A study of the adsorption of Fe (III) ions on natural sand collected from a tank in Ramanathapuram, India

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ABSTRACT

Adsorption of Fe(III) ions in aqueous medium by natural sand was studied by the batch mode technique. The influence of pH, particle size, contact time, initial concentration of the adsorbate and temperature were experimentally determined. The isotherm (Langmuir / Freundlich) model suitable for the adsorption process was determined. The results revealed that the adsorption of Fe (III) ions by natural sand is an exothermic process and the natural sand effectively removes the Fe (III) ions by adsorption and ion exchange processes.

Key Words: Adsorption, Natural sand, Langmuir, Freundlich models

INTRODUCTION

In recent years, low cost adsorbents are used as an alternative remedy for the removal of toxic heavy metals from the waste water. Now a day, various natural adsorbents have been used by many researchers for the treatment of water. Toxic heavy metals are released in the environment due to rapid industrialization and urbanization. Adsorption is an effective technique for the removal of heavy metals from aqueous solutions [1].

The consequences of urbanization and industrialization have a great impact on water which is used for agricultural purposes. Groundwater is explored in rural, especially in those areas where other sources of water like dams, river or a canal are not considerable [2].The heavy metals removal from the waste water is an important global issue [3]. Randall et al. worked on the removal of heavy metals using various barks and eventually expanded their work to peanut skins [4].

EXPERIMENTAL

Natural sand (~500g) from a tank in Ramanathapuram (~ one foot from the surface – during May 2013) was collected, washed well with water (to remove the soluble impurities) and filtered. Then, the material was stirred well with ~1N HNO_3 (to remove the acid – soluble impurities), filtered and washed repeatedly with distilled water (filtrate checked with litmus paper). Then, the sand material was filtered, washed well with double distilled water, dried, sieved to different sizes and kept in airtight glass containers. The sand thus obtained is abbreviated as TS (Tank Sand)

Batch equilibration method: All experiments were carried out in batch mode. Batch mode technique was selected because of its simplicity and reliability. In many applications the preliminary evaluation program may take the form of a simple feasibility study where capacities of adsorbents for the removal of chosen adsorbates are determined by simple batch experiments in laboratory. This study to gether with the knowledge of similar operating systems may provide sufficient capacity and design information to proceed with full scale design. In other cases considerable effort may be required for full scale implementation. Keeping this in view, batch experiments were done in different ground joint glass bottles of 125ml capacity. Prior to each experiment, a predetermined amount of adsorbent was added to each flask. The shaking was kept constant (100rpm) for each run throughout the experiment to ensure equal mixing. Each bottle was filled with 50ml of sample before shaking. The flask containing the sample was withdrawn from the

shaker at the predetermined time interval, filtered and the residual concentration of the sample was measured. Concentration of metal ions before and after adsorption was measured using a photo colorimeter (λ_{max} =480 nm). All experiments were conducted by following the batch mode adsorption technique in a 125 ml reagent bottles by varying parameters *viz.,* particle size (<75 µm to425µm - 500 µm), initial concentration of synthetic Fe(III) solutions (25 mg/l -200 mg/l), contact time (5 min - 50 min), pH (3 - 7) and temperature (27ºC-47ºC). The optimized size for TS was first examined followed by varying contact time, initial concentration, pH and temperature.

The metal ion retained in the adsorbent phase, q_e(mg/g) was calculated using the following equation [5]

$$q_e = \frac{(C_i - C_e)}{m} V$$

Where V= Volume (ml) of the equilibrated solution,
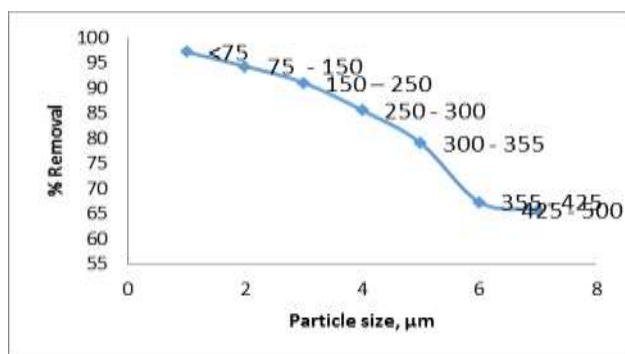 m= Mass of the adsorbent (g),

C_i = Initial concentration of synthetic Fe(III) solution (mg/l),
C_e = Fe (III) at equilibrium (mg/l).
The percentage removal (%) of Fe(III) ions was calculated using the following equation,

$$Removal\ (\%) = \frac{(C_i - C_e)}{C_i} X100$$

Effect of adsorbent particle size: Experiments were conducted using TS to evaluate the influence of adsorbent particle size on the removal of Fe(III) ions. The removal of Fe(III) ions at different particle sizes *viz.,*< 75 µm, 75 µm -150 µm, 150 µm -250 µm, 250 µm -300 µm, 300 µm – 355 µm, 355 µm -425 µm and 425 µm -500 µm were done. The results obtained with the variation of adsorbent particle sizes and the percentage of removal was graphically represented in Fig. 1. The high adsorption efficiency was shown by the particle size of <75 µm. The presence of a large number of smaller particles provides the sorption system with a larger surface area available for Fe(III) ions removal and it also reduces the external mass transfer resistance in addition to ion exchange[6].

Fig. 1 Variation in % removal of Fe (III) with particle size

Effect of pH: pH is one of the important factors to be considered in ion exchange/ adsorption process, since in many cases it alters the surface charge on the sorbent. The ion exchange of Fe (III) ions onto the sorbent at various pH values (3 –6.5) was
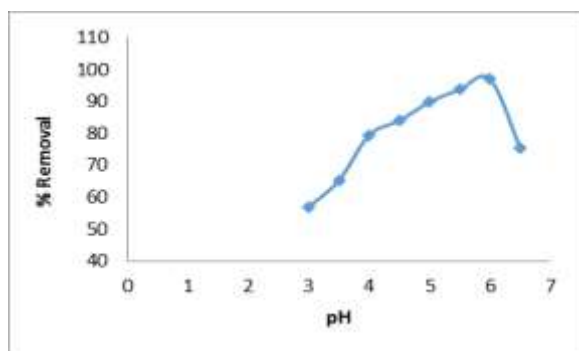
shown in Fig. 2. Initially the increase in pH value increases the removal capacity. The percentage removal of Fe (III) ion increases from 57.14 % to 97.09 % with the increase in pH from 3 to 6 and then it started decreasing [7].

Fig. 2 Variation in % removal of Fe (III) withpH

Effect of contact time: It was found that the removal of Fe (III) ion increases with increase in contact time to some extent. Further increase in contact time did not increase the percentage of Fe (III) removal.
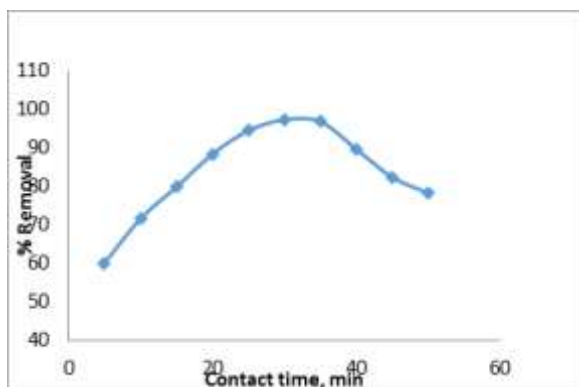

Fig. 3 Variation in % removal of Fe(III) with contact time

The adsorption starts increase from 5 min.to 35 min. as given in Fig. 3 and then started decreasing. The rate of Fe (III) removal is higher in the beginning due to the larger surface area of the adsorbent being available for the ion exchange/ adsorption of the Fe (III) ion. The adsorption capacity starts decreasing after 35 min. due to the desorption of Fe (III) ions from the sorbent material. Surface adsorption and ion exchange can be considered as the driving force of Fe (III) ion removal[8].

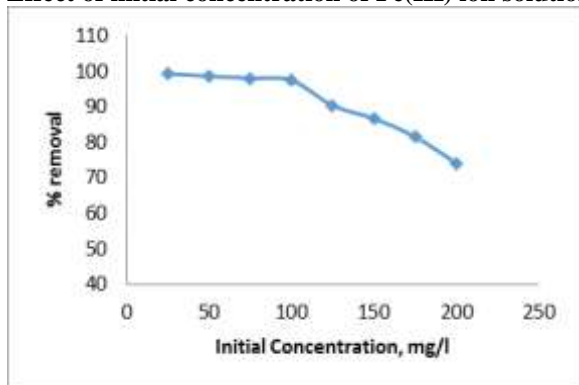**Effect of initial concentration of Fe(III) ion solution**

Fig. 4 Variation in % removal of Fe (III) with initial concentration

For an adsorptive reaction, in the optimized period of contact time (35 min.), the % removal varies directly with the initial concentration of synthetic Fe (III) solution. The ion exchange/ adsorption capacity of TS was systematically studied by varying the initial concentration of Fe(III) ions *viz.,*25 mg/l, 50 mg/l, 75 mg/l, 100 mg/l, 125 mg/l, 150 mg/l, 175 mg/l and 200 mg/l as given in Fig.4. The capacity of the adsorbent gets exhausted sharply with increase in the initial concentration of Fe (III) ions. Results show that the TS shows maximum removal of99.28% at 25 mg/l. The decrease in ion exchange/ adsorption capacity with respect to initial concentration of synthetic Fe (III) solution may be attributed to a high intermolecular competitiveness to occupy the lower energetic sites left behind [9].

Effect of temperature: Another important factor that greatly influences the ion exchange adsorption process is the temperature. The effect of solution temperature was investigated at 27ºC, 32ºC, 37ºC, 42ºC and 47ºC. The results summarized in Fig. 5 indicate that the adsorption rate decreased with increase in temperature. The result indicates that the low temperature favors the removal of Fe (III) ions by ion exchange/ adsorption on to TS in an exothermic manner. At higher temperature, the decrease in removal efficiency may be due to the decrease in the thickness of the boundary layer due to increased tendency of the molecules to escape from the adsorbent surface to the solution phase.
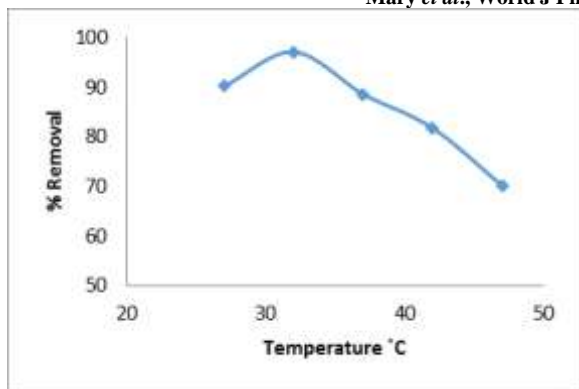
Fig. 5 Variation in % removal of Fe (III) with temperature

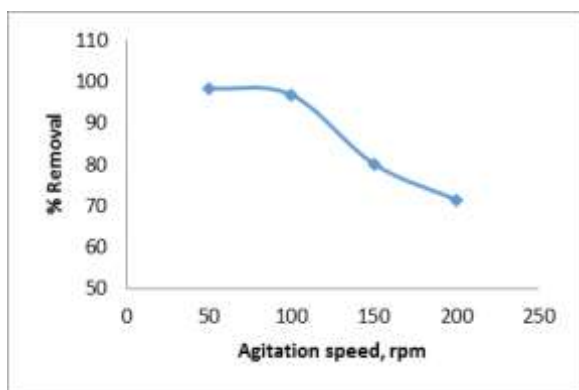**Effect of Agitation Speed:** The % removal of Fe (III) ions decreases with increase in agitation speed. This may be due to the domination of desorption with respect to adsorption. The maximum removal of 98.45 % was found at 50 rpm.

Fig. 6 Variation in % removal of Fe(III) with agitation speed

Isotherm Modelling: The abilities of two widely used isotherms *viz.,* the theoretical Langmuir and the empirical Freundlich isotherms were used to model the adsorption equilibrium data.

Langmuir Adsorption Isotherm: The formation of a monolayer adsorbate on the adsorbent was represented by the Langmuir isotherm model. Thereby, the Langmuir equation [10] represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is applicable for monolayer sorption onto a surface containing a finite range of indistinguishable sites.

The model assumes uniform energies of sorption onto the surface and no transmigration of adsorbate with in the plane of the surface. Based on these assumptions, Langmuir has drawn the subsequent equation

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$$

Langmuir sorption parameters were determined by remodeling the equation into linear type.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e}$$

Where,
C_e = the equilibrium concentration of adsorbate (mg/l)
q_e = the amount of Fe (III) ion adsorbed per gram of the adsorbent at equilibrium (mg/g)
Q_o = maximum monolayer coverage capacity (mg/g)
K_L = Langmuir isotherm constant (l/g)

The values of Q_0 and K_L were computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$ as given in Fig.7. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant mentioned as separation factor or equilibrium parameter.

$$R_L = \frac{1}{1 + (1 + K_L C_0)}$$

Where,
C_0 = initial concentration of Fe (III) solution,

K_L = the constant associated with the energy of adsorption (Langmuir constant).

R_L value indicates the nature to be unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$. From this analysis work, the utmost monolayer coverage capability (Q_0)

from the Langmuir isotherm model was determined to be 0.0005 mg/g, K_L was 500 ml/g and the separation factor, R_L was 0.006. The above parameters confirm the favorable ion exchange/ adsorption. The R^2 value (0.975) proved the fitness of Langmuir isotherm model on ion exchange/ adsorption.
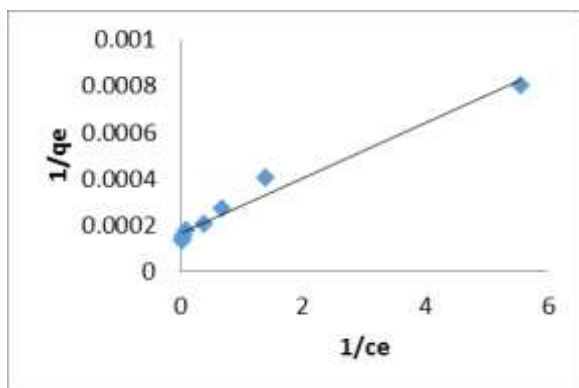

Fig. 7 Langmuir adsorption isotherm

Freundlich Adsorption Isotherm: This isotherm is used to describe the adsorption characteristics for the heterogeneous surface. These data often fit the empirical equation proposed by Freundlich [11].

$$Q_e = K_f C_e^{\frac{1}{n}}$$

Where K_f = Freundlich isotherm constant
n = adsorption intensity
C_e = the equilibrium concentration of adsorbate
Q_e = the amount of Fe (III)ions adsorbed per gram of the adsorbent at equilibrium

By linearizing the above equation,

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e$$

The constant K_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process. If n = 1 then the partition between the two phases are independent of the concentration. If the value of $1/n$ is below one it indicates a normal adsorption.

On the other hand, $1/n$ being above one indicates cooperative adsorption. The function has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants k and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface. However, K_f and n are the parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting. Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data where $1/n$ is a heterogeneity parameter, the smaller $1/n$, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when $1/n = 1$. If n lies between one and ten, this indicates a favorable sorption process. The value of $1/n = 0.294$ while $n = 3.4$ indicating that the ion exchange/ adsorption was favorable and the R^2 value (0.913) indicated the applicability of Freundlich isotherm on to ion exchange/ adsorption.
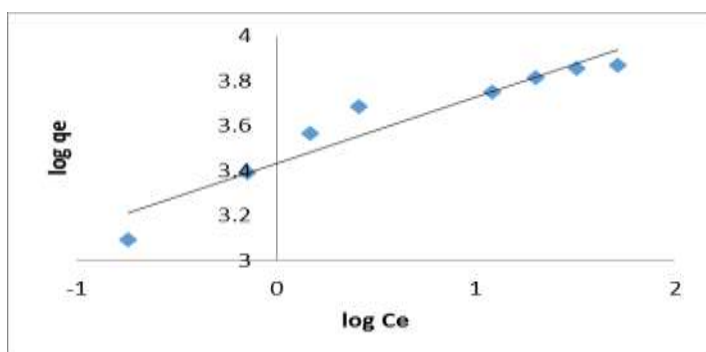

Fig. 8 Freundlich adsorption isotherm

CONCLUSION

From the above study, the optimum condition of various parameters for the Fe (III) ions adsorption using TS was found out. Also the isotherm modeling *viz.,* Langmuir and Freundlich isotherm were studied. Among the two, the Langmuir fitted well when compared to Freundlich which confirms that the adsorption/ ion exchange seems to follow the monolayer formation. Since, the present technique removes the Fe (III) ions from water using sand collected from a tank in Ramanathapuram, it can be considered as a green technique.

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