

BATCH ADSORPTION STUDIES FOR IRON(III) REMOVAL FROM AQUEOUS SOLUTION BY SAND AND CHARCOAL MIXTURE

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Abstract: In this study, batch adsorption of Fe(III) ions onto sand and charcoal mixture(2:1) was investigated. The factors controlling the adsorption process such as agitation time, initial pH, dosage and initial concentration have been examined. The equilibrium time was found to be 150 minutes. The adsorbent showed a high affinity to Fe(III) ions at pH values between 3.0 to 4.0. Fe(III) adsorption equilibrium was analyzed with both Langmuir and Freundlich isotherm equations. Maximum Fe(III) adsorption capacity of the mixture was calculated to be 19.23077 mg/g. Fe(III) adsorption kinetics fitted well with the pseudo second order model.

Keywords: batch adsorption; sand; charcoal; Langmuir; kinetics

1. Introduction:

Water contamination by heavy metals has become a major environmental problem owing to their non-biodegradability and harmful effects when they exceed the tolerance levels. Iron is present naturally in water, in the ferrous state in dissolved form or in the oxidised ferric state. However, when the concentration of iron exceeds the tolerance limit, it causes taste, odour, and indirect health-related and economic problems. Iron is an essential mineral helping in the transportation of oxygen in the blood, however, its presence in ground water above a certain level makes water unusable due to its metallic taste, discoloration, odour, turbidity and staining of laundry [1]. Iron overload in drinking water may cause vomiting, bleeding and circulatory disorders [2]. When the iron combines with tea, coffee and other beverages, it produces an inky, black appearance and a harsh, unacceptable taste. Vegetables cooked in water containing excessive iron turn dark and look unappealing [3]. Iron is considered a secondary or “aesthetic” contaminant and the recommended limit of 0.3 mg/L is based on taste and appearance rather than on any detrimental health effect [4,5]. Therefore, iron needs to be removed from water. Iron removal is most commonly performed by oxidation/filtration, ion exchange and sequestering. In many cases, chemical precipitation technique is used to precipitate out the contaminants by adding suitable chemicals. Adsorption is a process of removing specific components from waste water by adsorption on solid surfaces. It is a low cost and simple to handle method. Iron levels exceed the permissible limit in most parts of Assam. People in rural areas in Assam uses indigenous household sand filters to free drinking water from iron. Activated carbon is one of the most widely used adsorbents due to having extensive surface area, favourable pore size distribution and high degree of surface reactivity [6].

2. Materials and methods:

Adsorbent: Sand was collected locally and washed thoroughly with distilled water to get rid of soluble impurities. This was oven dried and sieved and the fractions between 0.595 mm and 0.063 mm were chosen. Charcoal was obtained commercially (Charcoal Activated, Merck). The sand is mixed with charcoal in 2:1 proportions for adsorption experimentation.

Adsorbate solution : The synthetic adsorbate solutions in water was prepared from anhydrous FeCl₃ (Qualigens, mol. wt = 162.21 g) . The required amount of FeCl₃ was weighed and dissolved in distilled water for each required concentration of Fe(III).

Adsorption experiment : The adsorption experiments are carried out in Erlenmeyer flasks by mixing a fixed amount of the adsorbent with 20 ml of aqueous Fe(III) solution. The mixture is agitated in a thermostatic water bath shaker (NSW, Mumbai, India) for a pre-determined time interval. The mixture is then filtered and Fe(III)

remaining unadsorbed in the supernatant liquid is determined spectrometrically (Flame Atomic Absorption Spectrometer, Perkin Elmer). All the experiments are done in triplicate to avoid experimental error. Batch adsorption experiments were carried out by varying: interaction time, pH, amount of adsorbent and initial concentration of Fe(III).

The amount of Fe(III) adsorbed per unit mass of the adsorbent (q_e) and adsorption % was calculated by Equations (1) and (2), respectively.

$$q_e = (C_o - C_e)V/m \quad (1)$$

$$\text{Adsorption \%} = \{(C_o - C_e) \times 100\} \div C_o \quad (2)$$

where, q_e is the amount of Fe(III) adsorbed(mg/g), m is the mass of adsorbent (g) and V is the volume of Fe(III) solution (L), C_o is the initial Fe(III) concentration (mg/L), C_e is the equilibrium concentration of the metal ion (mg/L).

3. Results and discussion:

Influence of contact time

The effect of contact time on the adsorption of Fe(III) was studied at initial concentration of 50 mg/L and normal pH. The adsorption is rapid in the first 60 minutes for sand- charcoal mixture after which it slowly attains equilibrium at ~ 150 min(Fig. 1).

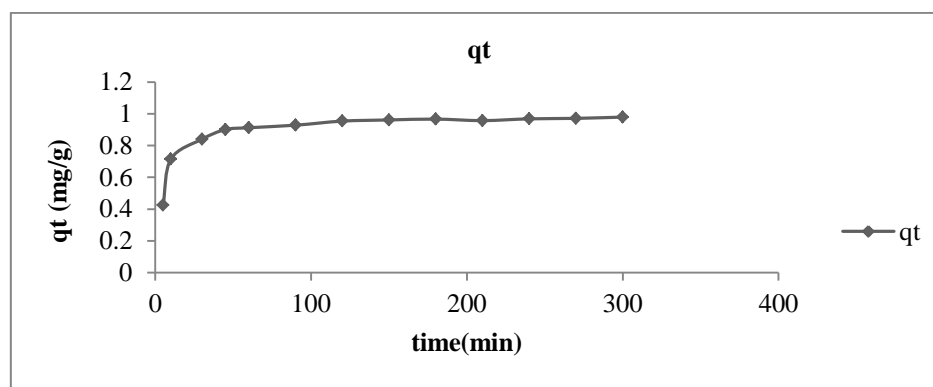


Figure 1: Influence of contact time.

At the onset of adsorption process, i.e., at low coverage, removal of Fe(III) is very rapid, but as the coverage increase, the number of available surface sites come down, and the rate decrease till equilibrium is approached. At equilibrium, the uptake is controlled by the rate at which the metal ions are transported from the external surface to the interior sites of clay [7].

Influence of pH

Since pH is one of the main variables affecting the sorption process, influencing not only the speciation of the metal ions, but also the surface charge of the sorbent and the degree of ionization of the adsorbate during the reaction[8]. Adsorption percentage increased from 15.37% to 95.09% for sand- charcoal mixture (2:1) on increasing pH from 2 to 4(Fig. 2). Adsorption at pH values higher than 4.0 was not studied due to precipitation of the metal as Fe(III)-hydroxide, which introduces uncertainty into the interpretation of the results.

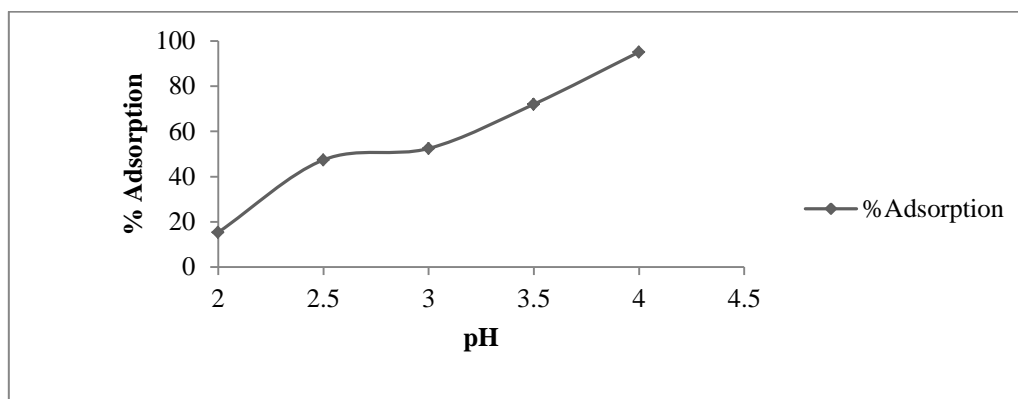


Figure 2: Influence of pH.

At very low pH, Fe(III) ions face stiff competition from H_3O^+ ions for the adsorption sites and consequently, adsorption of Fe(III) is low. As the pH increase, acidity decreases and the competition for the adsorption sites decreases.

Influence of adsorbent dose

Adsorbent dose is a significant factor to be considered for effective removal as it determined sorbent-sorbate equilibrium of the system [9]. Adsorption of Fe(III) was investigated at various adsorbent dosage with Fe(III) concentration fixed at 50 mg/L. Adsorption of Fe(III) was investigated at various dosage ranged from 0.5 g sand mixed with charcoal in the range of 0.5- 2.5 g per litre of Fe(III) solution in the ratio of 1:1, 1:2, 1:3, 1:4 and 1:5. Adsorption percent increased on increasing amount of sand- charcoal mixture from 1 g/L to 3 g/L from 56.25% to 80.13 % as shown in Fig. 3.

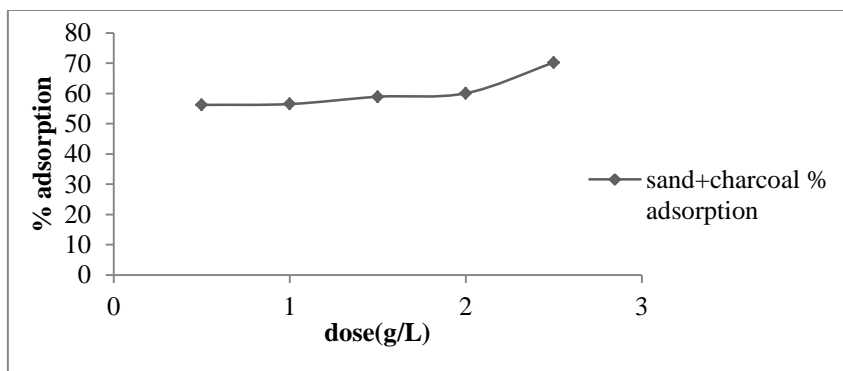


Figure 3: Influence of adsorbent dosage.

The increase in the adsorption percentage with an increase in adsorbent dosage can be attributed to increased surface area and the availability of more adsorption sites. The adsorption amount(q_e) decreases with an increase in adsorbent dosage. The decrease in the adsorption amount may be attributed to overlapping or aggregation of adsorption sites resulting in decrease in total adsorbent surface area [10].

Influence of initial concentration

Adsorption percentage decreased from 89.74% to 56.27 % for sand- charcoal mixture on increasing initial Fe(III) concentrations from 5 mg/L to 80 mg/L. Adsorbed amount of Fe(III) ions, on the other hand, was increased by increasing of initial Fe(III) concentrations (Fig.4).

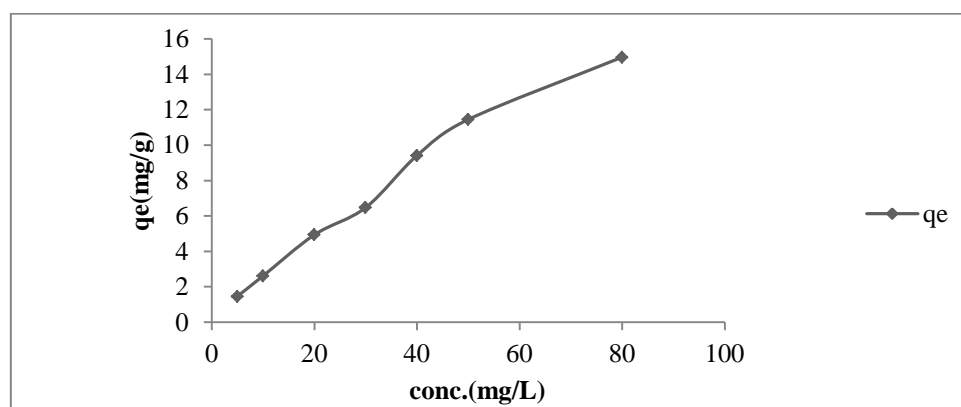


Figure 4: Influence of initial Fe(III) concentration.

When the initial concentration of Fe(III) is increased, the extent of adsorption (%) of Fe(III) comes down, and significantly, the amount adsorbed per unit mass, q_e , shows an increasing trend. At low initial metal ion concentration, the ratio of the number of Fe(III) ions to the number of available adsorption sites is small and consequently the adsorption is independent of the initial concentration. With an increase in Fe(III) concentration, the situation changes and the number of metal ions available per unit volume of the solution rises resulting in an increased competition for the binding sites [14]. At high concentration of Fe(III), unit mass of the adsorbent is exposed to larger number of Fe(III) ions and it takes up progressively higher number of ions as the appropriate binding sites are gradually filled up. This gives rise to an increase in q_e although the net adsorption comes down [11].

Equilibrium studies

Adsorption is a well-known equilibrium separation process for wastewater treatment. Adsorption isotherms are the equilibrium relationships between the concentrations of the adsorbed metal and the metal ion in the solution at a given temperature. Experimental adsorption data were applied to Langmuir and Freundlich equations, which have been widely used for the evaluation of adsorption data. The concentration variation method was used to calculate the adsorption characteristics of both adsorbent and process.

The Langmuir adsorption isotherm

The Langmuir adsorption isotherm suggests that when the adsorbate occupies a site further adsorption cannot take place at that site. All sites are energetically equivalent and there is no interaction between molecules adsorbed on neighboring sites¹³. The linearized Langmuir equation can be described as follows:

$$C_e/q_e = C_e/q_m + 1/bq_m \quad (3)$$

where C_e (mg/l) is the concentration of the Fe(III) solution at equilibrium, q_e (mg/g) is the amount of Fe(III) adsorbed at equilibrium, q_m is the maximum adsorption capacity, b is the Langmuir constant related to the affinity of the binding sites and energy of adsorption.

The Freundlich adsorption isotherm

Similarly, the Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface and suggests a multilayer adsorption. Adsorption energy exponentially decreases on completion of the adsorption centers of an adsorbent¹⁴. The Freundlich isotherm can be presented in linearized form as follows:

$$\log q_e = \log K_F + (1/n)\log C_e \quad (4)$$

where K_F and n are the Freundlich constants related to the adsorption capacity and the adsorption intensity of the adsorbent, respectively. $1/n$ is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. The adsorption capacity (K_F) and the adsorption intensity ($1/n$) are directly obtained from the slope and the intercept of the linear plot of $\log q_e$ versus $\log C_e$. The higher fractional values of $1/n$ signify that strong adsorption forces are operative on the system. The magnitude of $1/n$ also gives indication of the favorability and capacity of the adsorbent/adsorbate system. The value $1/n$, between 0 and 1, represents favorable adsorption. The results for equilibrium studies are shown in Table 1.

Table 1: Isotherm parameters.

Isotherm model	Parameter	Sand + charcoal
Langmuir constant	$q_m(\text{mg/L})$	19.23077
	$b(\text{L/mg})$	0.084388
	r	0.9441
	R_L	0.7078 - 0.1293
Freundlich constant	$K_F(\text{mg/g})(\text{L/g})^{1/n}$	2.078
	$1/n$	0.5677
	r	0.9929

The positive value of the Langmuir equilibrium coefficient, b indicates that the adsorbate-adsorbent interactions proceed in the direction of formation of the adsorption complex and hence, adsorption is the resultant process(Fig. 5). The Freundlich adsorption intensity, $1/n$, at 303 K, is 0.56 (by definition, the adsorption intensity, $1/n$, should have values less than unity for favourable adsorption)(Fig. 6).

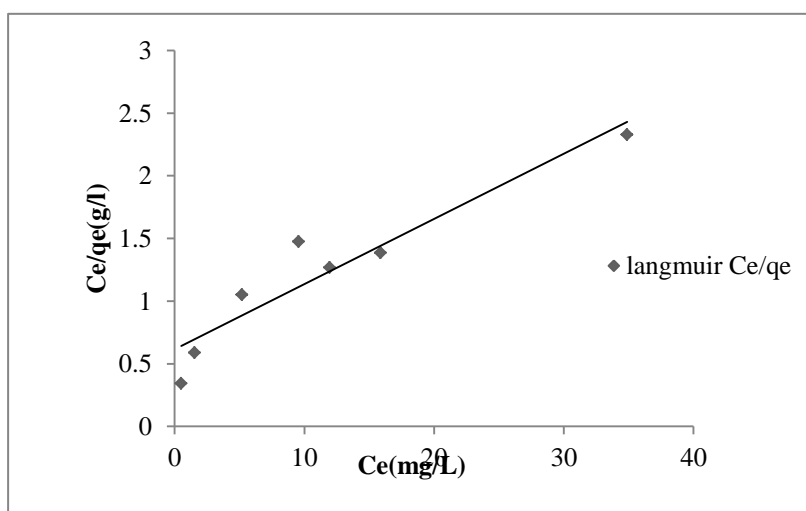


Figure 5: Langmuir adsorption isotherm of Fe(III) ions adsorption

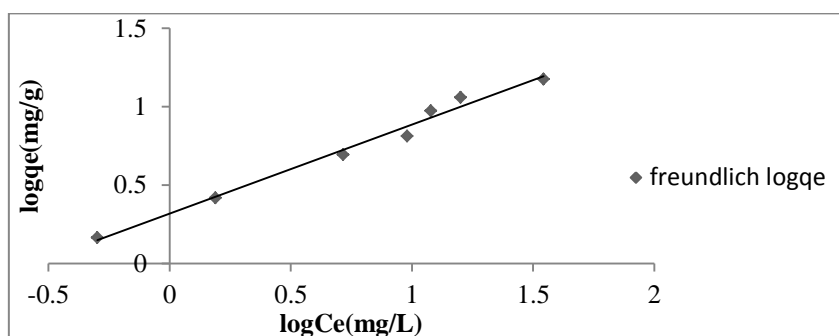


Figure 6: Freundlich adsorption isotherm of Fe(III) ions adsorption

Kinetics studies

Studies were carried out in order to understand the kinetic behavior of adsorption of Fe(III) on sand and charcoal mixtures. Different models have been applied to understand the kinetics of adsorption and the results are shown in Table 2.

The Lagergren curves are obtained by plotting $\log (q_e - q_t)$ vs. time (Fig. 7) according to the pseudo first order model [15,16] :

$$\ln (q_e - q_t) = \ln (q_e) - (k_1/2.303) t \tag{5}$$

where q_e and q_t (mg/g) are the solid phase concentrations of the solute at equilibrium and at time t , respectively and k_1 is the rate coefficient of pseudo-first order sorption (L/min).

Table 2. Kinetics study parameters.

Kinetic model	parameter	Sand + Charcoal
First order	$k_1 \times 10^2(\text{min}^{-1})$	3.24
	r	0.97
	qe(mg/g)	0.961
	% deviation	59.61
Second order	$k_2 \times 10^2$ ($\text{g mg}^{-1}\text{min}^{-1}$)	19.04
	r	0.99
	qe(mg/g)	0.992
	% deviation	-3.26

This curve is linear ($r \sim 0.97$) and the first order rate constant (obtained from the slopes) is $3.24 \times 10^{-2} \text{ min}^{-1}$ for the adsorbent (Table 2). However, linearity of the Lagergren plots does not necessarily assure a first order mechanism [17] due mainly to the inherent disadvantage of correctly estimating the equilibrium adsorption capacity, q_e . The q_e value obtained from the Lagergren plots differed from the experimental q_e value by 59.61 % . The first order kinetics is therefore less likely to explain the rate processes.

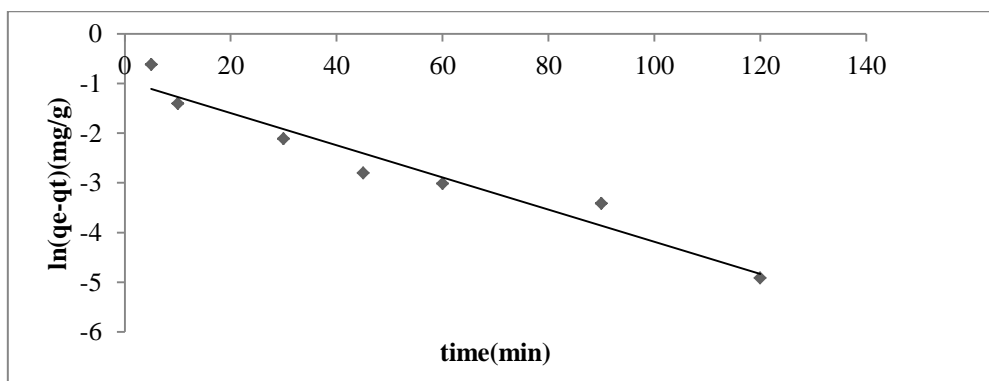


Figure 7: Lagergren plot for adsorption of Fe(III) (50 mg L^{-1}) on sand-charcoal mixture at 303 K.

The large deviation have led to verifying the kinetics of the interactions further by using the second order equation ¹⁸:

$$t / q_t = 1 / (k_2 q_e^2) + (1/q_e) t \tag{6}$$

where k_2 is the rate coefficient of adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$), q_e the amount of ions adsorbed at equilibrium (mg g^{-1}) and q_t (mg g^{-1}) the amount of ions adsorbed onto the surface at time, t .

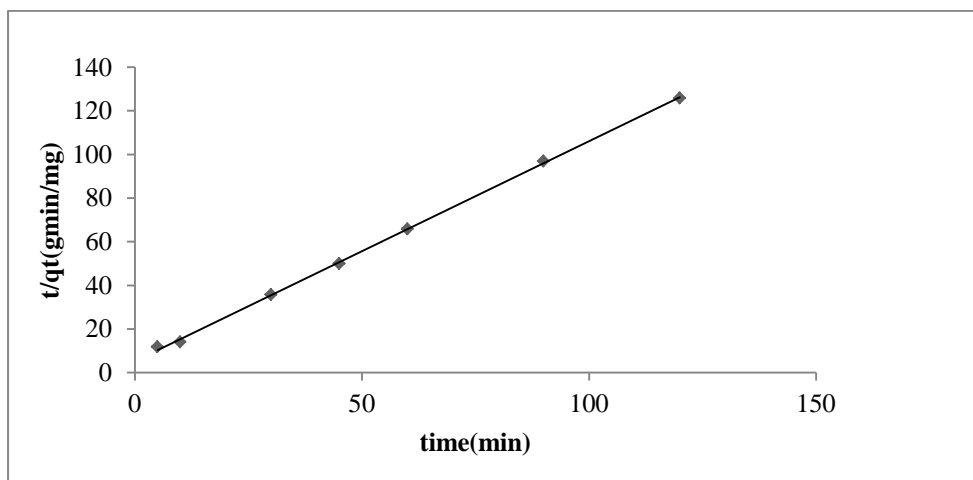


Figure 8: Second order plot for adsorption of Fe(III) (50 mg L^{-1}) on sand-charcoal mixture at 303 K

The second order plot shows better linearity ($r \sim 0.99$) and the rate coefficient, k_2 is $19.04 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$ at 303 K. The rate coefficient values reveal that the affinity of the sand- charcoal mixture towards Fe(III) is high. A comparison of q_e values (experimental and those obtained from the slopes of the second order plots) shows a better agreement and the deviation between the two sets of values is much smaller. The closeness of the two sets of values indicates a probable second order mechanism for the adsorption process.

3. Conclusion:

This study shows that sand and charcoal mixture is a suitable adsorbent for the removal of Fe(III) from aqueous solution due to its high capacity adsorption and availability. The Fe(III) removal depends contact time, pH and adsorbent dose. Fe(III) adsorption follows second order kinetics. Under optimum conditions, the maximum removal of capacity of adsorbent(based on Langmuir equation) was found to be 19.23077 mg/g .

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