



ADSORPTIVE REMOVAL OF FERROUS ION BY ACTIVATED BORASSUS *FLABELLIFER* BARK NANO CARBON – KINETIC AND THERMODYNAMIC STUDIES

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ABSTRACT

The present study was on adsorption of Fe (II) ions by activated Borassus flabellifer bark nano carbon (ABNC). Using batch adsorption techniques, the influence of contact time, initial concentration, dosage of adsorbent and effect of solution pH were investigated. The equilibrium adsorption data were correlated with Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Hurkins-Jura, Halsay, Radlich-Peterson, Jovanovic and BET isotherm models. The isotherm studies of R_L values showed that the adsorption process was favorable. Thermodynamic parameters such as ΔH^0 , ΔS^0 and ΔG^0 were evaluated. The data indicates that, the adsorption was spontaneous and endothermic in nature. Adsorption kinetics was tested for fitness with pseudo- second-order, Elovich model and Intra- particle diffusion models. Kinetic studies indicate an adsorption followed the pseudo-second-order reaction. The study shows that intra-particles diffusion played a vital role in the adsorption of Fe (II) ions. The ABNC has high adsorption capacity and adsorption rate for the removal of Fe (II) ions from aqueous solution.

KEY WORDS

Adsorption, Fe (II) ions, kinetics, Activated Borassus flabellifer bark nano carbon, Kinetics and Thermodynamic.

1. INTRODUCTION

One of the today's environmental challenges is the excessive use of heavy metals for industrial and domestic practices which contaminates ground and surface water [1]. Before these pollutants discharge to the environment, it is important to remove them from waste water [2]. The high Fe (II) concentrations causes gastrointestinal accumulation, low hemoglobin levels and neurotoxicity. Industries such as those involved in

the production of fertilizer, petrochemicals, electroplating, tanneries, metal processing, and mining industries are releasing Fe (II) into the environment [3 - 5]. Activated carbon has been used as an adsorbent in wastewater treatment application throughout the world, but because of its cost it is no longer attractive to be widely used in small-scale industries. In recent years research interest into the production of adsorbents to replace the costly activated carbon has intensified [6].

Several studies related to wastewater treatment were carried out using low-cost materials, *Borassus flabellifer* bark is used as an adsorbent because of its easy availability, economical viability and biodegradable nature [8,9].

In the present investigation, the adsorption of Fe (II) ion on activated nano carbon prepared from *Borassus flabellifer* bark by carbonization with sulphuric acid has been achieved. The kinetic and equilibrium adsorption data obtained were utilized to characterize the sample prepared [7]. The amount and rates of adsorption of Fe (II) 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.

2. MATERIALS AND METHODS

2.1. Adsorbent

The natural plant material *Borassus flabellifer* bark used in the present investigations was collected from Muthupet nearby Thiruvavur district. The bark wastes were washed with distilled water several times to remove the dirt and dust and was subsequently dried in a hot air oven at 110°C. After that, carbonization of the *Borassus flabellifer* bark was carried out by w/v ratio of concentrated sulphuric acid for 24 hours. The primary carbon obtained was activated at 1100°C for 6 hours under optimized conditions to obtain activated nano carbon. The activated nano carbon was thereafter transferred to room temperature in an inert atmosphere of nitrogen and washed with hot distilled water and 0.5 N hydrochloric, and until the pH of the material reached 7.0. The activated nano carbon was also dried in a hot air oven at 110°C, ground and sieved to obtain the desired particular size (45nm) and stored in desiccators for further use.

2.2. Batch adsorption studies

The effect of various parameters on the removal of Fe (II) on to activated *Borassus flabellifer* bark nano carbon (ABNC) 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) was prepared by dissolving the calculated quantity of ammonium ferrous sulphate deca 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

of known concentration was added with 25 mg of ABNC in a 250 ml stopper glass flask at 30, 40, 50 and 60 °C and the mixture was stirred on a mechanical shaker for 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) 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) concentration of 50 mg/L for a constant ABNC quantity. The pH values were adjusted with 0.1N HCl and in 0.1N NaOH solution. The adsorption process was carried out at different temperature (30°, 40°, 50° and 60°C). This was helped to estimate the impact of changes of thermodynamic parameters caused by the temperature change. The amount of adsorption at time t, q_t (mg/g), can be determined using the following formula;

$$q_t = (C_0 - C_t) V / W \dots \dots \dots (1)$$

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

$$q_e = (C_0 - C_e) V / (W) \dots \dots \dots (2)$$

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

$$\text{Removal \% of Fe (II)} = (C_0 - C_e) / C_0 \times 100 \dots (3)$$

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).

3. RESULTS AND DISCUSSION

3.1. Effect of contact time on the adsorption of Fe (II) ions.

In batch adsorption process contact time is one of the potent factors. In the resultant process all of the parameters except contact time, Temperature, adsorbent dose and agitation speed (120 rpm) were kept constant. The results are represented in Figure 1. The maximum removal of Fe (II) by ABNC required a contact time of 60 minutes, it was revealed that the removal of Fe (II) increase with increase in

contact time and the optimal removal efficiency was reached within 45 minutes. The maximum adsorption occurs at 45 minutes after which the adsorption phase reaches an equilibrium. At this point maximum amount of Fe (II) adsorbed under the particular conditions. It is noted that, the time variation curve is single, smooth and continuous and it shows the formation of monolayer coverage on the outer interface of the adsorbent [7-9].

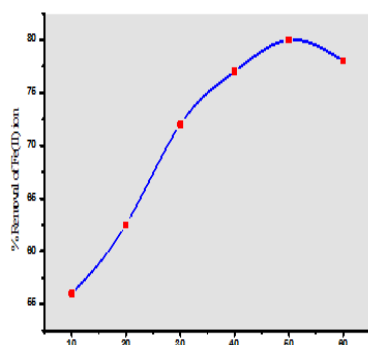


Fig.1-Effect of contact time on the adsorption of Fe (II) onto ABNC

3.2. Effect of Initial Fe (II) Concentration

To study the effect of initial Fe (II) ion concentration on the adsorption level experiments were conducted by varying Fe (II) ion concentration (10, 20, 30, 40 and 50 mg/L) under the constant temperature, pH 6.6 agitation speed (120 rpm) and 0.025 g of adsorbent dose. The removal efficiency by the effect of initial Fe (II) ions concentration obtained from the experimental results are presented in (Table 1), It shows that the increasing initial Fe (II) concentration results in decrease of the removal efficiency of Fe (II). In case of low Fe (II) ion concentrations the ratio of the initial number of moles of Fe (II) ions to available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration [10]. However, at higher concentrations of Fe (II) ions the available sites of adsorption become fewer and hence the percentage of Fe (II) ions adsorption which depends upon initial concentration, decreases.

Table: 1. Equilibrium parameters for the adsorption of Fe (II) onto ABNC

M ₀	C _e (Mg / L)				Q _e (Mg / L)				Removal %			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
10	1.6669	1.0001	0.6676	0.6335	16.666	18.000	18.665	18.733	83.331	89.999	93.324	93.665
20	3.6671	3.3353	3.0144	2.3344	32.666	33.329	33.971	35.331	81.664	83.324	84.928	88.328
30	8.0285	7.2690	6.3342	5.8688	43.943	45.462	47.332	48.262	73.238	75.770	78.886	80.437
40	11.696	10.696	10.146	9.5171	56.608	58.608	59.708	60.966	70.760	73.259	74.635	76.207
50	17.336	16.734	16.365	15.393	65.329	66.532	67.270	69.214	65.329	66.532	67.270	69.214

3.3 Effect of adsorbent dosage

The effect of varying adsorbent doses was investigated by employing (25, 50, 75, 100 and 125 mg). They were agitated with 50 ml of Fe (II) ions solution. The adsorbent dosages have impact on the adsorption of Fe (II) ions by ABNC. The results are presented in Figure2, It is revealed that the increased adsorbent doses increases the Fe (II) ions removal. This is because the contact surface areas of adsorbent have increased when the adsorbent dose increases. It would be more probable for Fe (II) ions, to be adsorbed on adsorption sites and hence the adsorption efficiency increased. Hence the entire studies are carried out with the adsorbent dosage of 25 mg/50 ml of adsorbate solution.

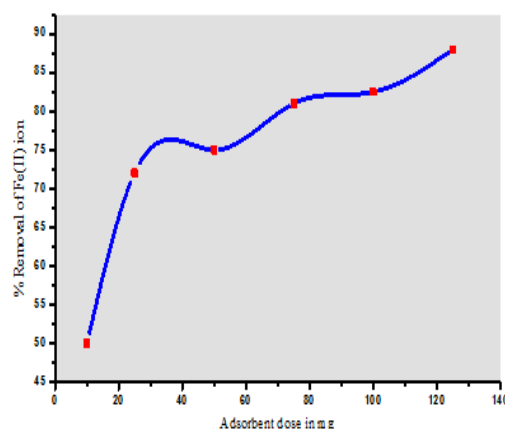


Fig.2-Effect of adsorbent dosage on the adsorption of Fe (II) onto ABNC

3.4 Effect of solution pH

The solution pH is one of the most important factors that control the adsorption of Fe (II) ions on the sorbent material. The adsorption capacity can be attributed to the chemical form of heavy Fe (II) ion in the solution at a specific pH (i.e. Pure ionic metal form or metal hydroxyl form). In addition, due to different functional groups on the adsorbent surface, which become active sites for the Fe (II) binding at a specific pH and the amount of adsorption can vary substantially. Therefore, an increase in pH may cause an increase or decrease in the adsorption, resulting different optimum pH values dependent on the type of adsorbent. To examine the effect of pH on the % removal of Fe (II) ions, the solution pH were varied from 2.0 to 10.0 by adding acid and base

to the stock solution. The increase in % removal increases may be due to the presence of positive charge on the surface of the adsorbent that may be responsible for the Fe (II) binding by ion exchange mechanism. However, as the pH is lowered, the hydrogen ions compete with Fe (II) ions for the adsorption sites in the adsorbent, the overall surface charge on the particles become positive and hinders the binding of positively charged Fe (II) ions. On other hand, decrease in the adsorption at pH above 6.6 may be due to occupation of the adsorption sites by OH⁻ ions which retard the approach of such ions further towards the adsorbent surface. From the experimental results, the optimum pH range for the adsorption of the Fe (II) ions was found to be 2.0 to 6.5 shown in (Figure.3).

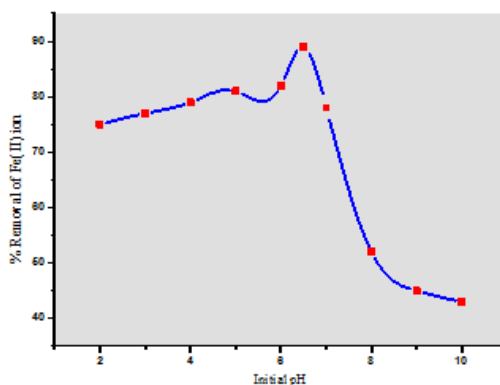


Fig.3-Effect of Initial pH on the adsorption of Fe (II) onto ABNC

3.5. Adsorption Isotherms

Adsorption isotherm (4-8) describes the relation between the amount or concentration of adsorbate that accumulates on the adsorbent and the equilibrium concentration of the dissolved adsorbate. Equilibrium studies were carried out by agitating a series of beakers containing 50 mL of Fe (II) ion solutions of initial concentration 10-50 mg/L with 0.025 g of activated nano carbon at 30 -60°C with a constant agitation speed. Agitation was provided for 1.0 h, which is more than sufficient time to reach equilibrium.

3.6.1 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

$$q_e = K_F C_e^{1/n_F} \dots\dots\dots (4)$$

Which, can be linearized as

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

Where, q_e is the amount of Fe (II) adsorbed at equilibrium (mg/g) and C_e is the concentration of Fe(II) 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 and the model parameters are shown in Table 2. The magnitude of K_F showed that ABNC had a high capacity for Fe (II) adsorption from the aqueous solutions studied. The Freundlich exponent, n_F , have the values within the range of 1 and 10 (i.e., $1/n_F < 1$) shows the favourable adsorption (9). The value of $1/n_F$ is less than one, which indicates that Fe (II) is favorably adsorbed by ABNC. The Freundlich isotherm did not show a good fit to the experimental data as indicated by SSE and Chi-square statistics.

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	K_f (mg/g) (L/mg) ^{1/n}	13.619	18.329	22.000	23.471
	n	1.7564	2.1260	2.4292	2.4309
Langmuir	Q_m (mg/g)	92.65	83.11	79.22	80.08
	b (L/mg)	0.1318	0.2150	0.3000	0.3496
Temkin	b_T (J/mol)	20.374	17.294	15.398	15.805
	K_T (L/mg)	1.0458	1.1079	1.1332	1.1462
Hurkins-Jura	A_H (g ² /L)	-323.07	-427.84	-512.80	-533.67
	B_H (mg ² /L)	-1.1615	-1.1543	-1.1456	-1.1073
Halsay	K_{Ha} (mg/L)	98.184	484.618	1824.235	2145.718
	n_{Ha}	1.7564	2.1260	2.4292	2.4309
Radlich-Peterson	g	0.4307	0.5296	0.5883	0.5886
	K_R (L/g)	0.0734	0.0546	0.0455	0.0426
Dubinin-Radushkevich	q_s (mg/g)	54.546	52.715	52.739	55.104
	$K_D \times 10^{-4}$ mol ² kJ ⁻²	1.4497	1.4319	1.4253	1.4338
Jovanovic	K_j (L/g)	0.0779	0.0765	0.0745	0.0780
	q_{max} (mg/g)	20.061	22.184	23.976	24.958
BET	C_{BET} (L/mg)	8.4593	16.4204	28.4502	30.1532
	q_s (mg/g)	0.1182	0.0609	0.0351	0.0332

Table: 2. Isotherms parameters for the adsorption of Fe (II) onto ABNC

3.6.2 Langmuir adsorption isotherm

The Langmuir adsorption isotherm is based on the assumption that all sorption sites possess equal affinity to the adsorbate. The Langmuir isotherm [10] in a linear form can be represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \dots\dots\dots (6)$$

Where q_e is the amount of Fe (II) adsorbed at equilibrium (mg/g), C_e is the concentration of Fe (II) in the aqueous phase at equilibrium (ppm), q_m is the maximum Fe (II) 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 . The data so obtained are 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 Chakraborti expressed the Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter (R_L) defined in the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad \dots\dots\dots (7)$$

Where, C_0 is the initial Fe (II) 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) 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) adsorptions on the ABNC were less than 1 and greater than zero, indicating favorable adsorption.

The Langmuir isotherm showed a better fit to the adsorption data than the Freundlich isotherm. The fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the ABNC surface, since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.

(C _i)	Temperature °C			
	30°C	40°C	50°C	60°C
10	0.2328	0.1569	0.1177	0.1027
20	0.1317	0.0851	0.0625	0.0541
30	0.0919	0.0584	0.0426	0.0367
40	0.0705	0.0444	0.0323	0.0278
50	0.0572	0.0359	0.0260	0.0224

Table: 3. Dimensionless separation factor (R_L) for the adsorption of Fe (II) onto ABNC

3.6.3 Temkin adsorption isotherm:

The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent-adsorbate interactions (11). The Temkin isotherm equation is given as:

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

Which, can be represented in the following linear form

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

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 lnC_e enables the determination of isotherm constants K_T and b_T from the slope and intercept. The model parameters are listed in Table 2. The Temkin isotherm appears to provide a good fit to the Fe (II) adsorption data.

The adsorption energy in the Temkin model, b_T, is positive for Fe (II) 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) on ABNC can be described reasonably well by the Temkin isotherm.

3.6.4 Hurkins-Jura adsorption isotherm

The Hurkins-Jura (12) adsorption isotherm can be expressed as:

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

This can be rearranged as follows:

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

Where, A_H (g²/L) and B_H (mg²/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 1/q_e² versus log C_e which enables the determination of model parameters A_H and B_H from the slope and intercept.

3.6.5 Halsay adsorption isotherm

The Halsay (13) adsorption isotherm can be given as

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

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

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

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

A plot of lnq_e Vs lnC_e 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 experimental data and the model predictions are based on the non-linear form of the Halsay models. The model parameters are listed in Table 2. This result also shows that the adsorption of Fe(II) on ABNC was not based on significant multilayer adsorption. The Halsay model is also not suitable to describe the adsorption of Fe (II) on ABNC, because this model also assumes a multilayer behavior for the adsorption of adsorbate onto adsorbent.

3.6.6 Radlich-Peterson adsorption isotherm

The Radlich-Peterson (14) adsorption 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:

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

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

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

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 $\ln C_e$ 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 ABNC is decreased with an increase temperature. Furthermore, the value of g lies between 0 and 1, indicating favorable adsorption.

3.6.7 Dubinin-Radushkevich adsorption isotherm

The Dubinin-Radushkevich (15) 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:

$$\ln q_e = \ln Q_D - B_D \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \dots\dots\dots(16)$$

Where, Q_D is the maximum sorption capacity (mol/g), and B_D is the Dubinin-Radushkevich constant (mol²/kJ²). A plot of $\ln q_e$ Vs $R \ln(1+1/C_e)$ enables the determination of isotherm constants B_D and Q_D from the slope and intercept were shown in Table.2.

3.6.8 Jovanovic adsorption isotherm

The model of an adsorption surface considered by Jovanovic (16) is essentially the same as that considered by Langmuir. The Jovanovic model leads to the following relationship:

$$q_e = q_{\max} \left(1 - e^{-K_j C_e} \right) \dots\dots\dots(17)$$

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

$$\ln q_e = \ln q_{\max} - K_j C_e \dots\dots\dots(18)$$

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

The q_{\max} is obtained from a plot of $\ln q_e$ and C_e , as shown in Table.2. 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 that Langmuir

and Temkin models are best to fit the Fe (II) adsorption on the ABNC. Both models show a high degree of correlation. This is clearly shown by the good fit of Langmuir and Temkin models with the experimental data for removal of Fe (II) from the solution.

3.6.9 The Brunauer-Emmett-Teller (BET) isotherm model

Brunauer-Emmett-Teller (BET) (17) 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 0.05Pa to 0.30 Pa corresponding to a monolayer coverage lying between 0.50 Pa and 1.50 Pa. Its extinction model related to liquid-solid interface is exhibited as:

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

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, the linear form is represented as

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

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 results of BET model are also shown in Table.2.

3.7 Kinetic parameters

The rate and mechanism of the adsorption process can be elucidated based on kinetic studies. Fe (II) adsorption on solid surface may be explained by two distinct mechanisms: (1) An initial rapid binding of Fe (II) molecules on the adsorbent surface; (2) relatively slow intra-particle diffusion. To analyze the adsorption kinetics of the Fe (II), the pseudo-first-order, the pseudo-second-order, and intra-particle diffusion models were applied (18). Each of these models and their linear modes of the equations are presented in below.

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

Where, q_e and q_t refer to the amount of Fe (II) adsorbed (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 the 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 will be 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.

C ₀	Temp °C	Pseudo second order				Elovich model			Intra-particle diffusion		
		q _e	k ₂	γ	h	α	β	γ	K _{id}	γ	C
10	30	17.0015	0.0110	0.9901	3.1916	4.2E-20	2.67E+00	0.9939	0.0215	0.9889	1.9050
	40	19.8849	0.0066	0.9902	2.6219	2.6E+01	3.59E-01	0.9866	0.1763	0.9881	1.6328
	50	19.7538	0.0118	0.9959	4.5881	6.2E+02	5.38E-01	0.9868	0.1080	0.9909	1.7726
	60	19.7527	0.0126	0.9929	4.9081	1.1E+03	5.67E-01	0.9879	0.1016	0.9920	1.7858
20	30	37.9555	0.0021	0.9963	3.0582	1.2E+01	1.50E-01	0.9922	0.2456	0.9942	1.4571
	40	38.1274	0.0024	0.9909	3.5262	1.7E+01	1.57E-01	0.9877	0.2262	0.9909	1.5043
	50	38.4725	0.0028	0.9943	4.1863	2.5E+01	1.65E-01	0.9872	0.2069	0.9935	1.5540
	60	38.9779	0.0033	0.9904	4.9837	4.8E+01	1.82E-01	0.9889	0.1780	0.9952	1.6189
30	30	48.5174	0.0024	0.9912	5.6788	6.1E+01	1.50E-01	0.9926	0.1743	0.9892	1.5369
	40	50.8258	0.0026	0.9970	6.8375	6.2E+01	1.38E-01	0.9867	0.1797	0.9883	1.5593
	50	53.7096	0.0022	0.9955	6.3469	3.7E+01	1.18E-01	0.9890	0.2048	0.9875	1.5332
	60	52.8529	0.0033	0.9971	9.3184	1.1E+02	1.39E-01	0.9868	0.1664	0.9877	1.6156
40	30	63.2983	0.0024	0.9945	9.4957	5.9E+01	1.02E-01	0.9906	0.1961	0.9896	1.5116
	40	65.3001	0.0022	0.9904	9.5233	6.3E+01	1.00E-01	0.9883	0.1941	0.9905	1.5263
	50	66.0698	0.0024	0.9934	10.5435	8.1E+01	1.03E-01	0.9930	0.1845	0.9926	1.5527
	60	67.3191	0.0024	0.9965	11.0172	9.3E+01	1.03E-01	0.9886	0.1799	0.9937	1.5697
50	30	73.1463	0.0013	0.9912	7.1700	4.3E+01	8.72E-02	0.9888	0.2074	0.9924	1.4250
	40	74.5563	0.0013	0.9972	7.3323	4.5E+01	8.58E-02	0.9881	0.2065	0.9945	1.4351
	50	74.5726	0.0014	0.9906	8.0378	6.3E+01	9.09E-02	0.9888	0.1906	0.9892	1.4688
	60	77.0198	0.0013	0.9930	7.8113	5.2E+01	8.50E-02	0.9917	0.1999	0.9892	1.4625

Table: 4. The kinetic parameters for the adsorption of Fe (II) onto ABNC

In the pseudo-second order model, the slope and intercept of the t/q_t 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 4. According to Table 4, the value of r^2 (0.999) related to the pseudo-second order model revealed that Fe (II) adsorption followed this model, which is in agreement with the results obtained by Karagoz et al. (19) Hameed et al.(20). Nevertheless, pseudo-first order and pseudo-second order kinetic models cannot identify the mechanism of diffusion of Fe (II) into the adsorbent pores.

3.7.1 Simple Elovich Model:

The simple Elovich model²¹ is expressed in the form,

$$q_t = \alpha + \beta \ln t \dots\dots\dots(23)$$

Where, q_t is the amount adsorbed at time t , α and β are the constants obtained from the experiment. A plot of q_t Vs $\ln t$ should give a linear relationship for the

applicability of the simple Elovich kinetic. The Elovich kinetics of Fe(II) on to ABNC for various initial concentrations (10, 20, 30, 40 and 50 mg/L) of volume 50 mL (each), adsorbent dose 0.025g, temperature 30°C and pH 6.6 were studied.

3.9 The intraparticle diffusion model

The Weber and Morris [20] 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

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

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) ions adsorbed (mg/g), at time t . From the plot of q_t Vs $t^{1/2}$, the intra-particle rate constant was 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 are presented in

Table.4. The γ values indicate that intra- particle diffusion process is the one which controls the sorption rate.

3.6. 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 [16].

$$\Delta G^0 = -RT \ln K_0 \dots \dots \dots (25)$$

Where, ΔG^0 is the free energy change of sorption process (kJ/ mol), K_0 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

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

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

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

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 for the sorption of Fe(II) ions on ABNC and the values are tabulated in Table.5. The negative values of free energy changes confirm the spontaneous nature of sorption of Fe(II) on ABNC and the positive values of ΔH^0 confirm the endothermic

nature of sorption process. The positive ΔS^0 values show increased randomness at solid-solution interface during the sorption of Fe(II) ions on the ABNC.

In order to support that physical adsorption is the predominant mechanism, the values of activation energy (E_a) 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 E_a and S^* were calculated from slope and intercept of the plot of $\ln(1-\theta)$ versus $1/T$ respectively 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 temperatures studied. Again, positive ΔH^0 value confirms that the sorption is endothermic in nature. The positive value of ΔS^0 reflects the affinity of the adsorbent for the Fe (II). The result shown in Table 5 indicate that the probability of the Fe (II) to stick on surface of biomass is very high as $S^* \ll 1$, and these values confirm that, the sorption process is physisorption.

(C ₀)	ΔG^0				ΔH^0	ΔS^0	E_a	S^*
	30°C	40°C	50°C	60°C				
10	-4054.0	-5717.4	-7083.2	-7457.6	31.246	117.374	27963.2	0.000002307
20	-3763.0	-4186.4	-4643.0	-5603.2	14.2461	59.103	12123.3	0.0015
30	-2536.2	-2966.9	-3539.6	-3914.3	11.7501	47.137	9046.67	0.0074
40	-2226.3	-2622.7	-2898.2	-3222.8	7.67066	32.746	5641.86	0.0309
50	-1596.0	-1788.0	-1934.7	-2242.9	4.70276	20.733	3162.62	0.0993

Table: 5. Thermodynamic parameters for the adsorption of Fe (II) onto ABNC

3.7 Effect of other ions

The effect of other ions like Cl^- on the adsorption process was studied at different concentrations. The chloride ions added to 20 mg/L of Fe (II) solutions and the contents were agitated for 60 min at 30°C. The results presented in the Figure 4 reveals that low concentration of Cl^- ions does not affect the percentage of adsorption of Fe (II) on ABNC, because the interaction

of Cl^- ions at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of other ion Cl^- ions increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption increases and hence decreases the percentage adsorption. This is so because ions with smaller hydrated radii decrease

the swelling pressure within the sorbent and increase the affinity of the sorbent for such ions [1,2].

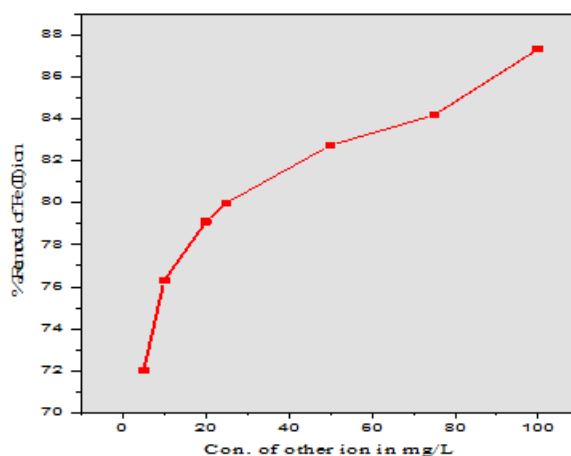


Fig.4-Effect of other chloride ion on the adsorption of Fe (II) onto ABNC

3.8 Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the ferrous ions. If the adsorbed ferrous ions can be desorbed using neutral pH water, then the attachment of the ferrous ion of the adsorbent is by weak bonds. The effect of various reagents were studied for desorption process. The results indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 90% removal of adsorbed ferrous ion. The reversibility of adsorbed ferrous ion in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of ferrous ion by mineral acids and alkaline medium indicates that the ferrous ion was adsorbed onto the ABNC through physisorption as well as by chemisorption mechanisms.

4. CONCLUSION

The adsorption of Fe (II) on to activated *Borassus flabellifer* bark nano carbon (ABNC) was investigated in this research work. The adsorption equilibrium is well correlated with both Langmuir and BET isotherm models. The adsorption kinetic process was found to follow pseudo-second-order model. Isotherm and kinetic study indicate that the ABNC can be effectively employed for the adsorption of Fe (II) ions. Thermodynamic results show that adsorption of Fe (II) ions on to ABNC was spontaneous and it was physical adsorption.

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