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Biosorption of iron(III) from aqueous solutions using the husk of *Cicer arientinum*

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Iron is a major pollutant released as a by-product during several industrial operations especially during acid mining of metal ores. In this paper, the use of Bengal gram husk (husk of channa dal, *Cicer arientinum*) in the biosorption of Fe(III) from aqueous solutions is discussed. Parameters like agitation time, adsorbent dosage and *p*H were studied at different Fe(III) concentrations. The adsorption data fit well with Langmuir and Freundlich isotherm models. The adsorption capacity (q_{max}) calculated from the Langmuir isotherm was 72.16 mg of Fe(III)/g of the biosorbent at an initial *p*H of 2.5. Desorption studies were performed at different concentrations of hydrochloric acid showing that quantitative recovery of the metal ion is possible. The infrared spectra of the biomass before and after treatment with Fe(III), revealed that hydroxyl, carboxyl and amide bonds are involved in the uptake of Fe(III) ions.

Keywords: Heavy metals, Iron, Biosorption, Langmuir isotherm, Infrared spectra
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The production of heavy metals has increased rapidly since industrial revolution[1]. Heavy metals usually form compounds that can be toxic, carcinogenic or mutagenic even in low concentrations[2]. Due to their mobility in natural water ecosystems and their toxicity to higher life forms, heavy metals in surface and groundwater supplies have been prioritised as major inorganic contaminants in the environment. Even if they are present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that through natural processes such as biomagnification, concentrations may become elevated to such an extent that they begin exhibiting toxic characteristics.

Apart from environmental issues, technological aspects of metal recovery from industrial wastewaters must also be considered[3]. Metal resources are non-renewable natural resources and are being depleted at faster rate due to increasing demand. It is therefore imperative that those metals considered environmentally hazardous or which are of technological importance and strategic significance or economic value, be recovered at their source through viable treatment options.

Conventional chemical (precipitation/neutralisation) or physical (ion exchange, activated carbon sorption and membrane technology) treatment techniques are inherently problematic in their application to metal bearing wastewaters. Chemical treatment methods can prove costly to the user, as the active agent cannot be recovered for reuse in successive treatment cycles. Also, the end product is usually a low-volume, highly concentrated metal bearing sludge, that is difficult to be dewatered and disposed off.

Biological methods of metal recovery termed as biosorption have been suggested as cheaper, more effective alternatives to existing treatment techniques. The process of adsorption is a well established and powerful technique for treating domestic and industrial effluents.

Biosorption is a collective term for a number of passive, metabolism independent, accumulation processes and may include physical and/or chemical adsorption, ion exchange, coordination, complexation, chelation and micro-precipitation accumulating heavy metals[4–7] such as Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{2+}, and Ni^{2+}.

The mechanism of binding of metal ions by adsorbents may depend on the chemical nature of metal ions (species, size, ionic charge), the type of biomass and environmental conditions (*p*H, temperature, ionic strength), and existence of competing organic or inorganic metal chelators[8-10].

In this regard, low cost biosorbents, such as seaweeds, moulds, yeast, bacteria, crabshells, agricultural products such as wool, rice, straw,

coconut husks, peat moss, exhausted coffee[11], waste tea leaves[12], walnut skin, coconut fibre[13], polymerized corn cob[14], melon seed husk[15], defatted rice bran, rice hulls, soybean hulls and cotton seed hulls[16,17], wheat bran, hardwood (*Dalbergia sissoo*) sawdust, pea pod, cotton and mustard seed cakes, petiolar felt sheath of palm[18-20] have been tried.

Iron exists in two forms, soluble ferrous iron (Fe^{2+}) and insoluble ferric particulate iron (Fe^{3+}). The presence of iron in natural water may be attributed to the dissolution of rocks and minerals, acid mine drainage, landfill leachate sewage or engineering industries. Iron in water is generally present in the ferric state.

Iron typically enters water bodies in the form of ferrous iron (Fe^{2+}), which can be oxidised to ferric iron (Fe^{3+}) by the oxygen dissolved in water. The rate of oxidation reaction depends primarily on the *p*H and on the level of dissolved oxygen in water (DO). At *p*H <4 and a relatively low dissolved oxygen, the oxidation process to ferric iron is very slow. At *p*H>4, however Fe^{2+} ions oxidise quickly to Fe^{3+} ions, which then react with water producing ferric hydroxide precipitate and acidity

$$Fe^{2+} + ¼\ O_2 + H^+ = Fe^{3+} + ½\ H_2O$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3\ (s) + 3\ H^+$$

If the *p*H drops below 3, the ferric ions cease to precipitate and remain in water in partially hydrolysed forms.

The presence of iron at concentrations above 0.1 mg/L will damage the gills of the fish[21]. The free radicals formed by the iron on the surface of the gills will cause oxidation of the surrounding tissue and this will lead to massive destruction of gill tissue and anemia.

The presence of iron in drinking water supplies, is objectionable for a number of reasons. Under the *p*H condition existing in drinking water supply, ferrous sulphate is unstable and precipitates as insoluble ferric hydroxide, which settles out as a rust coloured silt. Such water often tastes unpalatable even at low concentration (0.3 mg/L) and stains laundry and plumbing fixtures.

The objective of the present investigation was to examine the sorption of Fe(III) onto Bengal gram husk (bgh), an agromilling waste available in plenty in a tropical country like India.

Experimental Procedure

Biosorbent material

Bengal gram husk (*channa dal*), seed coat of *Cicer arientinum* was collected from a legume seed-splitting mill. The Bengal gram husk (bgh) was washed extensively in running tap water to remove dirt and other particulate matter. Following this, washing and boiling in distilled water was done repeatedly to remove colour. The washed and boiled Bengal gram husk was oven dried at 105°C for 24 h stored in a desiccator and used for biosorption studies in the original piece size.

Preparation of stock solution

An aqueous stock solution (1000 mg/L) of Fe(III) ions was prepared using ferrous ammonium salt as follows: 7.022 g of crystallized ferrous ammonium sulphate was dissolved in 500 mL of water and 50 mL of 1:1 sulphuric acid was added. The solution was warmed and oxidized with approximately 0.1% potassium permanganate solution until the solution remained faintly pink made upto 1 L with distilled water[22]. The *p*H of the solution was adjusted using 0.1 N HCl or NaOH. Fresh dilutions were used for each study.

Biosorption studies

The biosorption capacity of bgh was determined by contacting various concentrations (10-100 mgL^{-1}) of 100 mL iron solution in 250 mL conical flasks, with 1 g of bgh. The mixture was shaken in a rotary shaker at 120 rpm followed by filtration using Whatman filter paper (No. 1).

The filtrate containing the residual concentration of Fe(III) was determined spectrophotometrically at 530 nm after complexation with sodium salicylate[22]. For the determination of rate of metal biosorption by bgh from 100 mL (at 10, 20, 50, 100 mgL^{-1}), the supernatant was analysed for residual Fe(III) after the contact period of 15, 30, 60, 120, 180, 240 and 300 min. The effect of *p*H on Fe(III) sorption by bgh, was determined at *p*H values of 2, 2.5, 3, 3.5 and 4. The effect of adsorbent dosage was studied at different dosages ranging from 1 to 40 g/L with varied metal concentrations of 10, 20, 50 and 100 mg/L.

Adsorption isotherm studies were carried out with ten different initial concentrations ranging from 20 to 500 mg/L of Fe(III) while maintaining the adsorbent dosage at 1 g/100 mL. Langmuir and Freundlich models were applied to the adsorption isotherm and

different constants were generated. The Langmuir and Freundlich adsorption parameters and correlation coefficient were also calculated from the adsorption isotherm data.

Infrared spectra analysis

In order to determine the functional groups responsible for metal uptake, an un-reacted bgh sample and bgh pretreated with 100 mg/L iron solution were analysed using a Fourier transform infrared spectrometer.

Results and Discussion

Sorption equilibria studies

The equilibria of biosorption of iron were modeled using adsorption-type isotherms. The Freundlich and Langmuir models were used to describe the biosorption equilibrium.

The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by:

$$q = \frac{q_{max} b C_{eq}}{1 + b C_{eq}}$$

where q is milligrams of metal accumulated per gram of the biosorbent material; C_{eq} is the metal residual concentration in solution; q_{max} is the maximum amount of the metal ion per unit weight of the biosorbent to form a complete monolayer on the surface bound at high C_{eq}. q_{max} represents a practical limiting adsorption capacity when the surface is fully covered by metal ions and assists in the comparison of adsorption performance. b is the constant related to the affinity of the binding sites.

When the initial metal concentration rises, adsorption increases till the binding sites are not saturated. The linearised Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constants and is equated by the following equation.

$$C_{eq}/q = 1/q_{max}.b + C_{eq}/q_{max}$$

The linear plots of C_{eq}/q versus C_{eq} show that adsorption follows the Langmuir adsorption model (Fig. 1).

The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as:

$$R_L = 1/(1+bC_o)$$

where b is the Langmuir constant and C_o is the initial concentration of Fe(III). The R_L value indicates the shape of isotherm as shown in Table 1. An isotherm is favourable, if its fixation capacity grows rapidly with concentration in equilibrium in liquid phase, convex form. The maximum for a highly favourable isotherm is irreversible adsorption, where the amount adsorbed does not depend on the decrease in concentration, down to very low values, unlike unfavourable isotherms, which have a low adsorption capacity at low concentrations in equilibrium, concave forms.

The R_L values between 0 and 1 indicate favourable adsorption[23]. The R_L were found to be 0.754 to 0.1612 for the initial concentrations of 25-500 mg/L Fe(III), indicating that the adsorption of Fe(III) by bgh was favourable.

The Freundlich isotherm is represented by the equation[24],

$$q = K_f C_{eq}^{1/n}$$

where C_{eq} is the equilibrium concentration (mg/L), q is the amount adsorbed (mg/g) and K_f and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity, respectively. The linearised form of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$\ln q = \ln K_f + 1/n \ln C_{eq}$$

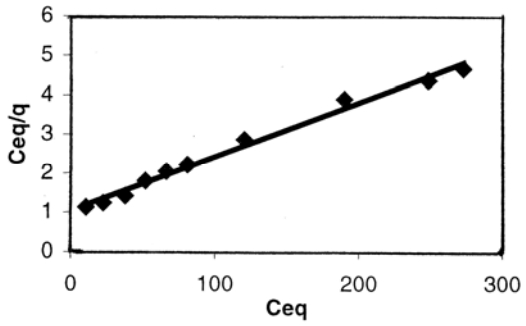

Fig. 1—Langmuir adsorption isotherm for Fe(III) biosorption by bengal gram husk at optimum conditions

Table 1—Relationship between R_L and the type of isotherm

R_L	Type of isotherm
R_L>1	Unfavourable
R_L=1	Linear
0< R_L<1	Favourable
R_L = 0	Irreversible

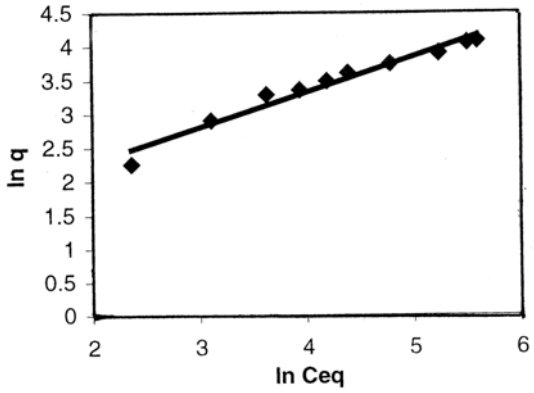

Fig. 2—Freundlich adsorption isotherm for Fe(III) biosorption by bengal gram husk at optimum conditions

Table 2—Sorption isotherm constants and coefficients of determination for bgh

	Langmuir equation			Freundlich equation		
	q_{max} (mg/g)	b (1/mg)	R^2	K_F (mg/g)	$1/n$	R^2
Iron	72.16	0.013	0.9897	3.492	0.516	0.9623

Table 3—Comparison of the Langmuir constants for iron

Adsorbent	q_{max} (mg/g)	Reference
Industrial biomass (*Aspergillus niger* grown on wheat bran)	19.2	25
Streptomyces rimosus	125	26
Chlorella vulgaris	24.49	27
Schizomeris leibleinii	101.70	28
Zoologea ramifera	65.49	29
Bengal gram husk	72	This study

K_f and n were calculated from the slopes of the Freundlich plots (Fig. 2).

The coefficients of determination (R^2) and the isotherm constants of Langmuir and Freundlich are given in Table 2.

The Langmuir capacity or q_{max} is used to compare the efficiency of Bengal gram husk with other materials, which have been tested as biosorbents for iron. Table 3 makes such a comparison and, shows that, for iron, the Bengal gram husk has a greater capacity than some of materials tested previously.

Effect of *p*H

The optimum *p*H for biosorption of ferric iron on to bgh (husk of *Cicer arientinum*) was observed at *p*H 2.5. The effect of *p*H at different concentrations of ferric ions is shown in Fig. 3. To avoid precipitation of ferric ions as their hydroxides, all the experiments

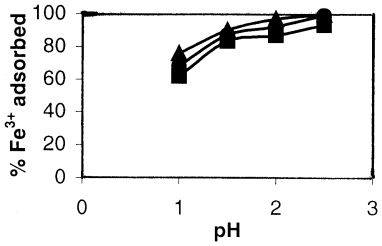

Fig. 3—Effect of *p*H on the biosorption of Fe(III) at different metal concentrations (▲ 10 ppm; ● 20 ppm; ■ 50 ppm), by 10 gL^{-1} at 120 rpm with equilibrium time of 200 min

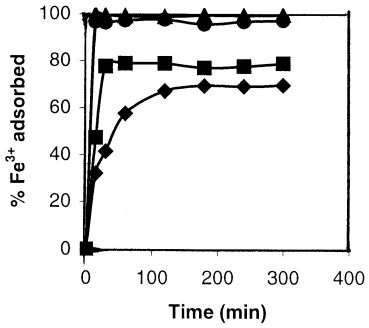

Fig. 4—Percentage biosorption of Fe(III) from solution at different metal concentration (▲ 10 ppm; ● 20 ppm; ■ 50 ppm; ♦ 100 ppm), *p*H 2.5, by 10 gL^{-1} bgh as related to the time of contact at 120 rpm

were carried out below *p*H 3. The *p*H of solution influences both the metal binding sites as well as metal chemistry in solution. The initial adsorption rates increased with increasing initial *p*H up to optimum *p*H values. At higher *p*H values, Fe(III) precipitated because of the high concentration of OH ions in the adsorption medium[28,30] and so adsorption experiments at *p*H>3 could not be performed. The percentage of iron adsorbed at *p*H 2.5 decreased with increasing metal concentration.

Effect of time and biomass concentration on the adsorption of bgh

The sorption of iron by bgh biomass was very rapid for 10 mgL^{-1} solutions and the equilibrium was achieved within 15 min. For 25 and 50 mgL^{-1} solutions, the equilibrium was achieved within 60 min and the percentage of Fe(III) adsorbed was 97 and 78% respectively. In 100 mgL^{-1}, the sorption equilibrium was achieved in 180 min and the percentage adsorbed is 70% (Fig. 4). It is clear from the results that the time required for maximum uptake of Fe(III) ions by bgh was dependent on the initial Fe(III) concentrations. This result is interesting, as the equilibrium time is an important parameter for

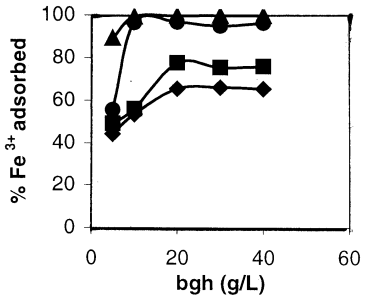

Fig. 5—Effect of quantity of bgh biomass on biosorption of Fe(III) from solutions at different metal concentrations (▲ 10 ppm; ● 20 ppm; ■ 50 ppm; ♦ 100 ppm), *p*H 2.5 for contact time of 200 min at 120 rpm

economical wastewater treatment operations. According to the above results, the agitation/ equilibrium time was fixed at 200 min for the rest of the experiments so that equilibrium is reached.

The bgh biomass was varied between 5 to 40 g L^{-1} with the variation in metal concentration to understand, whether the decline in metal adsorption with the increase in initial metal ion concentrations is due to the saturation of bgh sites by iron. This is illustrated in Fig. 5, which indicates that for 10 and 25 ppm metal solutions, the amount of biomass required to remove 99 and 96% of Fe(III) was 10 g L^{-1} and the amount of biomass required to attain the maximum sorption capacity for 50 and 100 ppm Fe(III) solutions was 20 g L^{-1}. Earlier studies have indicated that at a given equilibrium concentration, biomass adsorbs more metal ions than at higher loading[25,31-34].

Desorption studies

The desorption studies were carried out by filtering the Fe(III) loaded adsorbent from solution, washing gently with distilled water to remove unadsorbed Fe(III) and agitating the metal loaded adsorbent with varying concentrations of HCl. The results are shown in Fig. 6. It is evident that with increase in the HCl concentration, the desorption of Fe(III) ions increased. Above 1 M HCl, the structure of the biomass disintegrated, hence the experiments were terminated.

Infra-red spectral analysis

In order to determine the functional groups responsible for metal uptake, infra-red spectroscopy was used. An un-reacted bgh sample and bgh pretreated with 100 mg/L Fe(III) solution were analysed. The frequencies of vibrations and their corresponding groups are shown in Table 4. The

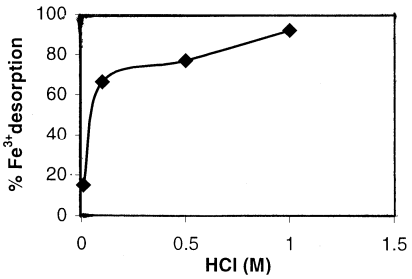

Fig. 6—Effect of HCl concentration on % desorption of Fe(III)

Table 4—IR absorption bands and the corresponding functional groups

Wave number (cm^{-1})	Functional group
3431	–OH, –NH
2925	–CH
2345	–OH
1110	–C–O, –C–N
1437	–CH
1060	–OH

results indicate that there are several functional groups that are available on the surface of bengal gram husk for binding the Fe^{3+} ions. The strong absorption peak at frequency level of 3400–3200 cm^{-1} represents –OH stretching of carboxylic groups and also representing stretching of –NH groups. The peak at 2925 cm^{-1} can be assigned to –CH stretching. The trough at 2345 and 1060 cm^{-1} can be attributed to the –OH group. The absorption peak at 1110 cm^{-1} is due to CO or CN groups.

Conclusion

In this study, the potential of using a milling agro-waste, bengal gram husk has been assessed for the biosorption of Fe(III). In batch mode studies, adsorption was dependent on contact time, *p*H, initial metal ion concentration and biosorbent dosage. Adsorption followed Langmuir and Freundlich isotherm models. The infra-red spectral analysis show that several functional groups like amide, hydroxyl and carboxyl groups are available for biosorption of metal ions. Moreover, the desorption experiments show that the metals can be desorbed after adsorption and Fe(III) can be recovered. Biomass residues, like bengal gram husk have several advantages such as costly nutrients are not required for its culturing and growth (unlike microbial biomass), the processing conditions are not restricted and a wider range of operating conditions such as *p*H, temperature and

metal concentrations are possible and metal can be desorbed and easily recovered. Finally, the use of such biomass studies can be viewed as part of the waste management strategy.

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