in ECOSORB release considerable amount of OH⁻ on dissolution which is responsible for the alkaline pH. This enables precipitation to occur without addition of any other reagent. A number of processes are thus responsible for metal uptake by ECOSORB; the primary ones being ion exchange accompanied by Lewis acid–base interaction, chemisorption and precipitation. The exact mechanism is dependant on the type of metal ion, concentration of the sorbed metal, pH of the solution etc. At low metal ion
Figure 4-13: Comparison of Metal Uptake Mechanism of ECOSORB and IRC-718
concentration monolayer adsorption/ion exchange is the primary removal mechanism. As metal ion concentration is increased both adsorption and precipitation become important. The sorption process is a synergistic process with the iron–rich compounds in ECOSORB responsible for heavy metal uptake and the aluminosilicates providing the hydroxyl ions for precipitation to occur. As metal concentration is further increased, precipitation dominates the sorption process

[13]

4.5 EFFECT OF PH ON METAL UPTAKE

It has been well established that metal oxyhydroxides have maximum affinity for \( H^+ \) ions. Therefore it is important to study the competitive effects of \( H^+ \) ions on metal uptake by ECOSORB, which contains considerable amount of iron oxyhydroxides. The chelating ion–exchanger IRC–718 also has maximum affinity for \( H^+ \) because of its weak–acid functionality. The effect of \( H^+ \) ion concentration on metal uptake was studied by lowering the pH of the feed solution (from 4.0 to 3.4) in both the column runs (ECOSORB and IRC–718) and monitoring the metal ion concentration in the effluent. Approximately 500 bed volumes of pH 3.4 influent (with the same composition as the feed solution used for the earlier column run), was passed through both fixed–beds at a flow rate of 2 cc/min. Figure 4–12 compares the variation in effluent pH for ECOSORB and IRC–718 column runs. It is observed that ECOSORB still has some residual basicity since the effluent pH remains above the influent pH, where as in the IRC–718 column run the effluent pH drops to the influent pH rather rapidly. Figures 4–14 through 4–17 show the variation in effluent metal ion concentration with number of bed volumes passed. The graphs indicate that leaching of heavy metals occurs from both adsorbents although elution occurs to a greater extent from IRC–718. Of course, with respect to Cu uptake, IRC–718
Figure 4-14: Effect of Lowering Influent pH (from pH 4.0 to 3.4) on Effluent Cd Concentration for ECOSORB and IRC-718 Column Runs
Figure 4-15: Effect of Lowering Influent pH (from pH 4.0 to 3.4) on Effluent Ni Concentration for ECOSORB and IRC-718 Column Runs
Figure 4-16: Effect of Lowering Influent pH (from pH 4.0 to 3.4) on Effluent Cu Concentration for ECOSORB and IRC-718 Column Runs
Figure 4-17: Effect of Lowering Influent pH (from pH 4.0 to 3.4) on Effluent pH for ECOSORB and IRC-718 Column Runs
is much more effective than ECOSORB at the lower pH too. As mentioned earlier, this is due to its imino-diacetate functionality which forms very strong complexes with Cu. This is an indication that ECOSORB may not be effective as a scavenger of heavy metals from solutions with pH below 3.5.

4.6 REGENERATION STUDIES

Metal removal by adsorption is achieved by concentrating the metals onto a solid surface, from which they are then desorbed into a much smaller volume for recovery or treatment by a conventional process such as precipitation, thus reducing the volume of sludge that has to be handled. Since the study envisages using ECOSORB in a similar process arrangement, experiments were conducted to determine the percentage of sorbed heavy metals that can be desorbed from the spent ECOSORB.

The metal recovery tests were conducted on the spent adsorbent obtained from the column runs performed with ECOSORB. The spent ECOSORB was removed from the column, washed with distilled water, oven-dried and then divided into two separate portions (designated as upper and lower-layer ECOSORB). The eluting agents used were 5% oxalate, 5% ethylenediamine tetra-acetate (EDTA) and 2% nitric acid solutions. The experiment essentially consisted of passing 1 liter of regenerant through a glass mini-column containing about 1 g of spent adsorbent.

The first mini-column run involved regenerating 1 g of upper-layer ECOSORB with 1 l of oxalate and then with 1 l EDTA solution. The regenerants were passed through the columns at a flow rate of approximately 0.5 cc/min. The effluent from the column run was then analyzed for various metals ions. A similar experiment was performed with the lower-layer ECOSORB. To test the
effectiveness of acid regeneration, a mini-column run was also conducted with upper-layer ECOSORB with 2% nitric acid as regenerant. The results of the three mini-column runs are tabulated in table 4–5.

Table 4–5: Results of Regeneration Experiments with Oxalate, EDTA and Nitric Acid

<table>
<thead>
<tr>
<th>Regenerant</th>
<th>Layer</th>
<th>Volume passed (ml)</th>
<th>Mass of metals recovered (mg per gram of spent ECOSORB)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>Na Oxalate</td>
<td>Lower</td>
<td>260</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>Upper</td>
<td>220</td>
<td>0.05</td>
</tr>
<tr>
<td>Na EDTA</td>
<td>Lower</td>
<td>950</td>
<td>4.50</td>
</tr>
<tr>
<td></td>
<td>Upper</td>
<td>950</td>
<td>5.75</td>
</tr>
<tr>
<td>2% Nitric Acid</td>
<td>Upper</td>
<td>500</td>
<td>5.85</td>
</tr>
</tbody>
</table>

From Table 4–5, it is evident that the amount of heavy metals recovered from the lower-layer is consistently lesser than that recovered from the upper-layer, for all the heavy metals studied. Keeping in mind the fact that the feed solution was passed through the bed in an upflow direction, it can be deduced that this is due to the elution of adsorbed heavy metals from the lower layer to the upper layer during the course of operation of the column run. Elution of heavy metals is caused by the displacement of the adsorbed heavy metal by another cation, most likely hydrogen.
Figure 4-18: Scanning Electron Micrograph of (a) Metal Loaded ECOSORB (1000X) and (b) Spent ECOSORB Regenerated with 2% H₂SO₄ (1000X)
ions. This is additional proof of the involvement of ion-exchange in the metal sequestering process.

It is observed that regeneration with oxalate is not effective, while regeneration with EDTA results in almost 70% heavy metal recovery. In the case of regeneration with EDTA some amount of iron (Fe) also desorbs from the bed. With nitric acid, percentage metal recovery is comparable to recovery with EDTA, except that much greater dissolution of the adsorbent occurs (indicated by high Fe concentration in the effluent). It must be noted that Table 4-5 gives the total amount of each heavy metal recovered per gram of spent ECOSORB, while Table 4-6 gives the percentage of heavy metals recovered from the spent ECOSORB. There is a discrepancy in the value obtained for percent Copper recovered – the amount desorbed is greater than the amount adsorbed. This could be due to the errors that are inevitable when analyzing for metals present in the parts per billion concentration range.

**Table 4-6: Percent Metals recovered from Spent ECOSORB using Na-EDTA**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Metal uptake Capacity (mg/gm)</th>
<th>Metal present in 2 gms of ESB (mg)</th>
<th>Metal recovered from 2 gm of spent ESB (mg)</th>
<th>Percent Recovered (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>7.05</td>
<td>14.10</td>
<td>10.70</td>
<td>76.1</td>
</tr>
<tr>
<td>Ni</td>
<td>8.80</td>
<td>17.6</td>
<td>7.60</td>
<td>43.1</td>
</tr>
<tr>
<td>Cu</td>
<td>0.90</td>
<td>1.80</td>
<td>2.80</td>
<td>155.7</td>
</tr>
<tr>
<td>Pb</td>
<td>24.2</td>
<td>48.4</td>
<td>23.3</td>
<td>48.2</td>
</tr>
</tbody>
</table>
4.7 COLUMN RUN WITH ECOSORB USING DISTILLED WATER AS FEED SOLUTION

A column run was performed with granules of ECOSORB constituting the bed and distilled water, the feed solution. The primary objective of this experiment was to check for leaching of heavy metals from ECOSORB (it is important to check for leaching of heavy metals because ECOSORB is the byproduct of a metal–recovery process) and to study ECOSORB's inherent buffer capacity. Figure 4–19 shows the variation of effluent pH with number of bed volumes of distilled water passed. The effluent from the column run was analyzed for sodium, calcium and heavy metals like Cd, Ni, Pb and Zn at regular intervals. Figure 4–20 shows that while sodium concentration in the effluent drops to around 2 ppm rapidly, the calcium concentration remains around 20 ppm even after passing 6000 bed volumes of distilled water through the ECOSORB bed. The slow leaching of alkalinity in the form of Ca could explain ECOSORB's sustained, high, acid neutralizing capacity. Effluent analysis also indicated leaching of Pb (about 50ppb) and Zn (about 200ppb) from the bed at the beginning of the column run. This problem will have to be redressed before ECOSORB is used commercially.
Figure 4-19: Effluent pH as a function of bed volumes passed for ECOSORB/Distilled water column run
Figure 4-19: Effluent pH as a function of bed volumes passed for ECOSORB/Distilled water column run
Figure 4-20: Effluent Na and Ca concentrations as functions of bed volumes passed for ECOSORB/Distilled water column run.
Figure 4-20: Effluent Na and Ca concentrations as functions of bed volumes passed for ECOSORB/Distilled water column run
4.8 COLUMN RUN WITH CaCO₃

A fixed bed column run was performed with amorphous CaCO₃ to compare its basicity with that of ECOSORB. Approximately 10g of amorphous CaCO₃ was placed in glass column of 11 mm internal diameter. Glass beads were interspersed with amorphous CaCO₃ to reduce pressure drop. Approximately 20 bed volumes of DI water was passed through the column and then the influent was switched to the pH 4 feed solution used in the earlier experiments. The effluent pH as a function of number of bed volumes passed is shown in figure 4-21. It is observed that the effluent pH remains above 9.0 for the DI feed, but drops to 6.0 the moment the feed is changed to the synthesized metal ion solution. This indicates that CaCO₃ releases its alkalinity rapidly, whereas ECOSORB releases its alkalinity slowly, as is evident from figure 4-3.

4.9 FIXED BED COLUMN RUNS WITH SPENT ECOSORB

In order to test for leaching of sorbed heavy metals from exhausted ECOSORB, column runs were performed using the spent ECOSORB obtained from the earlier column run described in section 4.2. One gram of oven-dried upper-layer ECOSORB was placed in a 9mm internal diameter glass column and 0.5 l of DI water followed by 1l of 2x10⁻³ N acetic acid was passed through the bed. The effluent pH and metal ion concentration were monitored at regular intervals. Figure 4-22 shows the effluent history for the column run. The effluent metal ion concentration is significant initially, before dropping to undetectable levels. This is an indication that some amount of leaching occurred from the bed initially, but
Figure 4-21: Effluent pH as a function of bed volumes passed for the CaCO₃ column run
Figure 4-21: Effluent pH as a function of bed volumes passed for the CACO₃ column run.
Figure 4-22: Effluent conc. as a function of bed volumes passed for the spent ECOSORB column run
insufficient contact time resulted in an effluent devoid of heavy metals. In order to ensure complete mass transfer between the solid and liquid phases, batch tests would have to be performed to obtain a better picture of the extent of leaching of metals from the exhausted sorbent.
Chapter 5

CONCLUSIONS AND REMARKS

5.1 REVIEW OF CONDUCTED STUDY

Presently available treatment methods for the control and recovery of heavy metals from wastewater have several shortcomings which tend to diminish their overall cost–benefit. In this study, the viability of using an iron–rich material as a sorbent was investigated. The material used in this study is an iron–rich byproduct of the process of metal recovery from Electric Arc Furnace (EAF) dust (called the Waelzing process). It is produced in large quantities in the U.S and is comparatively inexpensive. It has been given the trade–name ECOSORB.

Experiments were conducted to determine ECOSORB’s metal uptake capacity, the mechanisms responsible for metal uptake and the influence of pH on metal uptake. The effect of innocuous competing ions on heavy metal uptake was also studied. Tests were also performed with a chelating ion–exchanger, namely IRC–718, to compare ECOSORB’s performance with that of a commercially available ion–exchanger. Experiments were also performed to quantify ECOSORB’s acid neutralizing capacity.

Regeneration experiments were performed to determine the recoverability of heavy metals from the exhausted sorbent and to explore the possibility of multiple re–use of the sorbent.
5.2 CONCLUSIONS

- ECOSORB is capable of sequestering heavy metals from aqueous solutions, even when these metals are present at concentrations below their respective solubility limits. This indicates that precipitation at alkaline pH is not a significant mechanism by which heavy metals are removed by ECOSORB.

- Cation exchange accompanied by Lewis acid–base interactions is the proposed mechanism by which ECOSORB affects heavy metal uptake.

- Metal uptake by ECOSORB is an extremely rapid process.

- There is a generic similarity between commercially available chelating exchangers and ECOSORB in metal uptake mechanism.

- ECOSORB exhibits high selectivity towards bivalent transition metal cations. This was deduced by the occurrence of heavy metal uptake in the presence of a high background concentration of sodium ions.

- ECOSORB’s metal uptake capacity (0.7 meq/gram of sorbent) compares well with that of commercially available chelating ion exchangers (0.8 meq/gram of dry resin).

- The size of ECOSORB granules (20–50 mesh) permits its use in a process arrangement similar to that used for conventional ion–exchangers, that is in a fixed–bed process.

- ECOSORB has immense acid neutralizing capacity. Titration carried out using 0.1N HNO₃ indicate an acid neutralizing capacity of approximately 1.4 meq H⁺ per gram of ECOSORB.
Leaching of Zn and Pb from ECOSORB, albeit at low concentrations (50 ppb), may affect ECOSORB’s marketability, especially with regulations related to heavy metal discharge becoming more stringent.

Once exhausted, regeneration with chelating agents and acid resulted in about 50% recovery with the percentage varying with the type of metal ion. The results of batch tests performed on the regenerated ECOSORB indicate that ECOSORB loses its metal sequestering property on regeneration. Hence, unlike ion–exchangers, ECOSORB cannot be reused after elution of metals from the exhausted sorbent.

5.3 FUTURE WORK

Additional work has to be performed before ECOSORB can be marketed as a viable alternative to currently used sorbents. Specifically,

- Studies should be conducted to redress the problem of leaching of heavy metals (Zn and Pb) from ECOSORB.

- The effect of calcium and magnesium ions on metal uptake capacity should be studied since these ions are present in most wastewaters at relatively high concentrations.

- The influence of complexing ligands (e.g., Cl\(^-\), CN\(^-\), HCO\(_3\)^- and CO\(_3^{2-}\)) and organics on metal uptake should also be investigated.

- The ferromagnetic property of ECOSORB can be exploited to achieve heavy metal removal in a batch process. Separation of the sorbent from the other suspended particles in the slurry reactor can be accomplished by lowering an electromagnet into the reactor. The magnetic ECOSORB particles will attach to the electromagnet leaving the other suspended solids
in the reactor. Since batch processes require agitation of the contents of the reactor to achieve good mass transfer between the solid and liquid phases, the workability of this process would depend on ECOSORB’s ability to retain its granular form.
REFERENCES


A.1 METAL SOLUBILITY

The solubility of a metal in water is dependent on pH. The metals remain in solution up to a certain limiting pH. Exceeding that pH results in precipitation of the metals as hydroxides. The hydroxyl ions present in water also form monovalent and higher valence complexes with the metals. In this section, the maximum solubility of a metal ion at different pH conditions will be calculated from solubility product data.

The solubility product is an equilibrium relationship between the cationic and anionic part of a molecule in the aqueous phase. For dissolved metals in water, the solubility product dictates the maximum concentration of free metals that can be present at a particular pH. Mathematically, the solubility product of a metal ion is defined as:

\[ K_{sp} = [\text{Me}^{2+}] \cdot [\text{OH}^-]^2 \]

where,

- \( K_{sp} \rightarrow \text{Solubility product} \)
- \( \text{Me}^{2+} \rightarrow \text{Metal ion concentration} \)
- \( \text{OH}^- \rightarrow \text{hydroxyl ion concentration} \)

In the above equation, both the metal ion concentration and hydroxyl ion concentration are expressed as mole per liter. Thus knowing the system pH and solubility product, the maximum permissible metal ion concentration in a pure aqueous media can be determined.
A.2 METAL–HYDROXY COMPLEXES

Hydroxyl ions also form coordination complexes with metal ions. Due to these complex formation reactions between metal ions and hydroxyl ions, a number of charged and neutral species are formed in the aqueous phase. These complex formation reactions also affect the solubilities of the metal ions. The complex formation reactions between metal ions and hydroxyl ions can be represented as follows:

\[
\begin{align*}
\text{Me}^{2+} + \text{OH}^- & \rightleftharpoons [\text{Me(OH)}]^+, \quad K_1 \\
\text{Me(OH)}^+ + \text{OH}^- & \rightleftharpoons \text{Me(OH)}_2, \quad K_2 \\
\text{Me(OH)}_2 + \text{OH}^- & \rightleftharpoons [\text{Me(OH)}_3]^{-}, \quad K_3
\end{align*}
\]

where \( K_1 \) to \( K_4 \) are the step-wise stability constants for the corresponding reactions. The reactions given above are predominant when the aqueous phase pH is above 10. The total metal concentration in the aqueous phase is the sum of the free ion concentration and the concentration of the hydroxy complexes. The log of the solubility product [14] and stability constants [15] used to plot the solubility curves shown in figure A–1 are given below:

<table>
<thead>
<tr>
<th></th>
<th>(-pK_{sp})</th>
<th>(-pK_1)</th>
<th>(-pK_2)</th>
<th>(-pK_3)</th>
<th>(-pK_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>14.28</td>
<td>3.9</td>
<td>7.6</td>
<td>8.99</td>
<td>8.71</td>
</tr>
<tr>
<td>Nickel</td>
<td>15.7</td>
<td>4.1</td>
<td>9</td>
<td>11.33</td>
<td>–</td>
</tr>
<tr>
<td>Lead</td>
<td>19.85</td>
<td>6.3</td>
<td>10.9</td>
<td>14.58</td>
<td>–</td>
</tr>
<tr>
<td>Copper</td>
<td>18.7</td>
<td>6.5</td>
<td>11.8</td>
<td>15.25</td>
<td>16.41</td>
</tr>
</tbody>
</table>

For an aqueous system at equilibrium containing several metals and ligands, the total concentration of each metal is the sum of its free and complex ion concentrations.
Figure A-1: Hydroxide Solubility
APPENDIX B

B.1 DISTRIBUTION COEFFICIENT

The distribution coefficient of a solute is defined as the ratio of the concentration of the solute in the sorbent and in solution. It is represented mathematically as:

\[
\lambda_{Me} = \frac{q_{Me}}{C_{Me}}
\]  

where,

\( q_{Me} \) = concentration of metal ion (Me) in the solid phase (in milliequivalents per gram of sorbent).

\( C_{Me} \) = concentration of metal ion (Me) in the aqueous phase (in milliequivalents per milliliter of solution).

B.2 SEPARATION FACTOR

Separation factor is a surrogate parameter which indicates the preference of the sorbent for one species over another. The separation factor of solute A with respect to solute B, for a given sorbent is defined as:

\[
\alpha^A_B = \frac{\lambda^A}{\lambda^B}
\]  

where,

\( \lambda^A \) = distribution coefficient of solute A (in ml of solution/gram of sorbent)

\( \lambda^B \) = distribution coefficient of solute B (in ml of solution/gram of sorbent)

If \( \alpha^A_B \) is greater than unity, it indicates that solute A is preferred over solute B by the sorbent.

The values tabulated in Table B–1 were obtained using equations B.1 and B.2.
<table>
<thead>
<tr>
<th>Counterion</th>
<th>at. wt.</th>
<th>eq. wt.</th>
<th>aq. phase conc(mg/l)</th>
<th>aq. phase conc(meq/ml)</th>
<th>$C_{me}$</th>
<th>Resin phase mass(mg/gm of ECOSORB)</th>
<th>$q_{Me}$</th>
<th>Resin phase mass(meq/gm of ECOSORB)</th>
<th>Distribution Coefficient ($\lambda_{Me} = \frac{q_{Me}}{C_{Me}}$)</th>
<th>Separation Factor ($\alpha_{Cd} = \frac{\lambda_{Me}}{\lambda_{Cd}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>112.4</td>
<td>56.2</td>
<td>2.0</td>
<td>3.5587189E-05</td>
<td>7.043</td>
<td>0.125</td>
<td>3521.429</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>58.7</td>
<td>29.35</td>
<td>2.0</td>
<td>6.8143101E-05</td>
<td>8.800</td>
<td>0.300</td>
<td>4400.000</td>
<td>1.249</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>63.54</td>
<td>31.77</td>
<td>0.1</td>
<td>3.1476235E-06</td>
<td>0.904</td>
<td>0.028</td>
<td>9035.714</td>
<td>2.566</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>207.2</td>
<td>103.6</td>
<td>2.0</td>
<td>1.9305019E-05</td>
<td>24.200</td>
<td>0.234</td>
<td>12100.000</td>
<td>3.436</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
SYMBOALS & ABBREVIATIONS

\( \alpha_B^A \) ............... Separation factor of solute A with respect to solute B.

\( \lambda_A \) ............... Distribution Coefficient of solute A.

\( C_A \) ............... Concentration of solute A in the aqueous phase (in milliequivalents per gram of sorbent).

\( K_{sp} \) ............... Solubility Product.

\( K_1, K_2, K_3, K_4 \) ........... Stability Constants

\( q_A \) ............... Concentration of solute A in the solid phase (in milliequivalents per gram of sorbent).

EAF ............... Electric Arc Furnace.

EDTA ............... Ethylene Diamine Tetra-Acetate.

EBCT ............... Empty Bed Contact Time.


SEM ............... Scanning Electron Micrograph.

SLV ............... Superficial Liquid Velocity.

TCLP ............... Toxicity Characteristic Leaching Procedure.
VITA

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END
OF
TITLE