Original Research Article

COMPARATIVE EQUILIBRIUM STUDIES ON THE REMOVAL OF FE(III) FROM AQUEOUS PHASE BY LOW COST ADSORBENTS

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ABSTRACT: Increased anthropogenic activities due to modernization and fast growing civilization have immensely contributed to the contamination of water by heavy metals including iron. Iron, an essential element for living systems, occurs naturally in water. But when the iron concentration surpasses a definite tolerable limit, it becomes a matter of concern to the environment as well as human health. Due to iron overload in water, problems arises which are related to taste and smell, and indirect physiological and financial problems. Recent researches have highly emphasized on developing cost-effective adsorbents for removal of toxic ions. In the present study, the technical viability of two low-cost and easily available adsorbents for removal of iron from water has been studied. Instead of using expensive commercial activated carbon, low-cost materials like sand and saw dust were used which have high adsorption capacity and are available locally. The sawdust has been blended along with sand. The influence of contact time, pH, initial metal ion concentration, and adsorbent dosage on the rate of iron removal was evaluated. Isotherm models were employed for analyzing the equilibrium data. The adsorption capacities of sand and sand/saw dust composite from Langmuir model were found to be remarkable. Similarly, the Freundlich constant, $1/n$ value showed favorable adsorption. Kinetics studies indicated that adsorption of iron followed second order kinetics.

KEYWORDS: Iron, low-cost, sand, Langmuir, second order.

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1. INTRODUCTION

Water is the most precious and indispensable natural resource on the earth. Any type of inorganic, organic, biological or radiological substance that intervenes with the living system, either directly

or indirectly may be termed as a pollutant [1]. Water contamination by addition of heavy metals has become a major environmental hazard owing to their non-biodegradable nature and toxic effects that they imposed when they exceed the tolerance limits. Numerous methods have been utilized for elimination of such metals from aqueous systems like ion exchange, filtration, precipitation, solvent extraction, membrane separation, cementation, sedimentation, coagulation, floatation, complexing, electrochemical technique, biological process, reverse osmosis, ion exchange and adsorption. Among these methods, adsorption is a cost-effective technique and simple to operate [2-4]. Adsorption also has the advantage of specific removal of pollutant. Iron forms natural constituent of Earth's crust and is present in varying concentrations in every ecosystem. Iron, in natural water, may exist in soluble form as the ferrous iron (Fe^{2+} or $Fe(OH)^{+}$ in dissolved state) or the ferric iron (Fe^{3+} or $Fe(OH)_3$ in precipitated state). Occurrence of iron in natural waters can be obliged to the disintegration of rocks and minerals, land fill leachate, acid mine drainage, etc. [5]. Rain water as it moves down through the soil, minerals and rocks, collects iron from these sources and accumulates them in the groundwater. Some of the major anthropogenic sources which contribute to deposition of iron consist of various industrial sources such as mining activities, steel, car and aeronautics manufacturing industries, foundries and smelters. The incidence of iron is perhaps the most widespread problem encountered in water treatment [6]. It has been spotted frequently in municipal waste runoff, mostly in places where iron and steel are produced. It is also found in many industries involving metal finishing and manufacturing galvanized pipe [7].   Iron is generally divided into two main categories: "Clear water" and "Red water" type iron where the iron exists in soluble and insoluble forms respectively. The former type is found to be more common and more troublesome. When poured in a glass and allowed to stand, this type of iron will form reddish brown particles in the glass and eventually settle to the bottom. The subsequent type of iron displays rusty or shows red or yellow coloration, creating severe taste and appearance problems for the water user. Iron is one of the most indispensable metals for humans, and about 3000–5000 mg is present in the human body for normal functioning of the body. But when it surpasses the tolerance boundary, it creates plenty of medical conditions such as haemochromatosis, amenorrhea, skin pigmentation, joint diseases, enlarged liver, hair loss, and impotency. Excessive amounts of iron in public water systems will produce turbidity, disagreeable taste and odor. In deep wells, where the quantity of oxygen is small, the iron-loaded water is clear and devoid of color. When dissolved iron particles in water undergo oxidation, they get converted to white, yellow and ultimately rusty particles that precipitate down. If these particles are not that big enough to settle out, they will stay suspended in colloidal state for longer time, giving the water a red tint. Iron reacts with diverse naturally occurring acids, and therefore may be present as an organic composite. A blend of iron and acid, or organic iron, occurs in shallow wells and surface water most often. Dissolved iron gives water an unpleasant taste and may combine to react with tannins present in coffee, tea or some alcoholic potions, producing

a black sediment, which destroys both taste and appearance. Food when cooked in iron loaded water becomes dark and looks unappetizing. Iron contamination causes reddish-brown staining or discoloration of laundry, porcelain dishes and   utensils and even affects glassware. These stains cannot be removed by soaps and detergents, and using chlorine bleach and alkaline builders may cause even more damage. Besides, iron hydroxide precipitates introduce turbidity into the water, confining its utillity for drinking and industrial purposes. Moreover, these precipitates create problems in water supply by blocking pipes. Iron may also build up biologically inside the pipes, reducing the available supply and pressure of the water. Such accumulations pose an economic threat when the condition arises for replacement of water supply or water softening equipment, requiring lot of expenditure. Other problems associated with these accumulations include high power costs when the water has to be pumped through constricted pipes or when the water has to be heated using immersion coils, with iron or manganese mineral deposits coated on it. Another common problem resulting from high iron content in water is iron bacteria, which form rusty slime in toilet tanks and can congest water systems. The main issue of iron overload from an environmental outlook is not direct chemical hazard, but the influence of iron as an intermediate in the geochemistry of other possible toxic metals. Iron oxides can adsorb many trace elements and heavy metals. Therefore, excessive iron in water needs to be removed in order to make the water usable. The maximum acceptable limit of iron in drinking water has been fixed at 0.3 mg/L, based on taste and look and not on any unfavorable health effects [8, 9]. In adsorption processes of recent times, attempts have been made to use natural organic or inorganic materials, of low cost and easy availability as adsorbents. Some of these include natural materials include bark/tannin-rich materials, chitin/chitosan, lignin, seaweed/ algae/alginate, dead biomass, xanthate, clay, zeolite, fly ash, bone gelatin beads, leaf mould, moss, peat moss, iron-oxide-coated sand, modified wool and cotton [10]. Sand has been used for metal exclusion from water [11, 12]. Saw-dust is a by-product of saw mill. Uses of saw-dust as an adsorbent for the removal of heavy metals have been reported earlier [13-16]. In this work, the adsorption of iron (III) ions has been studied using low cost adsorbents by means of a batch technique with regard to the pH, contact time, initial concentration and adsorbent dose. The adsorbents used in the present study were sand and sand/sawdust composite. The removal efficiencies of the adsorbents were compared.

2. MATERIALSAND METHODS

Adsorbent: Sand and saw dust, collected locally was washed carefully with distilled water, oven dried and sieved. The sand is combined with saw dust in 2:1 proportions to get the adsorbent.

Adsorbate solution: The synthetic adsorbate solution in water was prepared from anhydrous $FeCl_3$ (Qualigens, mol. Wt.=162.21g) by dissolving $FeCl_3$ 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). Batch adsorption experiments were carried out by varying: interaction time, pH, amount of adsorbent and initial concentration of Fe(III).

The adsorbed amount of Fe(III) and adsorption % was calculated by Equations (1) and (2), respectively,

$$q_t = (C_o - C_t)V/m \tag{1}$$

$$\text{Adsorption percentage} = \{(C_o - C_t) \times 100\} \div C_o \tag{2}$$

where, q_t is the amount of Fe(III) adsorbed by the sand (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_t is the residual Fe(III) concentrations (mg/L) after the batch adsorption at time, t.

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 and 120 minutes for sand/sawdust composite after which it slowly attains equilibrium at ~ 90 min and~ 150 min respectively (**Figure 1**).
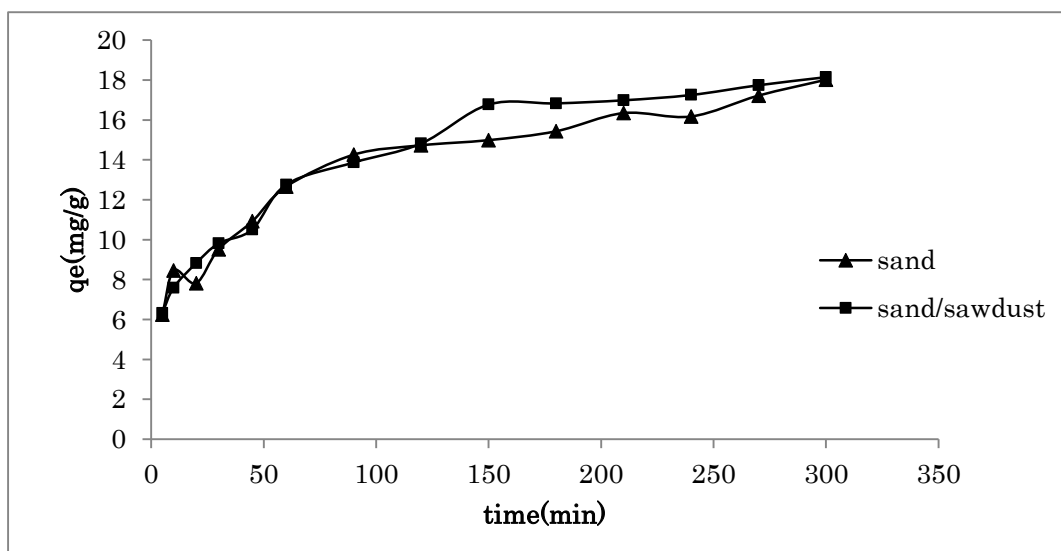

Figure 1. Influence of contact time

At the beginning of the process, there was a large number of vacant surface sites on which adsorption took place. As these vacant sites got filled after a certain duration of time, the remaining vacant surface sites becomes difficult to be occupied because of repulsive forces between the solute species on the solid and bulk phases [17].

Influence of pH

The effect of pH was studied with a constant dose of adsorbent of 2 g/L and a constant adsorbate concentration of 50 mg/L at 303 K. The time duration was kept fixed at 90 minutes and 150 minutes for sand and sand/sawdust composite respectively and the pH varied from 2.0 to 4.0. The adsorption percentage of Fe(III) increased sharply on increasing solution pH values from 2.0 to 3.0(**Figure 2**).
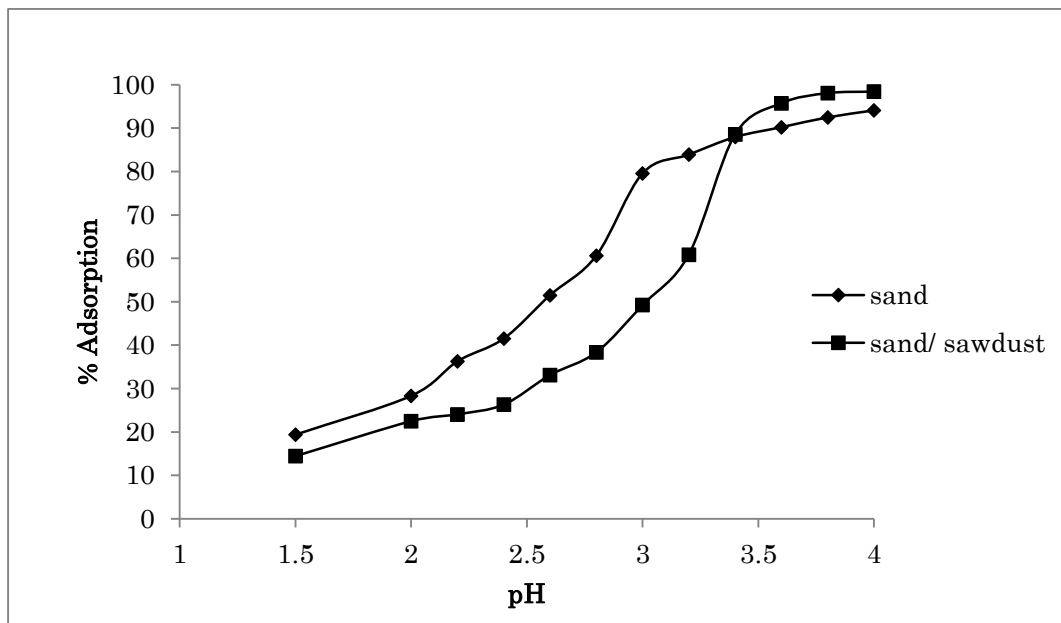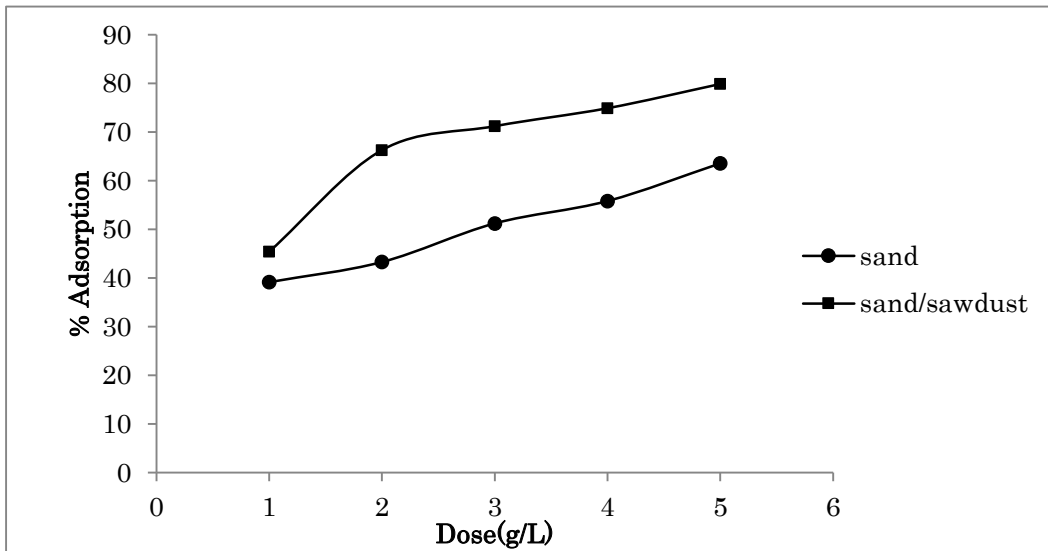

Figure 2. Influence of pH.

A little increase was observed after this point to pH of 4.0.Adsorption percentage increased from 19.35 % to94.06 % for sand and 14.43 % to 98.38 % for sand/sawdust composite (2:1) on increasing pH from 1.5 to 4. 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. 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 decrease [18].

Influence of adsorbent dose

Adsorption of Fe(III) was investigated at various adsorbent dosage with Fe(III) concentration fixed at 50 mg/L. Adsorption percent increased from 39.16 % to 63.51 % for sand and from 45.36 % to 79.84 % for sand/saw dust composite on increasing adsorbent dose from 1 g to 5 g per litre of Fe(III) solution (**Figure 3**). This increase in the adsorption percentage is because of availability of larger surface area and more adsorption sites [19].

Figure 3. Influence of adsorbent dose

Influence of initial concentration

Adsorption percentage decreased on increasing initial Fe(III) concentrations from 5 mg/L to 80 mg/L from 82.28 % to 37.15 % for sand and 86.86% to 43.14 % for sand/saw dust composite (**Figure 4)**.
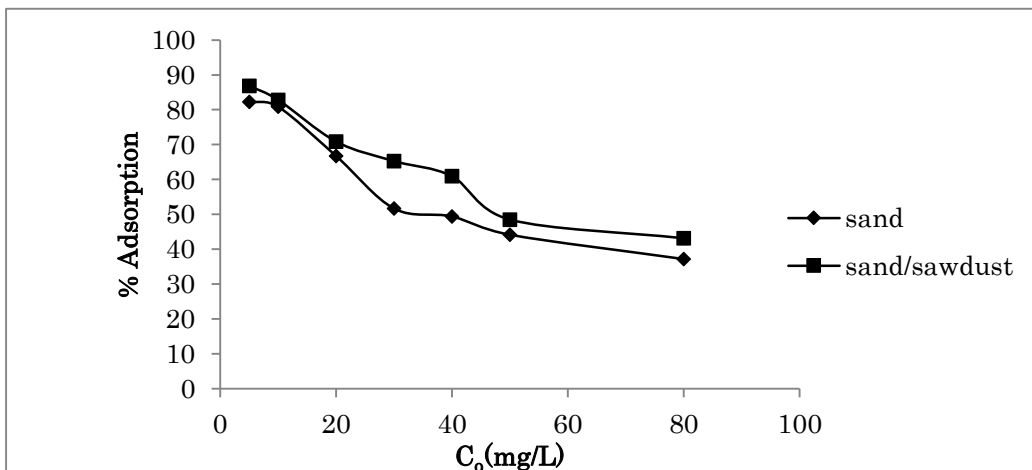
Figure 4. Influence of initial concentration of Fe(III)

Adsorbed amount of Fe(III) ions was increased by increasing of initial Fe(III) concentrations. Adsorption percentage decreased by increasing of initial Fe(III) concentrations due to saturation of adsorption sites on the adsorbent (12).

Isotherm studies

The adsorption process was investigated by Langmuir, Freundlich and Temkin isotherm models. The Langmuir isotherm is applicable for monolayer adsorption onto a surface having a finite number of identical sites [20].

The linearized Langmuir equation can be described as follows:

$$C_e/q_e = C_e/q_m + 1/bq_m \tag{3}$$

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. To predict whether the sorption process is favorable or not for the Langmuir model, the isotherm can be further tested by the values of 'R_L', the dimensionless separation factor which is given by;

$R_L = 1/(1 + bC_o)$ (4)

For R_L values greater than 1, the adsorption is unfavorable. R_L values between zero to one, indicates highly favorable adsorption [21].

Similarly, the Freundlich isotherm describes adsorption onto a heterogeneous surface and suggests a multilayer adsorption [22]. The linearized Freundlich isotherm can be presented as follows:

$\log q_e = \log K_F + (1/n)\log C_e$ (5)

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 qe Vs log Ce. The value of 1/n, between 0 and 1, represents favorable adsorption.

Temkin and Pyzhev considered the effects of some indirect interactions of adsorbate/adsorbent on adsorption isotherms and suggested that because of these the heat of adsorption of all the molecules in the layer would decline linearly with exposure [23].

The Temkin isotherm has been linearized can be linearized as:

$q_e = RT/b \ln K_T + RT/b \ln C_e$ (6)

where, b is the Temkin constant related to heat of sorption (J/mol); K_T is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K) and T the absolute temperature (K). Therefore, by plotting qe versus ln Ce enables one to determine the constants A and B.

Table 1. Results of Fe(III) adsorption isotherms at 303 K.

Isotherm model	Parameter	Sand	Sand/Sawdust
Langmuir constant	q_m(mg/L)	16.39	19.23
	b(L/mg)	0.113	0.118
	r	0.97	0.97
	R_L	0.66 – 0.11	0.63 – 0.095
Freundlich constant	K_F(mg/g)(L/g)$^{1/n}$	2.546	2.951
	1/n	0.449	0.475
	r	0.98	0.98
Temkin constant	b(J/mol)	891.1	747.07
	K_T(L/mg)	1.911	2.093
	r	0.96	0.97

Table 1 shows the the values of the various isotherm parameters. The positive values 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. The R_L values are less than unity indicating favorable sorption **(Figure 5)**. The Freundlich adsorption intensity, 1/n, at 303 K, have values less than unity which indicates favourable adsorption (**Figure 6**). The r values (**Figure 7**) confirm that Temkin isotherm provides a reasonable model for the adsorption of Fe(III).
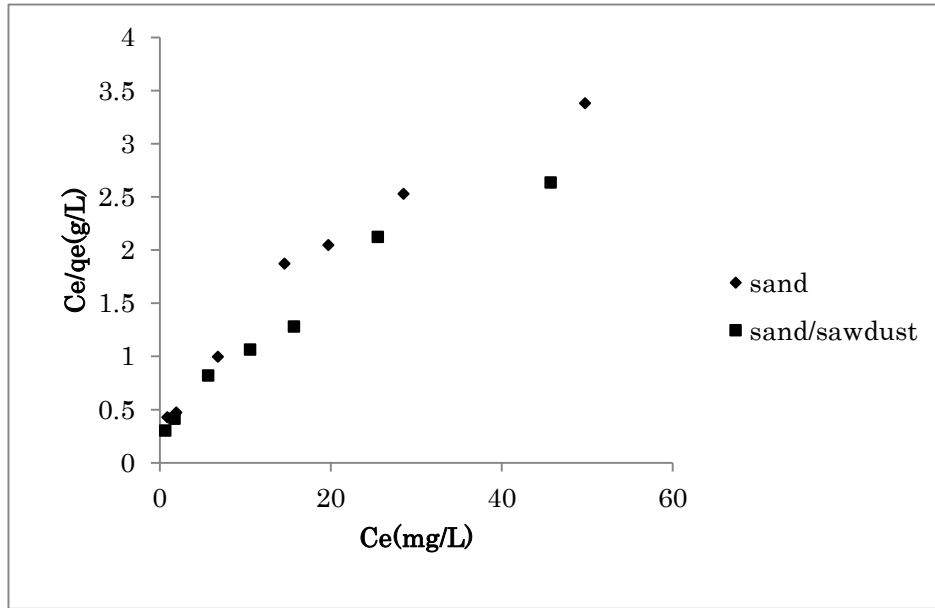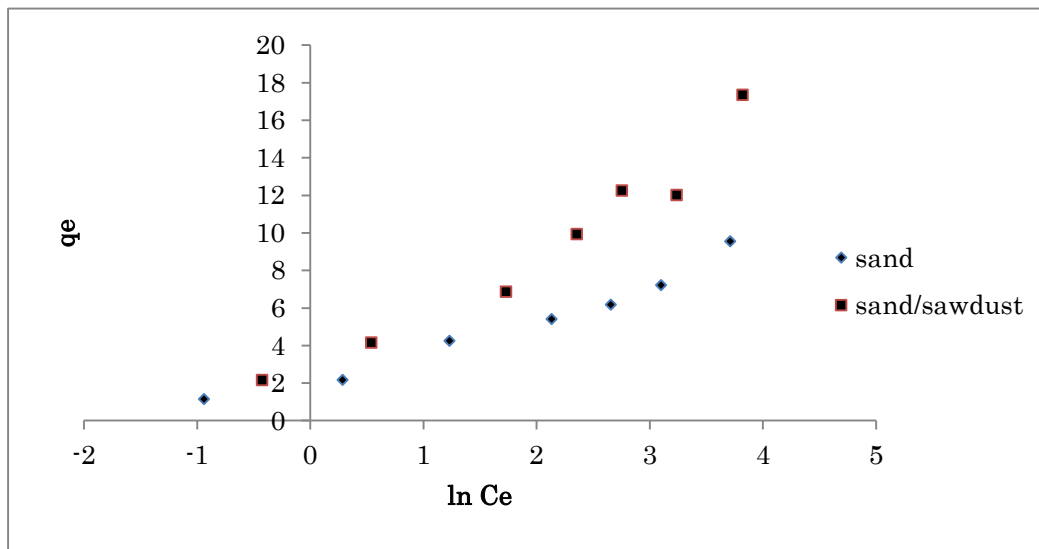

Figure 5. Langmuir adsorption isotherm of Fe(III) ions adsorption on sand and sand/sawdust composite.
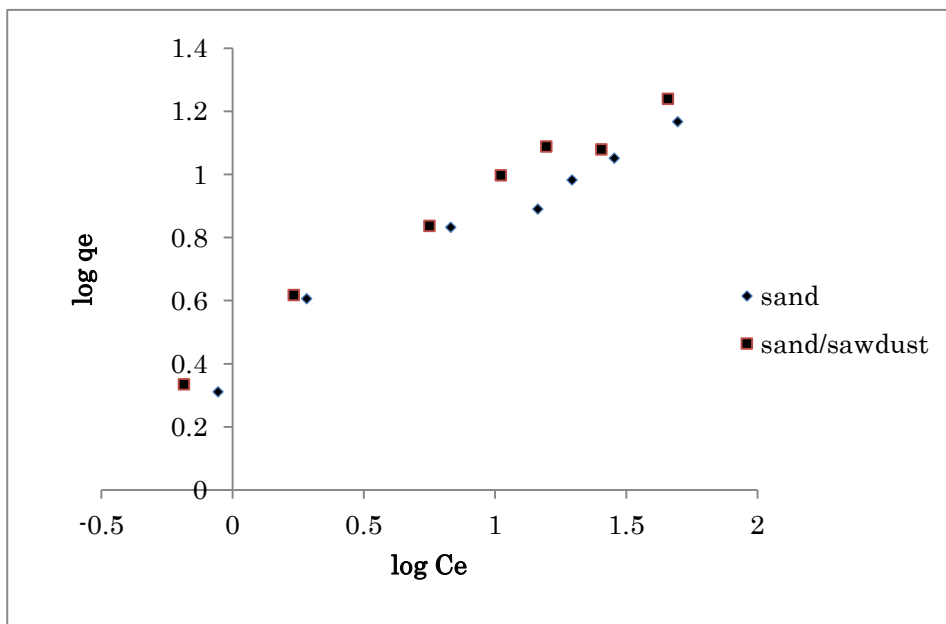
Figure 6. Freundlich adsorption isotherm of Fe(III) ions on sand and sand/sawdust composite.

Figure 7. Temkin adsorption isotherm of Fe(III) ions on sand and sand/sawdust composite.

Kinetics studies

To determine the order of the adsorbate-adsorbent interactions various kinetic models viz. the pseudo first order and the second order kinetic models were used. The experimental conditions are

Adsorbent dose: 2 g/L

Temperature, T: 303 K

Initial Fe(III) concentrations: 50 mg/L.

The pseudo first-order Lagergren plots were obtained by plotting ln $(q_e − q_t)$ vs. time (**Figure8)** according to the [24]:

$$\ln (q_e − q_t) = \ln (q_e) − (k_1/2.303)\, t \tag{7}$$

where,q_e and q_t were the amounts adsorbed per unit mass at equilibrium and at any time t, and k_1 was the first order adsorption rate constant.

The second order kinetics [25] governed by the equation:

$$t / q_t = 1/(k_2 q_e^2) + (1/q_e)\, t \tag{8}$$

where, k_2 is the rate coefficient of adsorption (g mg^{-1} 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. The value of q_e and k_2 can be determined by the slopes and intercepts of the straight line of the plots 't/q_t vs t', respectively as seen in **Figure 9**.

The adsorbate species are most probably transported from the bulk of the solution into the solid phase through an intraparticle diffusion process, which is often the rate-limiting step in many adsorption processes. The possibility of intraparticle diffusion was explored by using the intraparticle diffusion model [26]:

$$q = K_{id}t^{0.5} + C \tag{9}$$

where C is the intercept and K_{id} is the intraparticle diffusion rate constant (mg/g · min $^{0.5}$).
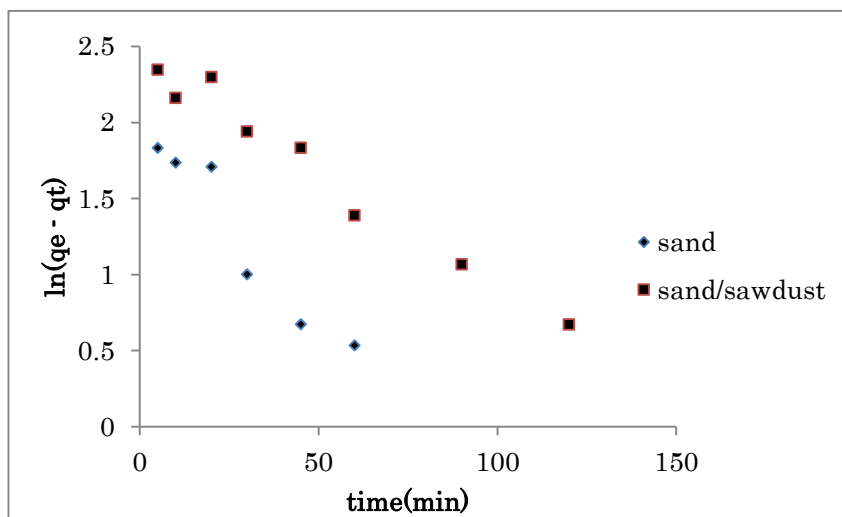
Figure 8. Lagergren plot for adsorption of Fe(III) on sand and sand/sawdust composite at 303 K.
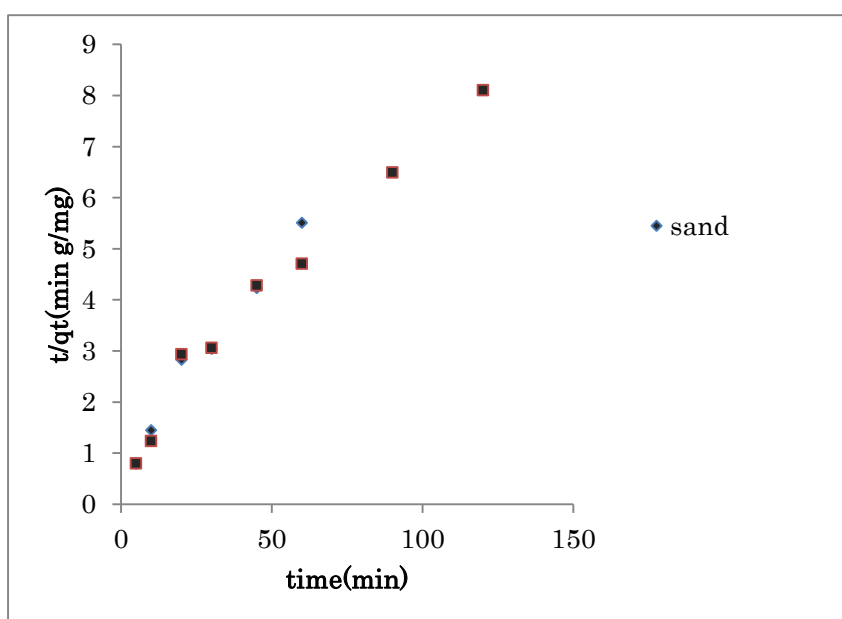

Figure 9. Second order plot for adsorption of Fe(III) on sand and sand/sawdust composite at 303K.
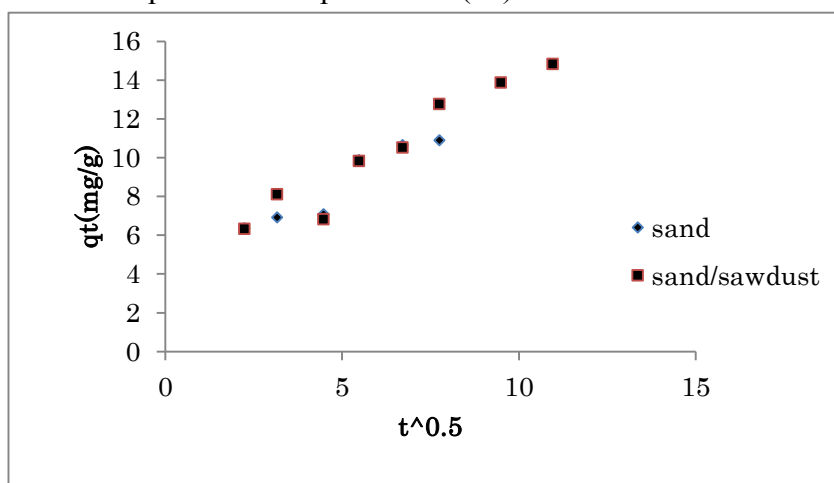

Figure 10. Intra-particle diffusion plot for adsorption of Fe(III) on sand and sand/sawdust composite at 303K.

The large deviations of q_e values from experimental q_e values do not support first order kinetics. The second order plot shows better linearity ~ 0.97 and 0.98 and the rate coefficient, k_2, varies from 10.4×10^{-3} to 2×10^{-3} g mg^{-1} min^{-1} at 303 K. The rate coefficient values reveal that the affinity of the sand/sawdust composite towards Fe(III) is more compared to sand. 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. The intra-particle diffusion plots (**Figure 10**) also yielded linear curves (r ~ + 0.93, 0.96) with the rate constant, K_i, having values from 1.019 to 1.022 mg g^{-1} min$^{-0.5}$ (**Table 2**). This suggests that a large number of Fe(III) ions might have diffused into the pores before being adsorbed. Significantly, the plots do not have a zero intercept as required by the above equation, indicating that intra-particle diffusion may not be the lone dominating aspect controlling the mechanism of the process.

Table 2. The adsorption kinetic model rate constants for adsorption of Fe(III) ions on Sand and Sand/Sawdust composite at 303K.

Kinetic model	Parameter	Adsorbent	
		Sand	Sand/Sawdust
First order	k_1 (min^{-1})	0.031	0.014
	r	0.95	0.98
	q_e(mg/g)	7.94	11.24
	% deviation	36.9	32.99
Second order	k_2 (g mg^{-1}min^{-1})	0.00104	0.002
	r	0.97	0.98
	q_e(mg/g)	12.195	16.67
	% deviation	3.21	0.62
Intra-particle diffusion	$K_i \times 10^2$ (mg g^{-1}min$^{-0.5}$)	1.019	1.022
	c	3.676	3.953
	r	0.93	0.96

4. CONCLUSION

This study shows that both sand and sand/saw dust composite are both suitable adsorbents for the removal of Fe(III) from aqueous solution due to high capacity adsorption, availability, and low cost. The Fe(III) removal was pH-, adsorbent amount-, and contact time-dependent. Fe(III) adsorption follows second order kinetics. However, the removal efficiency of sand was enhanced on mixing it with saw-dust. Under optimum conditions, the maximum removal capacity of sand/sawdust composite (based on Langmuir equation) was found to be 19.23, which is higher than that of sand

which has an adsorption capacity of 16.39 mg/g.

5. CONFLICT OF INTEREST

Authors have no conflict of interest.

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