Removal of Iron using Curry Tree Bark as Adsorbent-Batch Study

Sanchi S.Dange¹, R. M. Dhoble²

¹G.H.Raisoni College of Engineering, Nagpur, Maharashtra, India

²G.H.Raisoni Academy of Engineering & Technology, Nagpur, Maharashtra, India

Abstract: Iron is the most abundantly found metal on Earth and is used for different purposes in the day-to-day life of mankind. Iron is also a vital constituent of human body which helps in performing better regulation of the body. Certain amount of Iron is required for both the male and female body to avoid Iron deficiency in the body. The maximum permissible limit of Iron in Drinking Water according to the standards should be less than 0.3 mg/lit. The present paper describes a study carried out to determine Iron (II) removal capacity of barks of curry tree by Adsorption. The results of the Iron removal by curry tree barks were compared with commercial activated carbon. The removal of iron by curry tree barks was found within permissible limits values of iron in drinking water. The dose of 2.5 gm/lit of curry tree bark at pH 7, temperature 30°C, contact time 120 minutes removed iron within permissible limits and gave removal efficiency greater than 90%.

Keywords: Iron, Adsorption, Water, Earth, Environment

1.Introduction

Water is an essential natural resource for the survival of mankind. Sources of water i.e. surface water, ground water etc. are the major sources of water but due to increasing industrialization these sources of water are rapidly leading to pollution. Contamination of these water sources by heavy metals and other inorganics are a major problem in many developed and also in developed countries. Aluminum, Iron, Nitrate, Chromium, Manganese, Lead, Mercury, Cadmium, Copper, Cobalt, Nickel are the most concerned metals for contamination of water sources according to World Health Organization (WHO).

Around 80% of rural population and 50% of urban population in India are dependent on groundwater for their domestic purposes. Besides these it is found that around 33% of groundwater in India is unfit for drinking purposes which is a topic of concern (27). Not only in India but also in the other countries, provision of safe drinking water is a topic of immediate concern. Increasing discharge of pollutants into the water bodies is leading to the spread of harmful diseases affecting large number of people facing prolonged health issues especially children.

Iron is the second most abundantly found metal in the Earth's crust also it is used for various purposes by humans. Iron is an essential component of human body but if found in excess proportions in the body can cause harm leading to diseases like Alzheimer, Arteriosclerosis, Neurodegenerative diseases, Diabetes Mellitus, Cancer (suspected). Many states of India like Assam, West Bengal, Chhattisgarh, Karnataka, Orissa, Bihar, Punjab, Jharkhand, Madhya Pradesh, Kerala, Tamil Nadu, Maharashtra, Uttar Pradesh, Rajasthan, and also the union territory of Andaman & Nicobar are affected by excess amounts of iron in groundwater. The highest amount of Iron 49 mg/lit was found in a hand pump of Bhubaneswar (26).

Adsorption is proved to be a clean, cost effective, and safe process for removal of excess amounts of metals from

contaminated water. Many adsorbents are proved to be efficient in removing excess metal concentrations from aqueous medium. In the present study Curry Tree Bark is used as adsorbent and its removal capacity of Iron (II) from ground water is investigated.

2. Materials and Methods

All the chemicals used in the study were of analytical grade. Distilled water was used for the performance of batch experiments throughout the study. The glasswares used in the study were of Borosil grade. Testing of Iron concentrations was performed using UV-VIS Spectrophotometer.

1) Adsorbent preparation

Raw barks of curry tree were collected from a local market. The barks were dried in a hot air oven at 70°C for 2 days. The dried barks of curry tree were then treated with concentrated Sulphuric acid taken in equal proportions with distilled water. The barks were then subjected to continuous washing with distilled water to remove excess of acid from the barks. The barks were then dried in a hot air oven at 110°C for 1 day. The barks were then treated with 1N NaOH and then washed until clear colorless wash water was obtained and its pH was 7. The barks were then dried in a hot air oven at 110°C for 1 day and then grounded to powder form. The bark powder was then sieved and the powder passing through 300 μ m and retaining on 150 μ m was used for the performance of experiments. Comparison of curry tree bark results was done with commercial activated carbon.

2) Preparation of Iron (II) Solutions

In the present study metal Iron (II) was used for adsorption experiments. Stock solutions of 100(mg/lit) were prepared by dissolving Ferrous Ammonium Sulphate (FAS) in 100 ml distilled water.1,10 phenanthroline monohydrate was used as indicator. Hydroxyl Ammonium Chloride was used as reducing agent in the study. The same proportions of iron solutions were prepared for testing with commercial activated carbon.

3) Adsorption experiments

Batch experiments were performed in the study to determine Iron removal capacity by Curry Tree Barks. The agitation was done in Orbital shaking Incubator. Adsorption experiments were performed at 30±1°C. Different batch experiments were conducted for dose of curry tree bark powder (1, 2, 2.5, 4, 6, 8, 10 gm/lit), pH (4-10), contact time (30-420 min.), temperature (15°, 20°, 25°, 30°, 40°C), initial metal ion conc. (3mg/lit), metal ion conc. (2, 4, 5, 6, 7 mg/lit). The filter paper used was Whatman 1 filter paper. Batch experiments conducted for commercial activated carbon included varying doses (1, 2, 4, 6, 8, 10 gm/lit); while batch experiments for pH, contact time, temperature, and metal ion concentration where performed similar to as performed for curry tree bark powder. The percent removal of Iron after adsorption with curry tree bark adsorbent was calculated by

$$\% Removal = \frac{Initial \ conc. -Final \ conc.}{Initial \ conc.} \times 100$$

4) Characterization of Curry Tree Bark

The characterization of curry tree bark was carried out using XRF, FTIR.

3. Results and Discussion

1) Batch experiment for Dose

The initial conc. taken was 3 mg/lit. The dose of adsorbent i.e. curry tree bark was varied from 1, 2, 2.5, 4, 6, 8, 10 gm/lit. Removal of Iron was obtained within permissible limit at 2.5 gm/lit. Thus the further batch experiments were performed taking dose 2.5 gm/lit. The dose for commercial activated carbon was varied from 1, 2, 4, 6, 8, 10 gm/lit. For commercial activated carbon removal of iron was obtained within permissible limit at 1 gm/lit. For both curry tree bark as well as for commercial activated carbon as the dose increases removal efficiency of iron increases. These may be due to increasing avaibility of active sites of adsorbent with increasing dosages.

2) Batch experiment for pH

The study for pH was carried out by taking a range of 4-10 pH. The maximum removal of Iron (II) within permissible limit was obtained at pH 4 for both curry tree bark powder as well as for commercial activated carbon.

3) Batch experiment for contact time

The batch experiment for contact time was performed from time 30 min. to 360 min. The Iron (II) ions were removed within permissible limit in 120 minutes by curry tree bark while for commercial activated carbon iron ions were removed within permissible limits in 15 minutes.

4) Batch experiment for Temperature

The removal of Iron at temperatures 15°, 20°, 25°, 30°, 40°C was studied. The maximum removal for iron was obtained with increase in temperature. The increase in removal with

increasing temperature shows supportive chemisorptions for both curry tree bark adsorbent and also for commercial activated carbon.

5) Batch experiment for initial metal ion concentration

The batch experiment for metal ion concentrations was performed by varying iron concentrations. The concentrations varied from 2, 4, 5, 6, 7 mg/lit. The removal efficiency decreased with increase in concentration of iron these may be due to unavaibility of active sites of adsorbent with increase in metal ion concentrations.

6) Batch experiment for co-existing ions

The presence of different anions and cations in the groundwater affect the adsorption process. Batch experiment for co-existing ions were performed by taking cations Mg, Ca and anions Cl, SO₄, F.



Figure 1: Effect of dose for the removal of Fe (II) ions



Figure 2: Effect of pH for the removal of Fe (II) ions



Figure 3: Effect of contact time for the removal of Fe (II) ions

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Figure 4: Effect of temperature for the removal of Fe (II) ions



Figure 5: Effect of Initial conc. for the removal of Fe (II) ions



Figure 6: Effect of co-existing ions on Fe (II) ions





4. Adsorption Isotherms

The study of Adsorption isotherms is an important parameter in case of research carried out on the principle of adsorption. Adsorption isotherms provide details of the characteristics of adsorbent and adsorbate behavior. Langmuir and Freundlich isotherms are amongst the most commonly used isotherms in adsorption study.

1) Langmuir Isotherm Model

The basic assumption of Langmuir isotherm is that sorption takes place at specific homogeneous sites within the sorbent (9).

The Langmuir model was expressed as Langmuir (1916)

$$qe = \frac{qm \ \text{kL Ce}}{1 + k\text{L Ce}}$$

Where Ce is concentration of Fe ions at equilibrium (mg/L), q_e is amount of Fe ions adsorbed at equilibrium (mg/g), KL is Langmuir isotherm constant related to free energy of adsorption, qm is max. Adsorption capacity (mg/g).(11-13)

The Langmuir equation can be linearised to

$$\frac{C_e}{q_e} = \frac{C_e}{qm} + \frac{1}{qm \, kL}$$



Figure 8: Langmuir isotherm model for Fe (II) ions removal by curry tree bark adsorbent

2) Freundlich Isotherm Model

The Freundlich isotherm assumes a heterogeneous surface with a non-uniform distribution of heat of biosorption over the surface and a multilayer biosorption can be expressed Freundlich,(9)

The Freundlich equation is given as (1906) (14)

$$q_e = K_f C_e^{\frac{2}{n}}$$

Where K is Freundlich indicative of relative adsorption capacity of adsorbent, n is Freundlich indicative of the intensity of adsorption.

The Freundlich equation can be linearised as $logq_e = logK_f + \frac{1}{\pi} logC_e$

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Figure 9: Freundlich isotherm model for Fe(II) ions removal by curry tree bark adsorbent

According to the obtained R^2 values by Langmuir and Freundlich isotherm models the data fits best by Freundlich model as compared to Langmuir because of higher R^2 value of Freundlich model.

5.Adsorption Kinetics

1) Lagergren Pseudo-first order

Kinetic models are used to examine the rate of the adsorption process .The kinetic data obtained from batch studies have been analyzed by using pseudo first order and pseudo second order models.

$$\log(q_{e} - qt) = \log q_{e} - \left(\frac{\kappa_{1}}{2.303}\right)t$$

Where q_e and qt are the amounts of Fe ions adsorbed (mg/g) on the adsorbent at equilibrium and at time t respectively and k_1 is the rate constant of pseudo first order adsorption min-1.



Figure 10: Lagergren pseudo-first order model for Fe (II) ions removal by curry tree bark adsorbent

2) Lagergren Pseudo-second order

The equation of lagergren second order is expressed as(9)

$$\frac{c}{qt} = \frac{1}{k_2 q_e} + \frac{c}{q_e}$$

A plot of time in (min.) versus time/qt is plotted where k_2 is equilibrium rate constant of pseudo second order, t is the

time in (min.) and q_{e} and qt is mass of metal adsorbed at equilibrium at time t.





According to the R^2 values obtained by pseudo first and second order models pseudo second order model fits best to the adsorption data.

6. Characterization

1) XRF Scanning

| Na ₂ O % | MgO % | SiO ₂ % | Al ₂ O ₃ % |
|---------------------|--------------------------|----------------------------------|----------------------------------|
| 0.05 | 0.03 | 0.22 | 0.097 |
| | | | |
| $P_2O_5 \%$ | SO ₃ % | Fe ₂ O ₃ % | TiO ₂ % |
| 0.02 | 1.23 | 0.04 | 0.01 |
| | | | |
| K ₂ O % | SrO % | $Cr_2O_3\%$ | NiO % |
| 0.005 | 0.025 | 0.01 | 0.003 |
| | | | |
| CaO % | Cl % | CuO % | LOI % |
| 3.637 | 0.03 | 0.006 | 94.29 |







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7. Thermodynamic parameters

Van Hoff plot





The effect of temperature on curry tree bark adsorbent at temperature 20°C, 30°C, 40°C shows that the removal capacity of Fe (II) ions by curry tree bark adsorbent increases with the increase in temperature. This indicates that the adsorption process is endothermic in nature. The thermodynamic parameters including the change in Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from following equations:

$\Delta G^{o} = -RT \ln K$

Where R is the universal gas constant $(8.314 \times 10^{-3} \text{ kJ/mol} \text{ K})$, T is the temperature (K) and K (q_e/Ce) is the distribution coefficient. The enthalpy (ΔH°) and entropy (ΔS°) parameters were estimated from the following equation: $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$

It can be written as $-RT \ln K = \Delta H^{\circ} -T \Delta S^{\circ}$

Or

$$lnK = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

| Sr. | Thermodynamic | Temperature | Thermodynamic |
|-----|--|-------------|---------------|
| No. | Parameters | (K) | Values |
| 1 | ∆G° (kJ/mol) | 293 | 1.3778 |
| | | 303 | -0.5362 |
| | | 313 | -2.4502 |
| 2 | ΔH ^o (kJ/mol) | | 57.458 |
| 3 | $\Delta S^o \left(J / (mol \; k) \right)$ | | -0.1914 |

The obtained value of ΔG° became more negative with increase in temperature which indicates that with increase in temperature there is increase in spontaneity of adsorption process. The obtained value of ΔH° is positive which indicates that is endothermic in nature. The negative value of ΔS° indicates that the adsorption process resulted in the increase of randomness in the solid liquid interface.

8. Conclusion

In the study the adsorption capacity of Curry Tree Bark for the removal of Iron was studied. The curry tree bark was found efficient for the removal of Iron within permissible limits and gave greater than 90% efficiency of removal. The performed batch experiments indicate that curry tree bark as adsorbent is suitable for removal of Iron. The experimental data obtained from isotherm models and kinetic studies shows that data well fits with Freundlich isotherm model and fits the Lagergren pseudo second order kinetic model. The thermodynamic studies performed indicates that adsorption of Fe(II) ions is endothermic in nature. Thus curry tree bark is an efficient, low cost adsorbent and it can be considered as an eco-friendly adsorbent. While adopting any method for water treatment the essential aspect considered must be that the method should be efficient, eco-friendly, and should leave minimum adverse effects on the environment.

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