Experimental Study on Removal of Iron from Water using Egg shell as Adsorbent

Sonu Cherian¹, Prof.R Padhmavijayan²,
¹(Scholar, Environmental Engineering, Anna University Chennai, India, sonupady@gmail.com)
²(Assistant Professor, Department of Civil Engineering, The Kavery Engineering College, Salem)

Abstract— As the current global trend towards more stringent environmental standards, technical applicability and cost-effectiveness became key factors in the selection of adsorbents for water and wastewater treatment. Adsorption is by far the most versatile and widely used method for the removal of pollutants due to its high removal capacity and ease of operation at large scale. Recently, various low-cost adsorbents derived from agricultural waste, industrial by-products or natural materials, have been intensively investigated. In this respect, the eggshells from egg-breaking operations constitute significant waste disposal problems for the food industry, so the development of value-added by-products from this waste is to be welcomed. The egg processing industry is very competitive, with low profit margins due to global competition and cheap imports. Additionally, the costs associated with the egg shell disposal (mainly on landfill sites) are significant, and expected to continue increasing as landfill taxes increase. The aim of the present is to provide an overview on the use of chicken eggshell as adsorbent for the removal of iron from water by the adsorption process both on simulated and real effluents containing iron onto eggshell-derived adsorbent. This was accomplished by analyzing the uptake potential for selected iron concentration at different conditions. The effects of different parameters such as pH of the solution, varying ferrous ion concentration, varying adsorbent quantities, and agitation rate and contact time on the adsorption process are to be studied. Results obtained so far shows that eggshell can remove iron from different types of aqueous systems with great efficiency.

Keywords— Adsorption; Removal of iron; Eggshell as Adsorbent; Water treatment

1. INTRODUCTION

Environmental pollution is currently one of the most important issues facing humanity. It was increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures. Toxic heavy metals are considered one of the pollutants that have direct effect on man and animals. Industrial wastewater containing lead, copper, cadmium and chromium, etc. for example can contaminate groundwater resources and thus lead to a serious groundwater pollution problem. Water of high quality is essential to human life and water of acceptable quality is essential for agriculture, industrial, domestic and commercial uses. All these activities are also responsible for polluting the water. Billions of gallons of waste from all these sources are thrown to freshwater bodies every day. The requirement for water is increasing while slowly all the water resources are becoming unfit for use due to improper waste disposal. The task of providing proper treatment facility for all polluting sources is difficult and also expensive, hence there is pressing demand for innovative technologies which are low cost, require low maintenance and are energy efficient. The adsorption technique is economically favorable and technically easy to separate as the requirement of the control system is minimum. Instead of using commercial activated carbon, researchers have worked on inexpensive materials, such as coconut shell, sawdust, mango leaves, chitosan, egg shell, and other adsorbents, which have high adsorption capacity and are locally available.

A. NEED FOR THE STUDY

Iron is an essential element in human nutrition. Estimates of the minimum daily requirement for iron depend on age, sex, physiological status, and iron bioavailability and range from about 10 to 50 mg/day. The average lethal dose of iron is 200–250 mg/kg of body weight, but death has occurred following the ingestion of doses as low as 40 mg/kg of body weight. Autopsies have shown haemorrhagic necrosis and sloughing of areas of mucosa in the stomach with extension into the submucosa. Chronic iron overload results primarily from a genetic disorder (haemochromatosis) characterized by increased iron absorption and iron diseases that require frequent transfusions. Adults have often taken iron supplements for extended periods without deleterious effects, and an intake of 0.4–1 mg/kg of body weight per day is unlikely to cause adverse effects in healthy persons.

In remote areas, iron levels in air are about 50–90 ng/m³; at urban sites, levels are about 1.3 μg/m³. Concentrations up to 12 μg/m³ have been reported in the vicinity of iron- and steel producing plants.

The medium iron concentration in rivers has been reported to be 0.7 mg/litre. In anaerobic Ground water where iron is in the form of iron(II), concentrations will usually be 0.5–10 mg/litre, but concentrations up to 50 mg/litre can sometimes be found. Concentrations of iron in drinking-water are normally less than 0.3 mg/litre but may be higher in countries where various iron salts are used as coagulating agents in water-treatment plants and where cast iron, steel, and galvanized iron pipes are used for water distribution.

Iron occurs as a natural constituent in plants and animals. Liver, kidney, fish, and green vegetables contain 20–150 mg/kg, whereas red meats and egg yolks contain 10–20 mg/kg. Rice and many fruits and vegetables have low iron contents (1–10 mg/kg). Daily intakes of iron in food — the major source of exposure — range from 10 to 14 mg.
Drinking-water containing 0.3 mg/litre would contribute about 0.6 mg to the daily intake. Intake of iron from air is about 25 μg/day in urban areas.

B. Objectives And Scope Of The Work

The concurrent effects of a fast technological growth rate helps to develop a method that effectively remove iron from water using eggshell as adsorbent and to determine its optimum conditions like pH, concentration of adsorbent dosage, concentration of iron concentration, concentration of iron concentration.

It is a method for removing the iron content in water by an efficient way which is cheaper, environmental friendly and easily available.

2. REVIEW OF LITERATURE

The presence of large quantities of toxic metals such as mercury, lead, cadmium, zinc or others, poses serious health risks to humans, and this threat puts the scientific community under pressure to develop new methods to detect and eliminate toxic contaminants from wastewaters in efficient and economically viable ways. This section provides details on the latest developments and efforts in general heavy metals removal from wastewater.

A. Novel Method for Heavy Metal Removal Using Fish Scales

Effective removal of metal ions from industrial wastewater by using fish scales was studied in this article. A series of static tests was performed with 10 g of dried fish scale adsorbent pulverized to micron sizes of 37 or less. Such tests were conducted for lead ions (from lead nitrate solution) at concentrations of 25 ppm, 12.5 ppm, and 6.25 ppm. The dynamic equilibrium results were based on tests on 50 ppm of cobalt chloride solution (flow rate 1 ml/min), followed by 100 ppm of cobalt solution (flow rate 7 ml/min), and then a mixture of cobalt chloride (CoCl₂), lead nitrate (Pb(NO₃)₂), zinc nitrate hexahydrate (Zn(NO₃)₂.6H₂O) and strontium nitrate (Sr(NO₃)₂) solutions. The proposed sorption technique offers an acceptable solution for removal of heavy metal ions from wastewater streams. The potential application of this study is an enormous energy cost savings in the electroplating industry, which requires the replacement of wastewater and the burial of metal sludge in landfills. Also, the trimming of energy costs in oil drilling and pipeline corrosion is possible by potential formation of biopolymers developed from “adsorbed scale.

B. Seashells for Heavy Metals Clean-Up

On the banks of the Saigon River in Viet Nam, researchers have completed tests on a new way to combat water pollution that could save millions of lives in coastal cities in the developing world. Toxic metals like cadmium, zinc, lead and iron were cleaned using seashells. Dr. Köhler’s team has found that pouring metal and acid-laden water over a bed of crushed clam or mussel shells provides an easy fix. The shells are made of aragonite, a form of calcium carbonate that readily swaps its calcium atoms in favor of heavy metals, locking them into a solid form. The shells are alkaline – a pH of 8.3 when dissolved – and needs to be maintained so by adding more shells.

C. Removal Of Heavy Metals From Industrial Wastewaters By Adsorption Onto Activated Carbon Prepared From An Agricultural Solid Waste

Activated carbon was prepared from coirpith by a chemical activation method and characterized. The adsorption of toxic heavy metals, Hg(II), Pb(II), Cd(II), Ni(II), and Cu(II) was studied using synthetic solutions and was reported elsewhere. In the present work the adsorption of toxic heavy metals from industrial wastewaters onto coirpith carbon was studied. The percent adsorption increased with increase in pH from 2 to 6 and remained constant up to 10. As coirpith is discarded as waste from coir processing industries, the resulting carbon is expected to be an economical product for the removal of toxic heavy metals from industrial wastewaters.

3. METHODOLOGY

Adsorption experiments were carried out in batch mode at ambient temperature. Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Similar to surface tension, adsorption is a consequence of surface energy. Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid).

Fig 1 Mechanism of adsorption

The porous nature of eggshell makes it an attractive material to be employed as an adsorbent. The eggshell typically consists of ceramic materials which are arranged in a three-layered structure, namely the cuticle on the outer surface, a spongy (calcareous) layer and an inner lamellar (or mammillar) layer. The spongy and mammillar layers form a matrix composed of protein fibers bonded to calcite (calcium carbonate), representing more than 90% of the material. The two layers are also constructed in such a
manner that there are numerous circular openings (pores). The utilization of the eggshell and ESM by-products has started over 1970 with the development of several studies aiming at the calcium supplement and other nutrition sources from the albumin, membrane and matrix of the eggshell, which was processed by crushing and milling to obtain fine particles (flours) for animal use. Several researches have been conducted to evaluate the adsorption ability of eggshell as low cost adsorbent, in artificial wastewater with mono or multi components.

![Fig 2 Structure of egg](image-url)

**A. Preparation of Adsorbent**

The chicken eggshells were collected from kitchen waste and washed by deionized water for several times to remove the dirt particles. The sorbent used was eggshell powders. Shells were washed with distilled water and the membrane was recovered by hand and left in distilled water overnight. After complete removal of the organic fraction, shell was washed again. Afterwards, the material was dried at 105°C for 24h, milled and it is calcined at 1000°C for 2 hour.

**B. Preparation Of Simulated Solution**

Take 50 ml iron solution sample. Add 1ml hydroxylamine, 5ml sodium acetate, 5ml phenanthroline. Add 0.3g adsorbent.

**C. Adsorption Percentage**

The adsorption efficiency of iron can be calculated as:

\[
\text{Adsorption percentage} = \frac{(C_0 - C_f) \times 100}{C_0}
\]

where \(C_0\) and \(C_f\) (mg/L) are the liquid-phase concentration of iron at initial and equilibrium.

4. **EXPERIMENTS**

**A. Preparation Of Calibration Chart**

Prepare 6 samples in different iron concentration (say, 5, 10, 15, 20, 25, 30 mg/L). Take the corresponding absorbance readings by spectrometer.

**B. Determination Of Optimum Ph**

Take 50 ml iron solution (Fe concentration 5mg/lit) with different pH condition (3,5,7,9,11 PH). Add 0.3mg adsorbent. Give agitation at 1rpm for 1min & 20-30 rpm for 20min. Give retention time 30min. After that filter the sample. Take 50ml sample. Add 1ml hydroxylamine, 5ml sodium acetate, 5ml phenanthroline. After 10min measure the absorbance.

**C. Determination Of Optimum Iron Concentration**

Take 500 ml iron solution with different concentration (5, 10, 15, 20, 25, 30mg/lit) with optimum pH condition. Add 0.3mg adsorbent. Give agitation at 1rpm for 1min & 20-30 rpm for 20min. Give retention time 30min. After that filter the sample. Take 50ml sample. Add 1ml hydroxylamine, 5ml sodium acetate, 5ml phenanthroline. After 10min measure the absorbance.

**D. Determination Of Optimum Egg Shell Powder Concentration**

Take 500 ml iron solution with 5mg/lit Fe concentration with optimum pH condition and add egg powder in different amounts (0.3, 0.6, 0.9, 1.2, 1.5). Give agitation at 1rpm for 1min & 20-30 rpm for 20min. Give retention time 30min. After that filter the sample. Take 50ml sample. Add 1ml hydroxylamine, 5ml sodium acetate, 5ml phenanthroline. After 10min measure the absorbance.

**E. Determination Of Optimum Retention Time**

Take 500 ml iron solution (Fe concentration 5mg/lit) with optimum pH condition. Add 0.3g adsorbent. Give agitation at 1rpm for 1min & 20-30 rpm for 20min. Give retention in different times (30, 60, 90, 120, 150min). After that filter the sample. Take 50ml sample. Add 1ml hydroxylamine, 5ml sodium acetate, 5ml phenanthroline. Measure the absorbance after 10min.

5. **RESULTS AND DISCUSSION**

**A. Determination Of Optimum pH**

<table>
<thead>
<tr>
<th>No</th>
<th>pH Condition</th>
<th>Initial Iron Concentration [Co] (mg/lit)</th>
<th>Final Iron Concentration [Cf] (mg/lit)</th>
<th>Adsorption %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>5</td>
<td>1.5</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
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<td>30</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>5</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
<td>5</td>
<td>4</td>
<td>20</td>
</tr>
</tbody>
</table>


It shows that the adsorption capacities of Fe(III) increased significantly as the pH increased from 3–9 and started decreasing at pH range of 10–11. The adsorption capacities reached 22% at higher pH. At lower pH, little adsorption could be ascribed to the hydrogen ions competing with metal ions for adsorption site.

The effect of pH can be explained by ion-exchange mechanism of adsorption in which the important role is played by carbonate groups on the chicken eggshells that have cation-exchange properties. At lower pH values, ferrous ions adsorption was inhibited due to the competition between hydrogen and ferrous ions on the adsorption sites, which restricts the approach of metal cations. As the pH increased, the carbonate groups in chicken eggshells would be exposed, increasing the negative charges on the adsorbent surface, attracting the metal cations and allowing the adsorption onto the adsorbent surface.

RESULT: maximum adsorption % is at 9pH condition with initial concentration of Fe 5 mg/lit.

B. Varying Iron Concentration

<table>
<thead>
<tr>
<th>NO</th>
<th>Initial iron concentration [Co] (mg/lit)</th>
<th>Final iron concentration [Cf] (mg/lit)</th>
<th>Adsorption %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>5</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>2.</td>
<td>10</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>3.</td>
<td>15</td>
<td>13.5</td>
<td>10</td>
</tr>
<tr>
<td>4.</td>
<td>20</td>
<td>1</td>
<td>95</td>
</tr>
<tr>
<td>5.</td>
<td>25</td>
<td>11</td>
<td>56</td>
</tr>
<tr>
<td>6.</td>
<td>30</td>
<td>7.5</td>
<td>75</td>
</tr>
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</table>

The effect of initial metal ion concentration is as shown in table. From the figure it is evident that the metal uptake mechanism is dependent on initial heavy metal concentration. The metal ions are adsorbed onto the active sites of the adsorbent hence as the metal concentration increases specific sites are saturated and no further adsorption occurs. Batch experiments with varying initial metal ion concentration from 5mg/L to 25mg/L were carried out keeping other parameters constant. It was observed that metal ion uptake was more with a solution of 5mg/l and was observed that increase in metal ion concentration decreased adsorption. The feasibility and efficiency of a adsorption process not only depends on the properties of the adsorbents but also on the concentration of the metal ion solution. The initial metal ion concentration provides an important driving force to overcome all the mass transfer resistances of the metal between aqueous and solid phase. There are many factors which contribute to the absorbate concentration effect. The first and important one is that adsorption sites remain unsaturated during the adsorption reaction. The second cause is aggregation / agglomeration of adsorbent particles at higher concentration. Such aggregation leads to a decrease in the total surface area of the adsorbent particles available for adsorption.

RESULT: maximum adsorption % is at 20mg/lit of initial Fe concentration with 9pH condition.

C. Varying Egg Shell Powder Concentration

<table>
<thead>
<tr>
<th>NO</th>
<th>Initial iron concentration [Co] (mg/lit)</th>
<th>Egg powder amount (g)</th>
<th>Final iron concentration [Cf] (mg/lit)</th>
<th>Adsorption %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>5</td>
<td>0.3</td>
<td>3.9</td>
<td>80</td>
</tr>
<tr>
<td>2.</td>
<td>5</td>
<td>0.6</td>
<td>3.5</td>
<td>50</td>
</tr>
<tr>
<td>3.</td>
<td>5</td>
<td>0.9</td>
<td>3.3</td>
<td>10</td>
</tr>
<tr>
<td>4.</td>
<td>5</td>
<td>1.2</td>
<td>2.6</td>
<td>95</td>
</tr>
<tr>
<td>5.</td>
<td>5</td>
<td>1.5</td>
<td>2.4</td>
<td>56</td>
</tr>
</tbody>
</table>
As the number of active sites available for the adsorption of metal ion increases, the adsorption percentage also increases. This occurs as the concentration of the adsorbent increases. In the present case, batch study with adsorbent concentration ranging from 2.5mg/L to 10mg/L keeping all the other parameters constant was conducted. The results are shown in the figure below. It shows that 10mg/L of the adsorbent concentration adsorbs the maximum metal ion in both the cases.

RESULT: maximum adsorption % is at 20mg/lit of initial Fe concentration with 9pH condition.

D. Varying Retention Time

<table>
<thead>
<tr>
<th>NO</th>
<th>Initial iron concentration [Co] (mg/lit)</th>
<th>Egg powder amount (g)</th>
<th>Retention time (min)</th>
<th>Final iron concentration [Cf] (mg/lit)</th>
<th>Adsorption %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>5</td>
<td>1.5</td>
<td>30</td>
<td>2.4</td>
<td>52</td>
</tr>
<tr>
<td>2.</td>
<td>5</td>
<td>1.5</td>
<td>60</td>
<td>2.2</td>
<td>56</td>
</tr>
<tr>
<td>3.</td>
<td>5</td>
<td>1.5</td>
<td>90</td>
<td>1.8</td>
<td>74</td>
</tr>
<tr>
<td>4.</td>
<td>5</td>
<td>1.5</td>
<td>120</td>
<td>1.3</td>
<td>80</td>
</tr>
<tr>
<td>5.</td>
<td>5</td>
<td>1.5</td>
<td>150</td>
<td>1</td>
<td>80</td>
</tr>
</tbody>
</table>

The removal of ferric ion from the stock solution increases with the times and attains equilibrium value in about 120 to150 minutes. Initially within 30 to 90 minutes the uptake of metal ions from the bark is rapid, but gradually decreases with the time till it reaches equilibrium. In the beginning the number of active sites available for adsorption is more hence the metal uptake increases but later on the available of the active sites reduce and metal ion need to compete for the vacant sites. The figure shows that at the start of the adsorption the percent removal of metal is more and later reaches a constant value where upon no further adsorption was observed.

6. SUMMARY AND CONCLUSIONS

The removal of Fe(III) from water by using chicken eggshells has been experimented under several conditions such as at different pH, different ferrous ion concentration varying quantities of egg shell powder, agitation rate and retention time. The optimum pH for ferrous ion adsorption was found at pH 9. Since the metal ions uptake by chicken eggshells is highly dependent on the number of active binding sites or functional groups on the adsorbents, further research can be attempted to enhance the existing results by modifying the chicken eggshell adsorbents using acids or bases. As a result of chemical modification, it is expected that the number of active binding sites or functional groups on the adsorbents might be increased to improve the adsorption capacity of adsorbents. The analyses of the results indicate that egg shell like most other natural absorbents can be used in the treatment process of heavy metals and the treatment efficiency can be about 80% by choosing the adsorbent amount and other optimum parameters precisely. The concentration of ferrous ion has also an important effect on the treatment outcome. Egg shell waste is a cheap material and thus it would be convenient to use it in industrial wastewater treatment plants. From the evidences of all the performed experiments, it is possible to conclude that calcined eggshell is a promising adsorbent for the removal of iron.

REFERENCES