



Adsorption of Fe (III) Ions by Activated Calcite Powder - Equilibrium, Kinetic and Thermodynamics Studies

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ABSTRACT

The present work investigates the action of Fe (III) ions on Activated calcite powder. The influence of contact time, initial concentration, adsorbent dosage and solution pH has been done and reported. The equilibrium data were analyzed using Langmuir and Freundlich isotherm model. The pseudo – second –order, Elovich model and intra – particle diffusion were used to test the adsorption behavior, kinetic data's. Thermodynamic free energy (ΔG^0), Enthalpy (ΔH^0), and Entropy (ΔS^0) were calculated and the result shows that the adsorption process is physical adsorption.

KEYWORDS: Adsorption isotherm, Activated Calcite Powder (ACP), Iron Solution [Fe (III)], Kinetics, Thermodynamics.

INTRODUCTION:

The natures of the metal ions are non-biodegradable and it is necessary for the all living organisms, if the intake is above the permissible levels are highly toxic. So the presence of heavy metals in the environment above the permissible limit leads to severe threat to human life and environment [1]. Large quantities of wastewater containing various concentration of iron were generated from many industries such as coating cars, aeronautics and steels [2] Iron toxicity lead to many problems like anorexia, oliguria, diarrhea, hypothermia, diphasic shock, metabolic acidosis and even death and it causes vascular congestion of the gastrointestinal tract, liver, kidneys, heart, brain, adrenals and thymus with acute iron poisoning much of the damage happens to the gastrointestinal tract and liver which results from the high level of iron concentration and free radical production leading to hepatotoxicity via lipid per oxidation and destruction of the hepatic mitochondria. As a result of iron storage disease, the liver becomes cirrhotic. Hematoma, a primary cancer of the liver, has become the most common cause for death among patients with Hemochromatosis [3].

2 MATERIAL AND METHODS:

2.1 ADSORBENT:

The calcite stone was obtained from a granite quarry. It was washed with tap water and distilled water several times. Then it was transferred to the oven at 70°C to dry. The dried calcites were milled sieved and activated around 400°C then it was used as an adsorbent in batch adsorption techniques.

2.2 ADSORBATE:

All the reagents used were of analytical grade. A stock solution of Fe (III) ions was prepared accurately weighted amount of $[\text{NH}_4 \text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}]$ dissolved in 1000 ml of distilled water. The required concentrations of all experimental solution were prepared from the stock solution, aliquots containing different concentrations viz 25, 50, 75, 100 and 125 mg/L The pH of the each experimental solution was adjusted by using 1N NaOH (or) 1N HCl solution before mixing the adsorbent.

2.3 BATCH ADSORPTION TECHNIQUES:

The batch experiments were performed by fixed amount of 25 mg calcite powder added to 50 ml of iron solution taken in 250 ml stopper glass flasks. The flasks were placed in isothermal shaker with agitation speed 200 rpm for 90 min at constant temperature when the equilibrium was attained and the flasks were removed from the shaker. By centrifugation at 5000 rpm at 10 min the adsorbent was separated, the supernatant liquid was analyzed for the Fe(III)ions concentrations with the help of atomic absorption spectrophotometer (perkin Elmer 2380) the amount of Fe(III) ions adsorbed at equilibrium, q_e (mg/g) can be calculated based on the balance principle

$$q_e = \frac{(C_0 - C_e)V}{M} \dots\dots\dots (1)$$

where the q_e is the amounts of Fe(III) ions uptake per unit mass of the sorbent (mg/g), C_0 and C_e are the liquid phase concentration of iron (III) ions at initial and final (mg/L) respectively V is the volume of the solution(L), and M is the mass of dry adsorbent. Percentage removal (R %) was calculated using the formula;

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \dots\dots\dots (2)$$

3. RESULTS AND DISCUSSION:

3.1. EFFECT OF CONTACT TIMES AND INITIAL CONCENTRATION:

To see the effect of contact time and initial concentration on uptake of Fe(III) solution in different initial concentrations(25,50,75,100 and 125 mg/L) was agitated with 25 mg of ACP adsorbent . The solution pH was kept constant and the sorption results for iron on ACP at varies initial concentrations are shown in Figure 1. The contact time curve indicate that adsorption was rapid in the first 40 minutes and contact time needed for iron solution to reach the equilibrium was 50 minutes. The results reveal there is no change in the adsorption after 50 minutes at equilibrium levels and the adsorption capacity q_e was found to be 43.78 to170.40 mg/g with an increase in the initial concentration from 25 to 125 mg/L.

3.2. EFFECT OF ADSORBENT DOSAGES:

The effect of the activated calcite powder doses was studied at 30°C to 60°Cby varying the amount of adsorbent dose [25,50,75,100 and 125 mg] for the initial concentration 50 mg/L. Figure 2 reveals that increase in percentage removal of iron with increases in dose of adsorbent due to this increase in adsorbent surface area and the availability of more adsorption sites [4].

3.3. Effect of pH

The solution pH is the most important factor affecting the metal ion adsorption. This is because of the positive ion (ie, hydrogen ions) competing with the positively charged metal ions on the active sites of the adsorbent. The effect of pH on the adsorption of Fe (III) ions on to activated calcite powder has been studied by varying the pH ranges from 2 to 10 as shown in Figure3: The adsorption of Fe (III) ions initially increases up to 6.5 and then suddenly decreases. The optimum adsorption was at pH 6.5. Hence the further experiments were carried out at pH 6.5.

3.4. FREUNDLICH ISOTHERM:

The Freundlich model is based on multilayer adsorption for the heterogeneous surface [5]. The linear form of Freundlich equation is

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots\dots (3)$$

Where q_e is the amount of Fe (III) ions adsorbed per unit mass of sorbent (mg/g), C_e is the Fe(III) ions concentrations in the solution at equilibrium (mg/g), k_f is measure of adsorption capacity(mg/g), and n is the adsorption intensity. The values of k_f and n are calculated from the

intercepts and slope of the plot of $\log q_e$ VS $\log C_e$ and the values are given in Table 2. The value of n greater than 1 represents favorable adsorption condition. The k_f and n values indicates Freundlich isotherm was suitable for this adsorption. The k_f values also reveals that possibility of multilayer adsorption of Fe(III) on to activated calcite powder.

3.5 LANGMUIR ISOTHERM MODEL:

The linear form equation for the Langmuir isotherm model [6] is

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \dots\dots\dots (4)$$

where C_e is the equilibrium concentration of metal ions (mg/L), q_e is the amount of metal ions adsorbed at equilibrium(mg/g), Q_m is the constant related to the maximum adsorption capacity (mg/g), b is the Langmuir constant related to energy of adsorption (mg/L) .The linear plot of C_e/q_e against equilibrium Concentration(C_e). It is shows that the adsorption obeys the Langmuir model The constants Q_0 and b were determined from slope and intercept and the values of Q_m and b are tabulated in Table 2.

The important characteristics of the Langmuir isotherm model can be described by dimensionless separation factor R_L [7,8]

$$R_L = \frac{1}{1+bC_0} \dots\dots\dots (5)$$

R_L values indicates the nature of the adsorption process, if

- $R_L > 1$ unfavourable
- $0 < R_L < 1$ Favourable
- $R_L = 1$ Linear
- $R_L = 0$ Irreversible

R_L values were calculated at four different temperatures such as 30°, 40°, 50° and 60°C were shown in Table.3. The R_L data were lies within the range of 0 to 1 which shows the suitability of the Langmuir isotherm of Fe (III) ions on the activated calcite powder.

3.6 THERMODYNAMIC PARAMETERS:

The thermodynamic parameters viz standard Gibbs free energy (ΔG^0), Enthalpy (ΔH^0) and Entropy (ΔS^0) changes can be calculated by using the following equation 6,7,8 [9].

$$K_0 = C_{Solid} / C_{Liquid} \dots\dots\dots (6)$$

$$\Delta G^0 = -RT \ln K_0 \dots\dots\dots (7)$$

$$\text{Log}K_0 = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \dots\dots\dots (8)$$

Where K_0 is the equilibrium constant, R is the universal gas constant, T is the Temperature (K).

The ΔH^0 and ΔS^0 are changes in enthalpy and entropy of adsorption respectively. The enthalpy and entropy values for the iron adsorption can be determined from the plot of $\ln K_0$ vs $1/T$. Thermodynamic parameter values are obtained from the Eqs. (6),(7) and (8) for iron adsorption on to activated calcite powder. The values are given in Table 4. Here all the ΔG^0 values were negative, this confirm that the feasibility and the spontaneous nature of adsorption process. The all the values of ΔH^0 were positive, indicates that the sorption process was endothermic and physisorption. The all the ΔS^0 values were positive and this shows randomness at solid- liquid interface during sorption of iron on activated calcite powder.

3.7 THE PSEUDO SECOND ORDER MODEL:

The linear form of pseudo second order adsorption kinetic equation is given by Ho [10]. It is based on the adsorption capacity of the solid phase.

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \dots\dots\dots (9)$$

where k_2 ad, is the rate constant of pseudo second order adsorption (gmg.min), q_e is amount of metal ions adsorbed per unit mass of adsorbent at equilibrium (mg.g), q_t is amount of metal ions adsorbed at time (t). For the applying the boundary conditions, the integrated model of equation (8) becomes;

$$(q_e - q_t) = \frac{1}{q_e} + K_2 t \dots\dots\dots (10)$$

The initial adsorption rate h (mg/g.min), at t=0 can be defined as:

$$h = K_2 q_e^2 \dots\dots\dots(11)$$

The q_e and K_2 can be determined from the slope and intercept of the plot of t/q_t and time (t) respectively. The kinetic parameter and correlation coefficient values were summarized in Table 5. The correlation co-efficient values (γ) for the pseudo-second-order was greater than 0.9900(i.e $\gamma > 0.9900$) and also the calculated q_e values are good agreement with experimental q_e values suggested that the Fe(III) ions on to ACP follows pseudo-second-order model.

3.8. THE ELOVICH EQUATION:

The rate of Elovich model equation is generally expressed as [11,12],

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \dots\dots\dots (12)$$

Where α is the initial adsorption (mg/g/min), β is the adsorption constant (g/mg) during any one experiment. To simply the Elovich equation, by assuming $\alpha \beta t \gg T$ and by applying the boundary conditions $q_t= 0$ at $t=0$ and $q_t =q_t$ at $t=t$ equation (12) becomes

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \dots\dots\dots(13)$$

A plot of q_t vs $\ln(t)$ should yield a linear graph with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$. From the slope and intercept values the α , β and γ were calculated and shown in Table 5. The correlation co-efficient (γ) were greater than 0.9900 (i.e. $\gamma > 0.9900$) suggested that Elovich model can also suitable for the Fe(III) ions adsorption on to ACP.

The obtained pseudo second order high correlation value suggests the adsorption of Iron(III) follows second order kinetics.

3.9 INTRA- PARTICLE DIFFUSION MODEL:

The intra-particle diffusion model is the most commonly used to explains the mechanism of the adsorption process [13]

$$q_t = K_{id} t^{1/2} + C \dots\dots\dots (14)$$

where q_t is the amount of Fe(III) ions adsorbed at time “t” (mg.g^{-1}), K_{id} is the intra-particle diffusion rate constant ($t^{1/2}$), t is the time in minutes and C is the constant (ie, equal to intercept of the line (mg.g^{-1}). The K_{id} , I and γ values were calculated from the plot of q_t vs $t^{1/2}$. These values were given in table 5. The slope of the plot shows two separate regions in the curve, the first part of curved portion reflect the film (or) boundary layer diffusion effect while the final linear portion represents intra-particle diffusion effect. The diffusion rate parameters are summarized in Table .5. The data indicates that, the present system may be followed by intra-particle diffusion mechanism. Since plot is not passing through the origin, suggested that some other mechanism also involved in the adsorption process.

Table 1. Equilibrium parameters for adsorption of Fe (III) onto activated calcite adsorbent

C _i	C _e (Mg / L)				Q ₀ (Mg / g)				R (%)			
	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C
25	3.1705	2.8640	2.6560	2.5270	43.785	44.272	44.688	44.946	87.57	88.544	89.376	89.892
50	10.7935	9.7625	8.3735	7.3780	78.413	80.475	83.253	85.244	78.413	80.475	83.253	85.244
75	23.4245	21.1270	18.9205	16.9720	103.151	107.746	112.159	116.056	68.7673	71.8306	74.7726	77.3706
100	45.7730	42.8605	38.9205	36.7620	108.454	114.279	162.159	126.476	54.227	57.1395	81.0795	63.238
125	74.9725	71.2860	69.7995	64.2175	100.055	107.428	170.401	121.565	40.022	42.9712	68.1604	48.626

Table 2. Langmuir and Freundlich isotherm parameter for adsorption of Fe (III) ions onto activated calcite adsorbent

Temperature °C	Langmuir parameter		Freundlich parameter	
	Q ₀	B	K _f	n
30°	107.0011	0.3600	4.7783	3.6450
40°	115.1532	0.3184	4.8276	3.4729
50°	220.1746	0.0822	4.2458	1.9423
60°	130.7443	0.29412	4.9666	3.225

Table 3. Dimensionless separation factor (r_l)

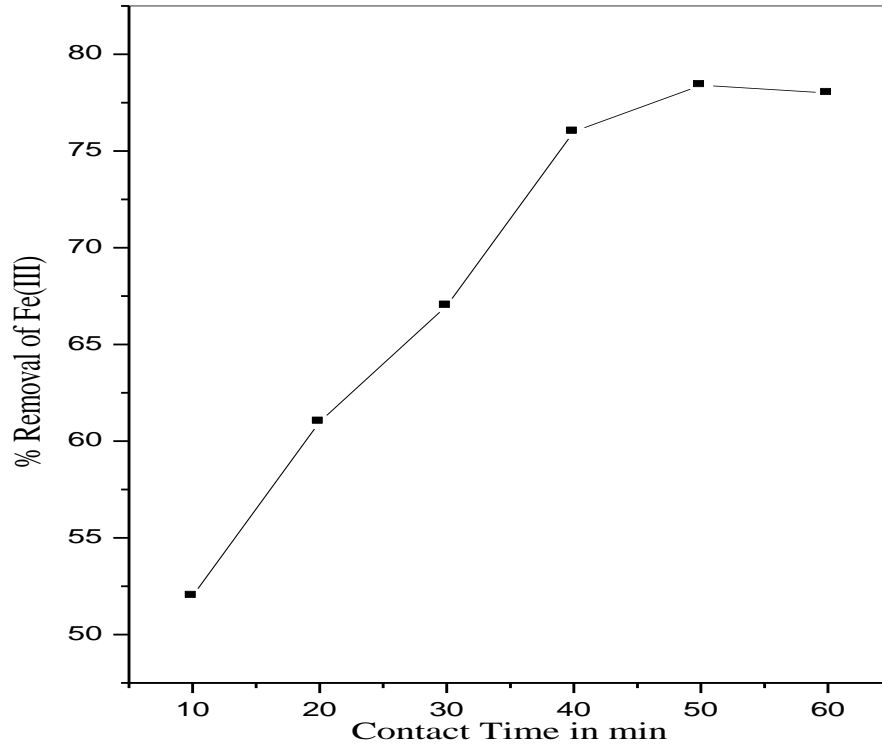
Initial Concentration(C _i)	Temperature °C			
	30°C	40°C	50°C	60°C
25	0.0999	0.1115	0.3272	0.1197
50	0.0526	0.05909	0.1956	0.0636
75	0.0357	0.0401	0.1395	0.0433
100	0.0270	0.0304	0.1084	0.0328

Table 4. Thermodynamic parameter for the adsorption of Fe (iii) ions on

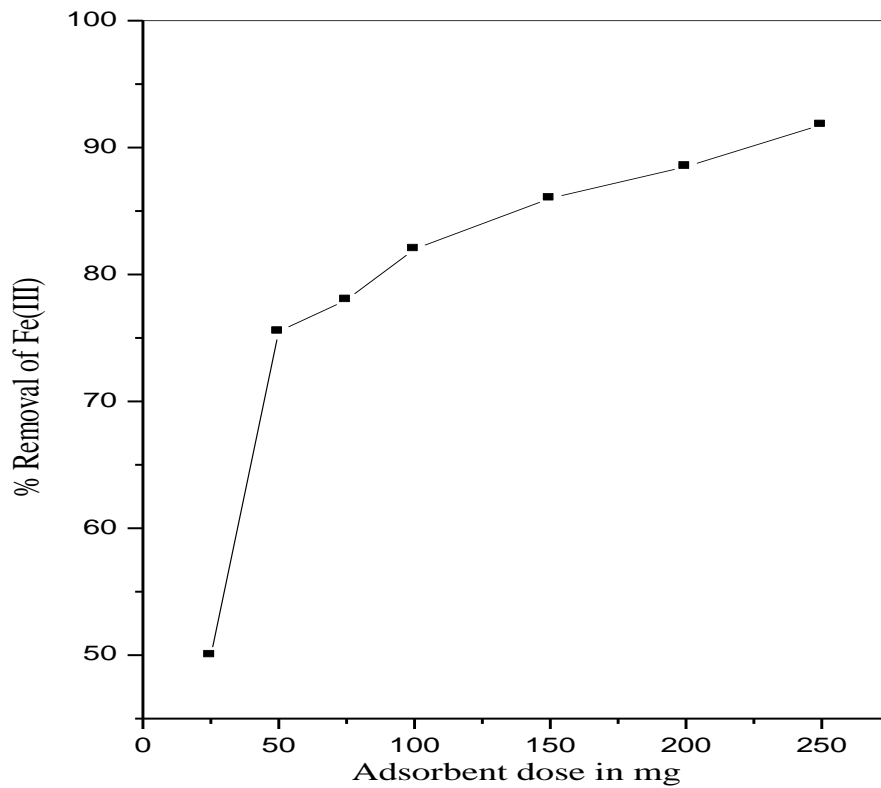
C _i	ΔG°				ΔH°	ΔS°
	30° C	40° C	50° C	60° C		
25	- 4918.185	- 5321.63	- 5719.242	- 6050.088	6.5891	38.0234
50	- 3249.437	- 3685.484	- 4306.517	- 4855.692	13.2275	54.2510
75	- 1988.269	- 2435.938	- 2917.776	- 3403.561	12.3323	47.2286
100	- 426.9556	- 748.2732	- 3907.784	- 1501.781	19.6977	67.1212
125	1019.115	736.5142	- 2044.017	152.1985	18.0271	56.7981

Table 5. The Kinetic Parameter For Adsorption Of Fe (Iii) Ions On Acp Adsorbent

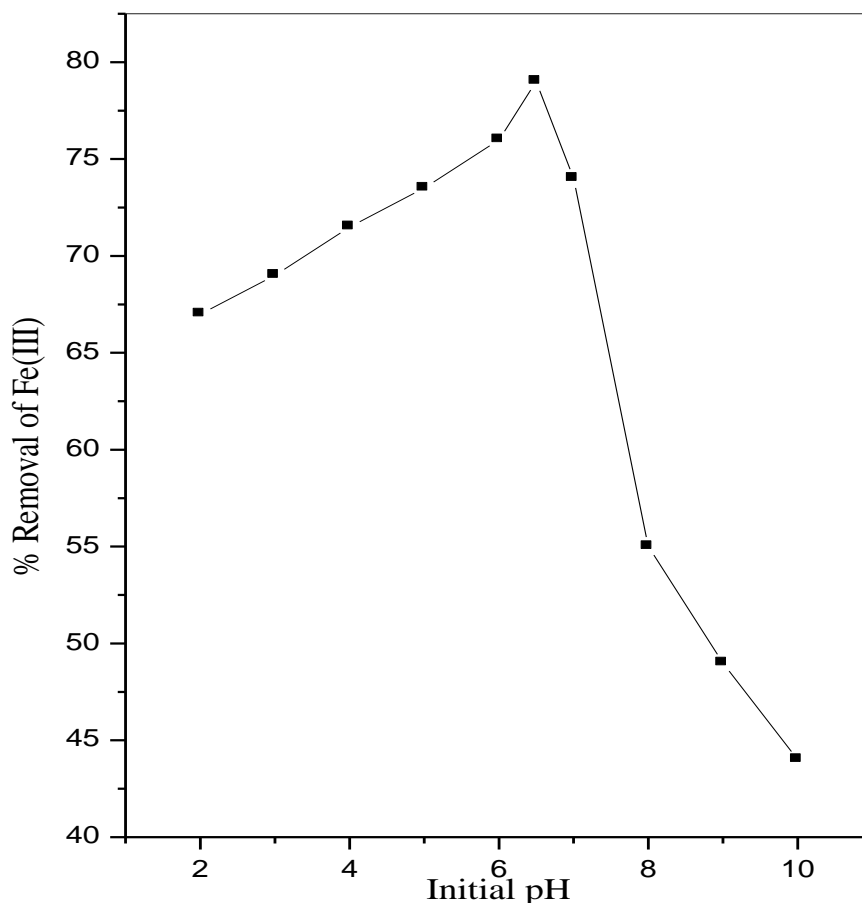
C _i	Temp °C	PSEUDO SECOND ORDER				ELOVICH MODEL			INTRAPARTICLE DIFFUSION		
		q _e	K _{2ad}	γ	H	α	β	γ	K _{id}	γ	I
25	30	50.9614	0.00174	0.9962	4.5114	17.3146	0.1107	0.9921	1.4974	0.9912	0.2460
	40	50.9096	0.00186	0.9963	4.8206	21.5532	0.1159	0.9924	1.5287	0.9914	0.2303
	50	52.8285	0.00201	0.9961	5.1921	27.3078	0.1213	0.9930	1.5579	0.9915	0.2160
	60	51.2191	0.00197	0.9960	5.1901	26.3776	0.1193	0.9915	1.5563	0.9917	0.2186
50	30	92.1793	0.00088	0.9964	7.5104	25.4943	0.0588	0.9940	1.4196	0.9918	0.2620
	40	93.9490	0.00090	0.9951	7.9499	29.6329	0.0590	0.9923	1.45023	0.9919	0.2505
	50	95.9066	0.00098	0.9952	8.9849	38.4464	0.0608	0.9928	1.4953	0.9921	0.2343
	60	98.2485	0.00096	0.9953	9.3534	39.7898	0.0592	0.9927	1.5073	0.9923	0.2344
75	30	126.2178	0.00051	0.9942	8.2023	22.09413	0.03950	0.9926	1.2848	0.9925	0.3052
	40	129.093	0.00056	0.9951	9.4039	27.9733	0.0401	0.9933	1.3427	0.9928	0.2837
	50	133.0713	0.0006	0.9956	10.6239	34.5720	0.0402	0.9935	1.3917	0.9938	0.2677
	60	135.8842	0.00049	0.9944	9.1152	38.5393	0.0429	0.9936	1.4176	0.9945	0.2444
100	30	149.2845	0.00026	0.9941	5.9354	12.3041	0.0294	0.9939	0.9755	0.9961	0.4208
	40	151.3299	0.0003	0.9944	6.881	14.9301	0.02980	0.9940	1.0595	0.9967	0.3856
	50	155.0632	0.00033	0.9922	7.9071	17.9935	0.0298	0.9941	1.1295	0.9969	0.3594
	60	157.778	0.00038	0.9932	9.5210	23.4261	0.0304	0.9943	1.2122	0.9968	0.3271
125	30	195.2934	0.0001	0.9933	3.2151	6.8818	0.0241	0.9937	0.4582	0.9977	0.6382
	40	189.0269	0.00010	0.9935	3.8320	7.9401	0.0237	0.9928	0.5767	0.9975	0.5876
	50	195.5088	0.00011	0.9936	4.2408	8.73306	0.0227	0.9920	0.6400	0.9974	0.5671
	60	185.0294	0.00016	0.9939	5.3636	10.7540	0.0232	0.9919	0.7822	0.9978	0.5026



Fig;1- Effect of Contact time on the removal of Fe(III)ion onto ACP
[Fe(III)]=50mg/L; Conact time=50min; Adsorbent dose=25mg/50ml;Temp=30 °C



Fig;2- Effect of Adsorbent dose on the removal of Fe(III)ion onto ACP
[Fe(III)]=50mg/L; Conact time=50min; Adsorbent dose=25mg/50ml;Temp=30 °C



Fig;3- Effect of Initial pH on the removal of Fe(III) onto ACP
 [Fe(III)]=50mg/L; Contact time=50min; Adsorbent dose=25mg/50ml;Temp=30°C

CONCLUSION:

The present study proved that activated calcite powder is a good adsorbent for Fe (III) ions from aqueous solution. The kinetics of adsorption follows pseudo – second –order, Elovich and intra- particle diffusion model. The adsorption follows both Freundlich and Langmuir models. Thermodynamically parameters indicate that the adsorption was a physisorption process.

ACKNOWLEDGEMENT:

The authors sincerely thank the University Grant Commission New Delhi for providing the fund from Major Research Project.

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