KINETIC, EQUILIBRIUM AND MECHANISTIC STUDIES OF Fe (II) ion ADSORPTION ON ACTIVATED NANO CARBON

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Abstract:

In this study, a series of batch laboratory experiments were conducted in order to investigate the feasibility of CissusQuadrangularis Stem activated carbon for the removal of iron from aqueous solution by adsorption process.Batch experiment was adopted to study the Removal efficiency of Fe^{2+}on varying contact time, temperature, adsorbent dosage, pHand concentrations.The adsorption was studied for Langmuir, Freundlich, Tempkin, Dubinin-Raduskevich, Hurkins-Jura, Halsey, Radlich-Peterson, Jovanovich and BET isotherms. The kinetic studies showed that the data were well described by the pseudo-second-order kinetic model.Thermodynamic parameters e.g. $\Delta G°$, $\Delta S°$ and $\Delta H°$ of the adsorption process was found to be endothermic. Finally it can be seen that activated carbon was found to be effective for removal of Fe^{2+}.

Keywords: Adsorption, Fe (II) ion, Kinetics and Thermodynamics, Isotherms.

Introduction:

Water is one of the most essential requirements for all life on earth and it is considered as very important resource for human civilization. Safe source for pure and affordable water is certainly one of the basic humanitarian goals, and is identified as a major global challenge for the 21st century. Water contamination is a most important critical issue facing the world due to an increase in population growth and has become aserious threat to environmental and human health. Therefore,decontamination of polluted water is become one of the mostimportant environmental matter in the recent decade. Ironis a natural constituent of the Earth's crust and is present in varying concentrations in all ecosystems. They are stable and persistent environmental contaminants since they cannot be degraded or destroyed. Human activity hasdrastically changed the biogeochemical cycles and balanceof some metals. The main anthropogenic sources of Iron arevarious industrial sources, including present and formermining activities, steel producing industries, foundries andsmelters, and diffuse sources such as piping, constituents ofproducts, combustion by –products, etc. These metals arealso known to have adverse effects on the environment andhuman health and are toxic even at low concentration tohuman beings and other living beings.Many processes have been developed that include chemical precipitation,electrode deposition, solvent extraction, ion exchange, activated carbon adsorption andbiological methods. The main limitations of these techniques are their low efficiency in metal ionremoval at trace levels or the high cost. Hence adsorption is reported to be the most effective method for this purpose,which works at low concentration.In the present investigation the adsorption of Iron ion on activated nano carbon prepared from CissusQuadrangularis Stem by carbonization with Sulphuric acid has been achieved. The kinetic and equilibrium adsorption data obtained were utilized to characterize the sample prepared. The amounts and rates of adsorption of Iron using above activated nano carbon from water were then measured. Three simplified kinetic models including pseudo first order, Pseudo second order equations and Elovich equations were used to describe the adsorption process.

Materials and Methods:

Preparation of the adsorbent:

CissusQuadrangularis Stem was collected from local area of Thanjavur district, Tamilnadu, India. It was dried, charred with excess quantity of concentrated sulphuric acid keeping at $120^{o}C$ for 10 hours. Then the resultant carbon was washed with excess quantity of distilled water and dried at $110^{o}C$ for 1 hour and the material obtained was soaked in 5% sodium bicarbonate solution and allowed to stand overnight to remove any residual acid. The material was thoroughly washed with hot distilled water until washings were nearly of neutral effect. To eliminate surface groups by thermal activation, the carbonized material was treated at 1100 ℃ for 6 hrs in a furnace. The resulting carbons were ground in a mill, washed with pure water and finally dried at 120 ℃. The dried powders were sieved by a mesh.

Batch adsorption Experiments:

The effect of various parameters on the removal of Fe(II) ion on to Activated CissusQuadrangularis StemNano Carbon was studied. All Chemicals used were in high level purity of the commercially available AR grade. A stock solution of the adsorbate containing 7.0210 mg/L of Fe(II) ion was prepared by dissolving the calculated quantity of Ammonium Ferrous SulphateDeca hydrate in de-ionized water. The stock solution was diluted to the required initial concentration (range 10 to 50 mg/L). In each adsorption experiment, 50 ml of Fe(II) ion solution with a known concentration was added 25 mg of Activated CissusQuadrangularis Stem Nano Carbon in a 250 ml stopper glass flask at 30, 40, 50 and 60˚C and the mixture was stirred on a mechanical shaker of 60 minutes.

The samples were withdrawn at the appropriate time intervals and the adsorbent was separated by centrifugation at 1000 rpm for 10 minutes. The supernatant was analyzed for the residual Fe(II) ion concentration and was measured before and after treatment with an atomic absorption spectrophotometer (Perkin Elmer 2380). The effect of pH on the rate of adsorption was investigated using Fe(II) ion concentration of 50 mg/L for constant Activated CissusQuadrangularis StemNano Carbon. The pH values were adjusted with 1N HCl and in 1N NaOH solution. The adsorption of process was carried out at different temperature (30°, 40°, 50° and $60^{o}C$). This was helped to estimate the impact of changes of thermodynamic parameters caused by the temperature effect. The amount of adsorption at time t, qt (mg/g), can be determined using the following formula;

$q_t = (C_0-C_t)V/ W$…………………(1)

Where, C_t is the Fe (II) ion liquid phase concentration(mg/L), at any time, $C_0$is the initial concentration of Fe (II) ion in solution (mg/L), V is the volume of solution (L) W is the mass of adsorbent(g) The amount of adsorption at equilibrium qe(mg/g) was computed by using the following equation

$q_e = (C_0 – C_e) V/(W)$………………(2)

Where, C_0 and C_e are the liquid phase concentration of Fe (II) ion (mg/L) initially and at equilibrium. The removal percentage of Fe(II) ion can be calculated as:

Removal % of Fe(II) ion = $(C_0-C_e)/ C_0 × 100$ …. (3)

Where, C_0 is the initial concentration of the Fe(II) ions in solution (mg/L), and C_e is the equilibrium concentration of Fe(II) ions in solution(mg/L).

Result and Discussion

Effect of Contact time

In order to establish the equilibration time for maximum uptake and to know the kinetics of the adsorption process, Fe (II) ionsadsorption on ACQNC adsorbent was investigated as a function of contact time and the results were shown in fig 1. The figure shows that the uptake rate was initially rapid with 50% of the adsorption was complete with in 30min, Equilibrium was achieved with in 50min therefore, an equilibration period of 1 h was selected for all further experiments. The time profile of Fe (II) ions uptake is a single Smooth and continuous curve leading to saturation suggesting the possible monolayer coverage of Fe (II) ions on the surface of the adsorbent. The equilibrium data were collected in Table 1 reveals that, percent adsorption decreased with increase in initial Fe(II) ion concentration, but the actual amount of Fe (II) ion adsorbed per unit mass of adsorbate increased with increase in Fe (II) ion concentration. It means that the adsorption is highly dependent on initial concentration of Fe (II) ion.
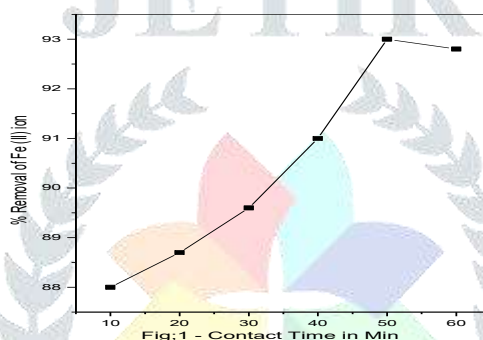

Fig;1 - Contact Time in Min

TABLE: 1. EQUILIBRIUM PARAMETERS FOR THE ADSORPTION OF Fe (II) IONS

M_0	C_e (Mg / L)				Q_e (Mg / L)				Removal %			
	30ºC	40ºC	50ºC	60ºC	30ºC	40ºC	50ºC	60ºC	30ºC	40ºC	50ºC	60ºC
10	0.3210	0.1926	0.1286	0.1220	19.358	19.615	19.743	19.756	96.790	98.074	98.714	98.780
20	0.7062	0.6423	0.5805	0.4496	38.588	38.715	38.839	39.101	96.469	96.789	97.098	97.752
30	1.5461	1.3998	1.2198	1.1302	56.908	57.200	57.560	57.740	94.846	95.334	95.934	96.233
40	2.2524	2.0598	1.9539	1.8328	75.495	75.880	76.092	76.334	94.369	94.850	95.115	95.418
50	3.3384	3.223	3.151	2.964	93.323	93.555	93.697	94.071	93.323	93.555	93.697	94.071

Effect of dosage

Effect of adsorbent dosages on the percentageremoval of Fe (II) ionsis shown in Fig. 2. As can be seenin the figure, the percentage removal of Fe (II) ionsincreases with an increase in the adsorbent dosage from25–125 mg/50ml, which can be attributed to the increasesin the surface area and the number of active sites.
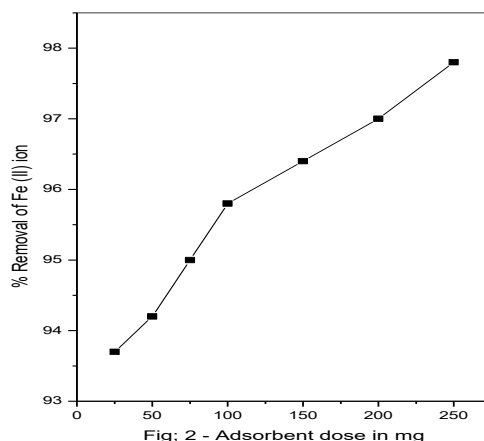
Fig; 2 - Adsorbent dose in mg

Effect of pH:

The study of effect of pH on the adsorption of the Fe (II) ionswas performed by contacting 0.025 g of the adsorbents with 25 mg/50ml concentration of Fe (II) ions solution within buffersolution ranging from pH 2 to 9. The pH of each solution wasadjusted to the desire values by drop wise addition of 0.1MHClor 0.1 M NaOH, both before and after adsorbents of 0.025 g wasadded to 50 mL of adsorbate solution. The flasks containing themixture were left in a thermostatic water bath shaker at 200 rpmand 30 °C for 60 min. The biomass was removed from the solutionby filtration. The residual metal ion concentration left in thesolutions was analyzed. Then the optimum pH was determinedas the pH with the highest adsorption efficiency of Fe (II) ions.
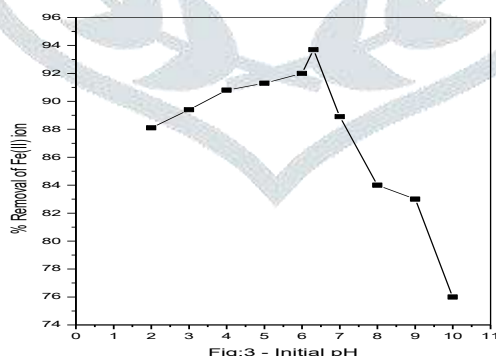

Fig;3 - Initial pH

Effect of Initial Concentration:

Batch adsorption study was made to determine the effect ofinitial Fe (II) ions concentration on the adsorption efficiency.Various iron concentrations (25, 50, 75, 100 and 125 mg/L.)of 50 mL were studied at the optimum conditions: pH of 6.5,adsorbent dose (0.025 g), shaking speed (200 rpm), contact time(60 min) and temperature (30 °C). After adsorption time wascompleted, the adsorbents were removed from the solution andthe concentration of residual metal ion in each solution wasdetermined using ACQNC.

Adsorption isotherm:

Freundlich adsorption isotherm

The Freundlich adsorption isotherm is based on the equilibrium sorption on heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to heat of adsorption. The adsorption isotherm is expressed by the following equation

$$q_e = K_F C_e^{1/nF}$$ ………………….. (4)

Which, can be linearized as

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e$$ ....(5)

Where, q_e is the amount of Fe(II) ion adsorbed at equilibrium (mg/g) and C_e is the concentration of Fe(II) ion in the aqueous phase at equilibrium (ppm). K_F (L/g) and $1/n_F$ are the Freundlich constants related to adsorption capacity and sorption intensity, respectively.

The Freundlich constants K_F and $1/n_F$ were calculated from the slope and intercept of the $\ln q_e$ Vs $\ln C_e$ plot, as shown in Fig. 4, and the model parameters are shown in Table 2. The magnitude of K_F showed that ACQNC had a high capacity for Fe (II) ion adsorption from the aqueous solutions studied. The Freundlich exponent, n_F, should have values in the range of 1 and 10 (i.e., $1/n_F < 1$) to be considered as favourable adsorption. A $1/n_F$ value of less than 1 indicated that Fe (II) ion is favorably adsorbed by ACQNC. The Freundlich isotherm did not show a good fit to the experimental data as indicated by SSE and Chi-square statistics.
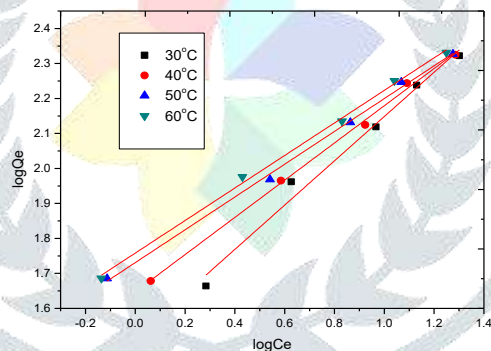

Fig; 4 - Freundlich adsorption isotherm

TABLE: 2. ISOTHERMS PARAMETER FOR THE ADSORPTION OF Fe (II) IONS

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	K_f(mg/g) (L/mg)$^{1/n}$	43.643	49.099	53.008	55.873
	n	1.5203	1.7954	2.0305	2.0509
Langmuir	Q_m(mg/g)	153.00	128.52	118.42	115.72
	b (L/mg)	0.4398	0.7207	0.9920	1.1804
Temkin	b_T (J/mol)	30.679	25.696	22.656	22.717
	K_T (L/mg)	1.8562	1.7432	1.6563	1.6679
Hurkins-Jura	A_H (g^2/L)	-423.82	-493.35	-556.12	-575.58
	B_H (mg^2/L)	-0.4181	-0.3930	-0.3743	-0.3430
Halsay	K_{Ha}(mg/L)	311.23	1086.6	3170.9	3831.4
	n_{Ha}	1.5203	1.7954	2.0305	2.0509
Radlich-Peterson	g	0.3422	0.4430	0.5075	0.5124
	K_R (L/g)	0.0229	0.0204	0.0189	0.0179
Dubinin-Radushkevich	q_s (mg/g)	80.257	74.485	72.283	74.872
	$K_D \times 10^{-4}$ mol^2 kJ^{-2}	1.5036	1.4802	1.4689	1.4738
Jovanovic	K_J (L/g)	0.4751	0.4781	0.4733	0.4921
	q_{max} (mg/g)	22.824	24.303	25.726	26.504

BET	C_{BET} (L/mg)	26.707	48.021	73.740	86.339
	qs (mg/g)	0.0374	0.0208	0.0136	0.0116

Langmuir adsorption isotherm

The Langmuir adsorption isotherm is based on the assumption that all sorption sites possess equal affinity to the adsorbate. The Langmuir isothermin a linear form can be represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad \text{………… (6)}$$

Where q_e is the amount of Fe (II) ion adsorbed at equilibrium (mg/g), C_e is the concentration of Fe (II) ion in the aqueous phase at equilibrium (ppm), q_m is the maximum Fe (II) ion uptake (mg/g), and K_L is the Langmuir constant related to adsorption capacity and the energy of adsorption (g/mg).

A linear plot of C_e/q_e Vs C_e was employed to determine the value of q_m and K_L, as shown in Fig. 5, and the data so obtained were also presented in Table 2. The model predicted a maximum value that could not be reached in the experiments. The value of K_L decreased with an increase in the temperature. A high K_L value indicates a high adsorption affinity. Weber and Chakrabortiexpressed the Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter (R_L) defined in the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \qquad \text{……………….. (7)}$$

Where, C_0 is the initial Fe (II) ion concentration (ppm). Four scenarios can be distinguished:

The sorption isotherm is unfavorable when $R_L > 1$, the isotherm is linear when $R_L = 1$, The isotherm is favorable when $0 < R_L < 1$ and the isotherm is irreversible when $R_L = 0$. The values of dimensionless separation factor (R_L) for Fe (II) ion removal were calculated at different concentrations and temperatures. As shown in Table 3, at all concentrations and temperatures tested the values of R_L for Fe (II) ion adsorptions on the ACQNC were less than 1 and greater than zero, indicating favorable adsorption.

Langmuir adsorption isotherm
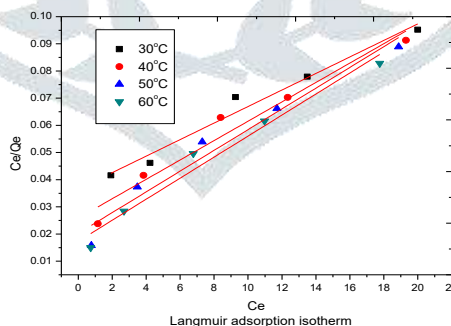
TABLE: 3. DIMENSIONLESS SEPERATION FACTOR (R_L) FOR THE ADSORPTION OF Fe (II) IONS

(C_i)	Temperature °C			
	30ºC	40ºC	50ºC	60ºC
10	0.0834	0.0526	0.0388	0.0328
20	0.0435	0.0270	0.0198	0.0167
30	0.0294	0.0182	0.0133	0.0112
40	0.0222	0.0137	0.0100	0.0084
50	0.0179	0.0110	0.0080	0.0067

The Langmuir isotherm showed a better fit to the adsorption data than the Freundlich isotherm as shown in Fig. 4 and Fig. 5. The fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the ACQNC surface, since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.
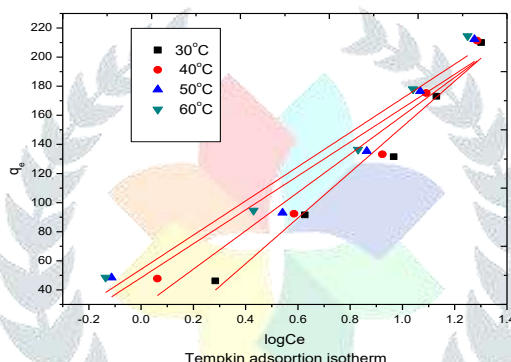
Temkin adsorption isotherm:

The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent-adsorbate interactions.The Temkin isotherm equation is given as:

$$q_e = \frac{RT}{bT} \ln(K_T C_e) \quad ....(8)$$

Which, can be represented in the following linear form

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e ....(9)$$

Where, K_T (L/g) is the Temkin isotherm constant, b_T (J/mol) is a constant related to heat of sorption, R is the ideal gas constant (8.314 J/mol K), and T is absolute temperature (K). A plot of q_e versus $\ln C_e$ enables the determination of isotherm constants K_T and b_T from the slope and intercept, as shown in Fig. 6 The model parameters are listed in Table 3. The Temkin isotherm appears to provide a good fit to the Fe (II) ionadsorption data.

Tempkin adsoprtion isotherm

The adsorption energy in the Temkin model, b_T, is positive for Fe (II) ion adsorption from the aqueous solution, which indicates that the adsorption is endothermic. The experimental equilibrium curve is close to that predicted by Temkin model. Consequently, the adsorption isotherm of Fe (II) ion on ACQNC can be described reasonably well by the Temkin isotherm.

Hurkins-Jura adsorption isotherm

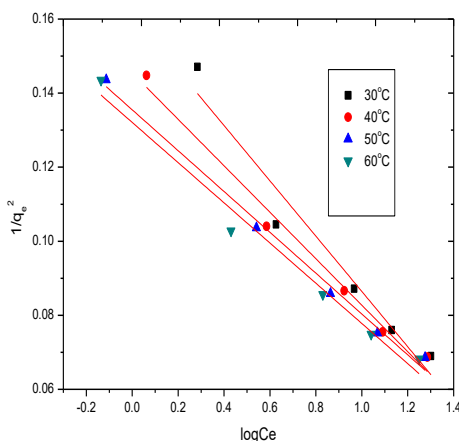The Hurkins-Jura adsorption isotherm can be expressed as:

$$q_e = \sqrt{\frac{A_H}{B_H + \log C_e}} ....(10)$$

This can rearranged as follows:

$$\frac{1}{q_e^2} = \frac{B_H}{A_H} - \frac{1}{A_H} \log C_e ....(11)$$

Where, A_H (g^2/L) and B_H (mg^2/L) are two parameters characterizing the sorption equilibrium.

The isotherm equation accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution. The Harkins–Jura isotherm parameters are obtained from the plots of of $1/q_e^2$ versus log C_e enables the determination of model parameters A_H and B_H from the slope and intercept in Fig. 7.

Hurkins-Jura adsorption isotherm for the adsorption of Fe (II) ions using ACQNC

Halsay adsorption isotherm

The Halsay adsorption isotherm can be given as

$$q_e = \exp\left(\frac{\ln K_{Ha} - \ln C_e}{n_{Ha}}\right) \ldots\ldots\ldots\ldots\ldots(12)$$

And, a linear form of the isotherm can be expressed as follows:

$$\ln q_e = \frac{\ln K_{Ha}}{n_{Ha}} - \frac{\ln C_e}{n_{Ha}} \ldots\ldots\ldots\ldots(13)$$

Where, K_{Ha} (mg/L) and n_{Ha} are the Halsay isotherm constants.

A plot of $\ln q_e$ Vs $\ln C_e$, (is also shown), enables the determination of n_{Ha} and K_{Ha} from the slope and intercept. This equation is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of adsorbent. The model parameters are listed in Table 2. This result also shows that the adsorption of Fe (II) ion on ACQNC was not based on significant multilayer adsorption. The Halsay model is also not suitable to describe the adsorption of Fe (II) ion on ACQNC, because this model also assumes a multilayer behavior for the adsorption of adsorbate onto adsorbent.

Radlich-Peterson adsorption isotherm

The Radlich-Petersonadsorption isotherm contains three parameters and incorporates the features of Langmuir and Freundlich isotherms into a single equation. The general isotherm equation can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \ldots\ldots\ldots\ldots(14)$$

The linear form of the isotherm can be expressed as follows:

$$\ln \frac{C_e}{q_e} = g \ln C_e - \ln K_R \ldots\ldots\ldots\ldots(15)$$

Where, K_R (L/g) and a_R (L/mg) are the Radlich-Peterson isotherm constants and g is the exponent between 0 and 1. There are two limiting cases: Langmuir form for g = 1 and Henry's law for g = 0.

A plot of $\ln C_e/q_e$ versus $\ln C_e$ (is also shown), enables the determination of isotherm constants g and K_R from the slope and intercept. The values of K_R, presented in Table 2, indicate that the adsorption capacity of the ACQNC decreased with an increase temperature. Furthermore, the value of g lies between 0 and 1, indicating favorable adsorption.

Dubinin-Radushkevich adsorption isotherm

The Dubinin-Radushkevich adsorption isotherm is another isotherm equation. It is assumed that the characteristic of the sorption curve is related to the porosity of the adsorbent. The linear form of the isotherm can be expressed as follows:

$$\ln q_e = \ln Q_D - B_D \left[R T \ln\left(1 + \frac{1}{C_e}\right)\right]^2 \quad \text{..............(16)}$$

Where, Q_D is the maximum sorption capacity (mol/g), and B_D is the Dubinin-Radushkevich constant (mol^2/kJ^2). A plot of $\ln q_e$ Vs $R_T \ln(1+1/C_e)$ enables the determination of isotherm constants B_D and Q_D from the slope and intercept.

3.6.8 Jovanovic adsorption isotherm

The model of an adsorption surface considered by Jovanovicis essentially the same as that considered by Langmuir. The Jovanovic model leads to the following relationship:

$$q_e = q_{max}\left(1 - e^{K_J C_e}\right) \quad \text{............(17)}$$

The linear form of the isotherm can be expressed as follows:

$$\ln q_e = \ln q_{max} - K_J C_e \quad \text{..............(18)}$$

Where, K_J (L/g) is a parameter. q_{max} (mg/g) is the maximum Fe (II) ion uptake.

The q_{max} is obtained from a plot of $\ln q_e$ and C_e. Comparison of the experimental data and Jovanovic model is also shown. Their related parameters are listed in Table 2.

By comparing the values of the error functions, it was found the Langmuir and Temkin models are best to fit the Fe (II) ion adsorption on the ACQNC. Both models show a high degree of correlation. This one is clearly confirmthe good fit of Langmuir and Temkin models with the experimental data for removal of Fe (II) ion from the solution.

The Brunauer–Emmett–Teller (BET) isotherm model

Brunauer–Emmett–Teller (BET)isotherm is a theoretical equation, most widely applied in the gas–solid equilibrium systems. It was developed to derive multilayer adsorption systems with relative pressure ranges from 0.05 to 0.30 corresponding to a monolayer coverage lying between 0.50 and 1.50. Its extinction model related to liquid–solid interface is exhibited as:

$$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)(C_e/C_s)]} \quad \text{..............(19)}$$

Where, C_{BET}, C_s, q_s and q_e are the BET adsorption isotherm (L/mg), adsorbate monolayer saturation concentration (mg/L), theoretical isotherm saturation capacity (mg/g) and equilibrium adsorption capacity (mg/g), respectively. As C_{BET} and C_{BET} (C_e/C_s) is much greater than 1,
In the linear form as used is represented as

$$\frac{C_e}{q(C_s - C_e)} = \frac{1}{q_s C_{BET}} + \left(\frac{C_{BET} - 1}{q_s C_{BET}}\right)\left(\frac{C_e}{C_s}\right) \quad \text{..............(20)}$$

Where, C_e is equilibrium Concentration (mg/l), C_s is adsorbate monolayer saturation concentration (mg/l) and C_{BET} is BET adsorption relating to the energy of surface interaction (l/mg) the BET model is also shown.

Kinetic parameters

The rate and mechanism of the adsorption process can be elucidated based on kinetic studies. Fe (II) ionadsorption on solid surface may be explained by two distinct mechanisms: (1) An initial rapid binding of Fe (II) ion molecules on the adsorbent surface; (2) relatively slow intra-particle diffusion. To analyze the

adsorption kinetics of the Fe (II) ion, the pseudo-first-order, the pseudo-second-order, and intra-particle diffusion models were applied. Each of these models and their linear modes of them equations presented in below.

Kinetic Models and Their Linear Forms			
Model	Nonlinear Form	Linear Form	Number of Equation
Pseudo-first-order	$dq_t/d_t = k_1(q_e-q_t)$	$\ln(q_e-q_t) = \ln q_e - k_1 t$	(21)
Pseudo-second-order	$dq_t/d_t = k_2(q_e-q_t)^2$	$t/q_t = 1/k^2 q_e^2 + (1/q_e)t$	(22)

Where, q_e and q_t refer to the amount of Fe (II) ionadsorbed (mg/g) at equilibrium and at any time, t (min), respectively and k_1(1/min), k_2(g/mg.min) are the equilibrium rate constants of pseudo-first order and pseudo-second order models, respectively.

Pseudo-first order model is a simple kinetic model, which was proposed by Lagergren during 1898 and is used for estimation of the surface adsorption reaction rate. The values of $\ln(q_e - q_t)$ were linearly correlated with t. The plot of $\ln(q_e - q_t)$ Vs t should give a linear relationship from which the values of $k_1$were determined from the slope of the plot. In many cases, the first-order equation of Lagergren does not fit well with the entire range of contact time and is generally applicable over the initial stage of the adsorption processes.

In the pseudo-second order model, the slope and intercept of the t/qt Vs t plot were used to calculate the second-order rate constant, k_2. The values of equilibrium rate constant (k_2) are presented in Table 5. According to Table 5, the value of R^2(0.999) related to the pseudo-second order model revealed that Fe (II) ionadsorption followed this model, which is in agreement with the results obtained by Karagoz et al. Hameed et al.. Nevertheless, pseudo-first order and pseudo-second order kinetic models cannot identify the mechanism of diffusion of Fe (II) ioninto the adsorbent pores.

TABLE: 5. THE KINETIC   PARAMETERS FOR THE ADSORPTION OF Fe (II) IONS

C_0	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q_e	k_2	γ	h	α	β	γ	K_{id}	γ	C
10	30	19.3869	0.0780	0.9901	29.3289	4.411	1.3901	0.9939	0.0037	0.9889	1.9843
	40	19.8813	0.0490	0.9902	19.3742	5.913	1.8600	0.9866	0.0279	0.9881	1.9404
	50	19.9174	0.0750	0.9959	29.7559	4.621	2.7900	0.9868	0.0184	0.9909	1.9607
	60	19.9213	0.0792	0.9929	31.4355	8.822	2.9400	0.9879	0.0174	0.9920	1.9627
20	30	39.2248	0.0188	0.9963	28.9915	2.011	7.8001	0.9922	0.0341	0.9942	1.9207
	40	39.3221	0.0204	0.9909	31.4787	9.211	8.1701	0.9877	0.0324	0.9909	1.9257
	50	39.4414	0.0226	0.9943	35.1036	4.912	8.5701	0.9872	0.0307	0.9935	1.9312
	60	39.6108	0.0244	0.9904	38.2186	1.714	9.4501	0.9889	0.0276	0.9952	1.9390
30	30	57.5350	0.0183	0.9912	60.4991	2.717	7.7701	0.9926	0.0230	0.9892	1.9335
	40	57.9671	0.0200	0.9970	67.1408	1.316	7.1501	0.9867	0.0249	0.9883	1.9348
	50	58.4353	0.0174	0.9955	59.5354	5.913	6.1401	0.9890	0.0289	0.9875	1.9305
	60	58.4207	0.0238	0.9971	81.2161	3.316	7.2301	0.9868	0.0244	0.9877	1.9408
40	30	76.4459	0.0181	0.9945	105.815	8.515	5.3001	0.9906	0.0254	0.9896	1.9309
	40	76.8216	0.0170	0.9904	100.234	4.715	5.2001	0.9883	0.0258	0.9905	1.9319
	50	77.0059	0.0179	0.9934	106.415	1.416	5.3301	0.9930	0.0251	0.9926	1.9346
	60	77.2562	0.0179	0.9965	106.685	1.616	5.3301	0.9886	0.0250	0.9937	1.9362
50	30	94.3201	0.0109	0.9912	96.785	6.216	4.5301	0.9888	0.0241	0.9924	1.9242

40	94.5815	0.0107	0.9972	95.697	3.716	4.4601	0.9881	0.0245	0.9945	1.9247
50	94.6623	0.0113	0.9906	101.137	4.317	4.7201	0.9888	0.0230	0.9892	1.9280
60	95.0829	0.0105	0.9930	94.698	3.016	4.4101	0.9917	0.0246	0.9892	1.9267

The intra-particle diffusion model

The Weber and Morris suggest the following kinetic model to identifying the mechanism involved in the adsorption process is of an intra- particle diffusion model or not. It is generally expressed as

$$q_t = K_{id} \, t^{1/2} + C \ldots\ldots\ldots\ldots\ldots\ldots\ldots(24)$$

Where, K_{id} is the intra-particle rate constant (mg/g/min$^{1/2}$), c is the intercept, q_t is the amount of Fe (II) ion ions adsorbed (mg/g), at time t. From the plot of q_t Vs $t^{1/2}$, the intra-particle rate constant can be determined from the slope of the plot. The value of C gives an idea about the boundary layer thickness. The calculated intra- particle diffusion parameters present in Table .5. The γ values indicate that, intra- particle diffusion process is the controls the sorption rate.

Thermodynamic parameters

Thermodynamic parameters such as standard free energy (ΔG^0) standard enthalpy change (ΔH^0) and standard entropy changes (ΔS^0) were calculated by using equilibrium constant (K_0) change with temperature (T).The free energy change can be determined by the following equation.

$$\Delta G^0 = -RT \ln Ko \ldots\ldots\ldots\ldots\ldots\ldots (25)$$

Where, ΔG^0 is the free energy change of sorption process (kJ/ mol), K_o is the equilibrium constant, T is the temperature in (K), R is the universal gas constant. The free energy change may be expressed in terms of enthalpy change of sorption as a function of temperature as follows

$$\Delta G^0 = \Delta H - T\Delta S \ldots\ldots\ldots\ldots\ldots\ldots (26)$$

The adsorption coefficient K_0 can be obtained by combined and rearranging Eqs (25) and (26)

$$\ln K_0 = \Delta H^0 / RT + \Delta S^0 / R \ldots\ldots\ldots\ldots..(27)$$

Where, ΔH^0 is the standard heat changes of the sorption, ΔS^0 is the entropy change of sorption (KJ/mol). The standard enthalpy and entropy changes values are evaluated from the slope and intercept of linear plot $\ln k_0$ against 1/T. Thermodynamic parameter values are obtained from the equation (8) for the sorption of Fe (II) ion ions on Activated CissusQuadrangularis Stem Nano Carbon and the values are tabulated in Table.4. The negative values of free energy changes confirm the spontaneous nature of sorption of Fe (II) ion on Activated CissusQuadrangularis Stem Nano Carbon and the negative values of ΔH^0 confirm the sorption process of an exothermic nature. The positive ΔS^0 values show increased randomness at solid – solution interface during the sorption of Fe (II) ion ions on the Activated Nano Carbon.

TABLE: 4. THERMODYNAMIC PARAMETER FOR THE ADSORPTION OF Fe (II) IONS

(C$_0$)	ΔG^o				ΔH^o	ΔS^o	E_a	S^*
	30ºC	40ºC	50ºC	60ºC				
10	-8580.9	-10227.7	-11657.6	-12165.3	28.536	123.253	27963.2	0.000000444
20	-8332.4	-8862.8	-9426.2	-10444.4	12.4807	68.387	12123.38	0.0003
30	-7337.1	-7851.2	-8488.6	-8971.3	9.46528	55.432	9046.67	0.0014
40	-7101.3	-7581.5	-7973.0	-8405.8	5.94432	43.112	5641.86	0.0060
50	-6644.1	-6961.7	-7248.1	-7653.0	3.37540	33.025	3162.62	0.0191

In order to support that physical adsorption is the predominant mechanism, the values of activation energy (Ea) and sticking probability (S*) were calculated from the experimental data. They were calculated using modified Arrhenius type equation related to surface coverage (θ) as follows:

$$\theta = \left(1 - \frac{C_e}{C_i}\right) \dots\dots\dots (28)$$

$$S^* = (1-\theta)_e \frac{-E_a}{RT} \dots\dots (29)$$

The sticking probability, S*, is a function of the adsorbate/adsorbent system under consideration but must satisfy the condition $0 < S^* < 1$ and is dependent on the temperature of the system. The values of Ea and S* can be calculated from slope and intercept of the plot of $\ln(1-\theta)$ versus 1/T respectively (is also shown) and are listed in Table 5.

From Table 5 it is clear that the reaction is spontaneous in nature as ΔG^0 values are negative at all the temperature studied. Again positive ΔH^0 value confirms that the sorption is endothermic in nature. The positive value of ΔS^0 reflects the affinities of the adsorbents for the Fe (II) ion. The result as shown in Table 5 indicate that the probability of the Fe (II) ion to stick on surface of biomass is very high as $S^* << 1$, these values confirm that, the sorption process is physisorption.

Conclusion

The adsorption of Fe (II) ion on to Activated CissusQuadrangularis Stem Nano Carbon was investigated in this research work. The adsorption equilibrium well correlated with both Langmuir and BET isotherm models. The adsorption kinetic process was found pseudo-second-order model. Isotherm and kinetic study indicates that the ACQNC can be effectively employed for the adsorption of Fe (II) ion ions. Thermodynamic results show that adsorption of Fe (II) ion ions on to ACQNC was spontaneous and physical adsorption.

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