Ageratum conyzoides LEAF POWDER FOR DECONTAMINATION OF IRON (III): REMOVAL, ADSORBENT CHARACTERIZATION AND EQUILIBRIUM MODELING

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ABSTRACT

The present study explores the use of Ageratum conyzoides leaf powder (ACLP) for the effective removal of Fe(III) from aqueous solution. Experiments were conducted in batch mode to observe the influence of various parameters such as contact time (0-4 hrs), pH (1-2.5), adsorbent dosage (0-30 g/L), temperature (20-60°C), agitation speed (50-200 rpm) for different Fe(III) concentrations. The adsorption was found to increase with increase in contact time and biosorbent dosage. The results revealed that pH (2.0) and process temperature 40°C were optimum for Fe(III) biosorption. The Langmuir and Freundlich isotherm models were used to analyze the batch biosorption data and Langmuir model showed better representation of data with correlation coefficient of 0.994. The maximum biosorption capacity ($q_{max}$) was obtained 20.9 indicating strong binding capacity of the biosorbent. The biosorbent was analyzed using Fourier Transform Infrared Spectroscopy (FTIR) to identify various functional groups involved in iron binding. Scanning electron microscope coupled with energy dispersive x-ray spectroscopic analysis (SEM-EDX) was carried out for both untreated and treated biomass to detect the presence of iron in adsorbed biomass.

Key Words: Adsorption isotherm models, Biosorbent, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Energy Dispersive X-ray spectroscopy (EDX)

INTRODUCTION

Water is an essential resource for living systems, industrial processes, agricultural productions and domestic uses. An increase in population and rapid industrialization has intensified the accumulation of pollutants such as heavy metals, toxic industrial byproducts and synthetic compounds in various terrestrial aquatic environments causing acute water pollution. Due to their mobility in natural water ecosystems and their toxicity to higher life forms, heavy metals in surface and ground waters are considered as major inorganic contaminants in environment1. Also as heavy metals are non-biodegradable and persistent, they pose a significant threat to both environment and public health.

Iron can be a troublesome chemical in water supplies. It is one of the earth’s most plentiful resources as it makes up at least 5 percent of the earth’s crust. As rain water infiltrates the soil and underlying geologic formations, it dissolves iron, causing it to seep into aquatic systems like ground and river waters. Iron is mainly present in water in two forms, either soluble ferrous iron or insoluble ferric iron. Water containing ferrous iron is clear and colorless because the iron is completely dissolved. Ferrous iron further oxidized to ferric iron by dissolved oxygen in water. Rate of oxidation depends on pH and dissolved oxygen level of water. Oxidation rate is slower at pH <4
and at relatively low Dissolved Oxygen (DO) level. Oxidation rate increases with increase in dissolved oxygen and pH of the water forming insoluble ferric hydroxide precipitate. Hence, water turns cloudy and a reddish brown. Although iron is not directly hazardous to health but it is considered as secondary or aesthetic contaminant. Excess of dissolved ferrous iron gives water an unwanted metallic smell and unacceptable taste. Iron concentration as low as 0.3 mg/l may leave a reddish brown stain laundry and table wares that are very hard to remove. Hence the level of iron in water must be kept under control. The commonly used methods for removing metal ions from effluents include chemical precipitation, ion exchange, reverse osmosis, solvent extraction, lime coagulation, membrane separation and electrolysis. However most of the methods have disadvantages like incomplete metal removal, high reagent and energy requirement, generation of toxic sludge and waste products that require careful disposal. Hence, an efficient, environmental friendly and cost effective technology is highly essential. The process of heavy metal removal by biological material is known as biosorption. Various biosorbents have been used like yeasts, moulds, bacteria, various agricultural products, waste tea, exhausted coffee, rice and soybean hulls, different dried leaf powder, husks etc. In our study, we have used leaf power of Ageratum conyzoides as biosorbent for the removal of iron from aqueous solution.

**MATERIAL AND METHODS**

**Preparation of biosorbent material**

The plant weeds Ageratum conyzoides were collected from Selaqui area of Dehradun district, Uttarakhand, India. The leaves of the plant were separated and washed initially with tap water followed by distilled water for 5 times to remove dirt and particulate materials from the surface of the leaves. The washed leaves were then completely dried in sunlight for 1 week. The dried leaves were ground by using a domestic mixer-grinder and later sieved to obtain various standard particle sizes ranging from 53-180 μm.

**Preparation of iron stock solution**

An aqueous stock solution of Fe(III) ions of concentration 1000 mg/l was prepared by using ammonium ferric hydrate salt [NH₄Fe(SO₄)₂·12H₂O] (Merck India) as follows: 8.64 g of ammonium ferric hydrate salt was dissolved in 500 mL of water and 50 mL of 1:1 H₂SO₄ was added. Then the solution was oxidized with 0.1% KMnO₄ solution until faint pink color appears and further the volume was made upto 1l with distilled water. Following that, the stock solution was diluted to various concentrations for further experiments. The pH of the solution was adjusted using 0.1N HCl or NaOH.

**SEM/EDX analysis**

The surface structure of biosorbent was analyzed by scanning electron microscope coupled with energy dispersive X-ray analysis (SEM-EDX) [Model: JEOL JSM5800 with Oxford EDS Detector (JEOL Japan)]. The microscope has tungsten hairpin filament and a maximum acceleration voltage of 30 kV. Dried untreated and treated leaf samples of Ageratum conyzoides were coated with thin gold layer using sputter coater and SEM photographs were taken at 4000X magnification. To determine the chemical composition of biosorbents energy dispersive X-ray spectroscopic analysis were performed on biomass before and after iron biosorption.

**Batch biosorption experiments**

Different batch biosorption experiments were carried out using dried leaf powder of Ageratum conyzoides as biosorbent to optimize various biosorption parameters like time, temperature, pH, rotational speed (rpm), biosorbent dosage and initial iron concentrations. The effect of contact time on Fe(III) biosorption by Ageratum conyzoides was carried out by taking 50 mL Fe(III) solution of concentrations 10, 30, 50 and 80 mg/l in different conical flasks with 200 mg of biosorbent added in each of the flasks. The flasks containing solutions were shaken in a rotary water bath shaker at constant speed of 120 rpm for different time periods (10 – 240 mins) at temperature 20 ± 0.5 ºC. After different time gaps, filtrations were carried out using Whatman No. 1 filter paper and filtrates containing residual Fe(III) concentration were analyzed spectro-
photometrically via complex formation with potassium thiocyanate at 465nm. The removal efficiency of Fe(III) by the biosorbent was calculated by using the following equation,

\[
\text{Removal} (\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)
\]

Where, \(C_0\) and \(C_e\) are the initial and equilibrium liquid phase iron concentrations (mg/l) respectively. Further, the amount of Fe(III) adsorbed by biomass was calculated using the following equation:

\[
q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)
\]

Where, \(q_e\) (mg/g) is the amount of iron adsorbed per unit mass of biosorbent, \(V\) is the volume of the iron solution, \(m\) is the mass of the biosorbent and \(C_0\) and \(C_e\) are the initial and equilibrium liquid phase iron concentrations (mg/l) respectively.

The effect of pH on Fe(III) biosorption was determined at different pH values of 1, 1.5, 2 and 2.5 for Fe(III) solution of concentration 10, 30 and 90 mg/l with 200 mg of biosorbent (150 µm adsorbent size) in a water bath shaker (Remi make) at temperature 20 ± 0.5 ºC and at a constant speed of 120 rpm. The effect of biosorbent dosage was carried out with different biosorbent dosage ranging from 1 – 30 g/l at temperature 20 ± 0.5 ºC, pH 2 for a time of 120 minutes in a water bath shaker at a constant speed of 120 rpm for solutions with different Fe(III) concentrations. The effect of temperature on iron biosorption was also studied at various temperatures like 20, 30, 40, 50 and 60 ºC with initial Fe(III) concentration of 80 mg/l adding 200mg of biosorbent (150 µm adsorbent size) keeping constant agitation speed of 120 rpm at pH 2. Finally the effect of agitation speed on adsorption was measured at different agitation speeds of 50, 100, 150 and 200 rpm for 120 minutes by adding 200 mg of biosorbent (150 µm adsorbent size) to each flask containing 50 ml of 80 mg/l Fe(III) solution at temperature 20 ± 0.5ºC and pH 2.

**Adsorption isotherms**

The adsorption isotherms are one of the most important data to understand the mechanism of adsorption. Isotherm expresses the relation between the amounts of adsorbate removed from the liquid phase by unit mass of adsorbent at constant temperature under equilibrium conditions. Several isotherm models are often used to interpret the equilibrium data. Batch adsorption studies were carried out at a concentration range of 10-90 mg/l using adsorbent dosage of 200 mg (adsorbent size 150 µm) at pH 2 with agitation speed of 120 rpm for 120 minutes at 20 ± 0.5 ºC. In our study Langmuir and Freundlich Models were used to explain the experimental results. The Langmuir model is based on the hypothesis that uptake occurs on a homogeneous surface by monolayer sorption without any interaction between adsorbed molecules. It is expressed as,

\[
q_e = \frac{q_{\text{max}} b C_e}{(1 + b C_e)} \quad (3)
\]

Where, \(q_{\text{max}}\) represents maximum biosorption capacity and \(b\) is the Langmuir constant related to the energy of biosorption. Equation (3) can be rearranged into the following equation from which both the parameters (\(q_{\text{max}}\) and \(b\)) can be calculated by plotting \(1/q_e\) vs \(1/C_e\).

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}} b} \frac{1}{C_e} + \frac{1}{q_{\text{max}}} \quad (4)
\]

The Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, \(R_L\), defined as,

\[
R_L = \frac{1}{1 + b C_0} \quad (5)
\]

Where, \(b\) is the Langmuir constant and \(C_0\) is the initial concentration of Fe(III). The \(R_L\) values indicate the favorability of the isotherms as \(R_L > 1\) indicates isotherm is unfavorable, \(R_L = 1\) indicates linear type of isotherm, \(0 < R_L < 1\) condition indicates isotherm is favorable.

The Freundlich model proposes a monolayer sorption with heterogeneous energetic distribution of active sites and with interaction between adsorbed molecules. It can be expressed as follows,

\[
q_e = K_c C_e^{1/n} \quad (6)
\]

The above equation can be rearranged into the linear form as follows,

\[
\ln q_e = \frac{1}{n} \ln C_e + \ln K_c \quad (7)
\]

Where, \(K_c\) and \(n\) are the Freundlich coefficients.
indicating adsorption capacity and adsorption intensity respectively. The Freundlich coefficient \( n \) should have value lying in the range of 1 to 10 for classification as favorable adsorption.

**FT-IR spectral analysis**

To determine the functional groups responsible for metal uptake Fourier transform infra-red spectroscopy was used. An untreated biomass of *Ageratum conyzoides* and a pre-treated biomass with \( 80 \text{ mg/} \ell \) Fe(III) solution were analyzed using FT-IR spectrophotometer. The adsorption bands were identified in the spectra corresponding to their functional groups. Also the treated and untreated biosorbent samples were compared to detect the functional groups which are responsible for the iron biosorption.

**RESULTS AND DISCUSSION**

**SEM/EDX analysis**

The morphology of *Ageratum conyzoides* was analyzed by scanning electron microscopy (SEM) before and after the Fe(III) adsorption at 4000X magnification Fig. 1(a) and Fig. 1(b). The figure shows that adsorbent has an irregular porous surface which may be responsible for metal biosorption. Corresponding EDX spectrum showed the presence of alkali \( (K^+) \) and alkaline earth metals \( (Ca^{2+}) \) in the biosorbent Fig. 2(a). Losing of these ions after Fe(III) biosorption Fig. 2(b) indicates the ion-exchange mode of biosorption. After biosorption 17.64% of Fe (by weight) was found in the treated sample which was absent in untreated sample Table 1.

**The effect of contact time on adsorption**

The effect of contact time on the removal of Fe(III) is presented in Fig. 3. It is evident from the figure that rate of Fe(III) adsorption is very rapid during the initial time period (upto nearly 10 mins). Thereafter no significant change occurs in the rate of Fe(III) removal and attains nearly a constant value. Availability of large number of vacant surface sites during the initial stages of adsorption can be attributed to this result. After certain time, as most of the vacant sites become occupied remaining sites are difficult to be occupied due to the repulsive forces between adsorbate molecules on the solid surface. Further solution with lower initial concentration attains equilibrium much faster and show higher percentage of Fe(III) removal.

The pH of the solution also plays a major role in biosorption studies. In our study also we investigated the role of pH in Fe(III) biosorption (Fig. 4). Biosorption study was carried out at different pH values (pH 1, 1.5, 2 and 2.5) for Fe(III) solutions with different initial concentrations of 10, 30 and 90 mg/\ell (Fig. 4). All the experiments were carried out below pH 3 to avoid precipitation of ferric ions as ferric...
Fig. 2(a): EDX spectrum of untreated *Ageratum conyzoides*

Fig. 2(b): EDX spectrum of *Ageratum conyzoides* treated with Fe(III) solution

Table 1: EDX data for untreated and treated biosorbent (*Ageratum conyzoides*)

<table>
<thead>
<tr>
<th>EDS data for untreated biosorbent</th>
<th>EDS data for treated biosorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element type</strong></td>
<td><strong>Element %</strong></td>
</tr>
<tr>
<td>Ca</td>
<td>77.47</td>
</tr>
<tr>
<td>K</td>
<td>10.18</td>
</tr>
<tr>
<td>Cl</td>
<td>12.35</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

hydroxide. Result shows initial adsorption rate increases with increasing pH of the solution up to pH 2. At pH 2 percentage of Fe(III) removal by biosorption is highest. The percentage of iron removal decreases further with increase in pH above pH 2. The pH of the solution may influence both the metal binding sites as well as metal chemistry causing the variation in metal adsorption. The optimum pH for biosorption was found to be pH 2.
The effect of biosorbent dose on adsorption

Adsorbent dosages also play a significant role in the biosorption process. Experimental studies were carried out for different biosorbent dosage ranging from 1–30 g/l for solutions with different initial iron concentrations (10, 30, 50 and 80 mg/l) at temperature 20 ± 0.5 °C, pH 2 for a time of 120 minutes. Results show a progressive increase in the percent iron removal with increase in biosorbent dosage (Fig 5). Further increase in biosorbent doses cause a decrease in the amount adsorbed per unit mass (q_e), i.e. adsorption density (Fig 6). The result is evident from the fact that with increasing biosorbent dosage number of available adsorption site increases, hence leading to an increase in the rate of percent iron removal and decrease in the adsorption density with increase in the adsorption dose is due to the unsaturation of adsorption site through the adsorption process 19.

The temperature is also an important factor in the context of biosorption in the solid phase. Increase in temperature increases the rate of diffusion of adsorbate molecules in the internal pores as well as across the external boundary layers leading to an increase rate of adsorption. Also change in temperature causes a change in equilibrium capacity of the adsorbent for a particular adsorbate 20,21. Effect of temperature was carried out at different temperatures 20, 30, 40, 50 and 60 °C with initial Fe(III) concentration of 80 mg/l using adsorbent dosage 200 mg (adsorbent size 150 µm) at pH 2 with agitation speed of 120 rpm for 120 minutes (Fig 7). Result showed a rapid increase in the rate of biosorption upto 40°C, as increase in the rate of diffusion due to increase in temperature causes increase mobility of the adsorbate molecules. With increase in temperature further upto 60°C did not lead to significant change in the percent iron removal.
Attainment of dynamic equilibrium between adsorption and desorption processes may be attributed to this result.

**The effect of agitation speed on adsorption**

Kinetic investigation is also an important factor that plays a major role in the biosorption process. Effect of agitation speed was carried out in the range between 50-200 rpm with initial Fe(III) concentration of 80 mg/l using adsorbent dosage 200 mg (adsorbent size 150 µm) at pH 2 for 120 minutes (Fig 8). Results shows that the rate of Fe(III) adsorption increases to some extent with increase in agitation speed in the range between 50 to 200 rpm. This may be due to the fact that better and more uniform mixing occurs with increase in agitation speed. The optimal agitation speed was found to be 200 rpm.

**Adsorption isotherm**

Batch adsorption studies were carried out at a concentration range of 10-90 mg/l and the results were analyzed using Langmuir and Freundlich isotherms. The separation factor ($R_L$), biosorption capacity ($q_e$ and $K_f$), maximum biosorption capacity ($q_{max}$), intensity of biosorption ($b$ and $n$) were calculated using equations 4, 5 and 7 (Fig. 9 and Fig. 10). Results obtained shows that experimental data were better fitted in the Langmuir equation ($R^2 = 0.994$) compared to the Freundlich equation ($R^2 = 0.861$). The isotherm studies were summarized in the Table 2. The $R_L$ values were calculated for different initial iron concentrations shown in Table 3. The maximum biosorption capacities ($q_{max}$) of some other adsorbents Fe(III) uptake are compared in Table 4.
Infra red spectral analysis

FTIR analysis was carried out for the treated and untreated *Ageratum conyzoides* leaf powder samples and spectral data were obtained (Fig. 11). Functional groups which are responsible for the biosorption were identified from the shifting of peaks in the spectra between treated and untreated samples and listed in Table 5. The results indicate that presence of several functional groups that are available for the binding of ferric ions. The strong adsorption peak at frequency level 3400-3200 cm\(^{-1}\) represents –OH stretching of carboxylic group and also stretching of –NH groups, hence the 3369.76 cm\(^{-1}\) band can be due to the –OH or -NH functional groups present on biosorbent. The trough at 1637.71 cm\(^{-1}\) can be attributed to the C=O stretching mode conjugated to a NH deformation mode. The trough that occurs at 815 cm\(^{-1}\) and 1261.99 cm\(^{-1}\) indicate stretching mode of C-H and C-N functional groups respectively. The band at 1053.71 cm\(^{-1}\) represents the presence of OH groups in the biosorbent. Shifting of the bands in the spectrum of treated sample compared to the untreated sample clearly indicate the involvement of these functional groups in the iron biosorption.

**Table 3 : Values of separation factors (R\(_L\)) for different initial iron concentrations**

<table>
<thead>
<tr>
<th>Initial concentrations C(_o) (mg/l)</th>
<th>R(_L) = 1/(1 + bC(_o))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.392</td>
</tr>
<tr>
<td>30</td>
<td>0.177</td>
</tr>
<tr>
<td>40</td>
<td>0.139</td>
</tr>
<tr>
<td>70</td>
<td>0.084</td>
</tr>
<tr>
<td>90</td>
<td>0.067</td>
</tr>
</tbody>
</table>

**Table 4 : Maximum adsorption capacities of various adsorbents for iron adsorption**

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>q(_{max}) (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Streptomyces rimosus</em></td>
<td>125(^{22})</td>
</tr>
<tr>
<td>Bengal gram husk</td>
<td>72(^{1})</td>
</tr>
<tr>
<td><em>Zoologea ramifera</em></td>
<td>65.49(^{23})</td>
</tr>
<tr>
<td><em>Chlorella vulgaris</em></td>
<td>24.49(^{24})</td>
</tr>
<tr>
<td><em>Aspergillus niger</em> grown on wheat bran*</td>
<td>19.2(^{25,26})</td>
</tr>
<tr>
<td>Dried leaves of <em>Ageratum conyzoides</em></td>
<td>20.9</td>
</tr>
</tbody>
</table>

**Table 5 : IR adsorption bands and corresponding possible functional groups**

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>3369.76</td>
<td>-OH, -NH</td>
</tr>
<tr>
<td>1637.71</td>
<td>-COO(_2), &gt;C=O</td>
</tr>
<tr>
<td>1412.03</td>
<td>-C-C-</td>
</tr>
<tr>
<td>1261.99</td>
<td>-CN</td>
</tr>
<tr>
<td>1053.71</td>
<td>-OH</td>
</tr>
<tr>
<td>815.92</td>
<td>C-H</td>
</tr>
</tbody>
</table>
CONCLUSION

*Ageratum conyzoides* leaf powder can be promising low cost biosorbent for the removal of Fe(III) from waste waters. The optimal condition for biosorption was pH 2, temperature 40°C, agitation speed 200 rpm and contact time 120 minutes. Biosorption fits the Langmuir model ($R^2 = 0.994$) better compared to the Freundlich model ($R^2 = 0.861$). Maximum adsorption capacity ($q_{\text{max}}$) was obtained 20.9 indicating strong binding capacity of the biosorbent for ferric ions also the $R_L$ values were found less than 1 for all iron concentrations indicating that the nature of biosorption was favorable. Further SEM-EDX spectrum data conclusively proves the presence of iron in the treated biosorbent.22-26

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