Adsorption Studies on the Removal of Fe(II) Ion onto *Posidonia Oceanica* Nano Carbon

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Abstract: Adsorption of Fe(II) ions by activated *Posidonia oceanica* nano carbon was studied by 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 indicate that, the adsorption was spontaneous and is an endothermic nature. Adsorption kinetics was tested with pseudo- second-order, Elovich model and intra – particle diffusion models. Kinetic studies indicate an adsorption pseudo-second-order reaction. This study shows that intra-particles played a major role in the adsorption of Fe(II) ions mechanism. The activated *Posidonia oceanica* nano carbon has high adsorption capacity and adsorption rate for the removal of Fe(II) ions from aqueous solution.

Introduction

One of today's environmental challenges is the excessive use of heavy metals for industrial and domestic practices contaminates ground and surface water[1], before these pollutants discharge to the environment, it is important to remove from water and wastewater[2]. The high Fe(II) concentrations also caused 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 released 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 in efficiency 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, *Posidonia oceanica* is used as adsorbent because of its easily available, economically viable and biodegradable[7] and also Jordanian Pottery materials was chosen as adsorbent due to its low cost, its granular structure, insolubility in water, chemical stability and local availability[8].

In the present investigation the adsorption of ferrous ion on activated nano carbon prepared from *Posidonia Oceanica* Ash by carbonization with sulphuric acid has been achieved. The kinetic and equilibrium adsorption data obtained were utilized to characterize the sample prepared[9]. 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.

Experimental

The *Posidonia oceanica* collected (Figure 1) from nearby Thiruvarur district was carbonized with con. H_2SO_4 and activated around 1100 ^0C in a muffle furnace for 5 hours then it was taken out, ground well to fine powder and stored in a vacuum desiccators.

Figure 1. Photograph of *Posidonia oceanica*

Table 1. Physicochemical characteristics of adsorbent

Analysis	Value
pH_{slurry}	5.500
pH_{zpc}	6.000
Specific gravity	0.195
Moisture content, %	0.105
Bulk density, g cm^{-3}	0.117
Particle density, g cm^{-3}	0.285
Conductivity, μS/cm	41.63
Surface area, m^2/g	25.25
Na$^+$, mg L^{-1}	98.00
K$^+$, mg L^{-1}	440.0

Adsorbent characterization

Adsorbent characterization was performed by means of spectroscopic and quantitative analysis (Table 1). The surface area of the adsorbent was determined by quanta chrome surface area analyzer. The pH of aqueous slurry was determined by soaking 1 g of biomass in 50 mL distilled water, stirred for 24 h and filtered and the final pH was measured[8]. The physico-chemical characteristics of the adsorbent were determined using standard procedures[9]. The concentrations of sodium and potassium were determined by Flame Photometer (Model No. Systronics126). The equilibrium Cr(VI) concentration was determined by using 1,5-diphenylcarbazide as the complexing agent and a UV-Vis Spectrophotometer (Systronics, Vis double beam Spectro 1203) at a λ_{max} of 540 nm. For stirring purpose magnetic stirrer was used. The pH of zero-point charge or pH_{ZPC} was determined based on the previous method[10]. The Fourier transform infrared (FTIR) spectra of the adsorbent was recorded with Fourier transform infrared spectrophotometer in the range of 400-4000 cm^{-1}.

Batch adsorption studies

The effect of various parameters on the removal of Fe(II) onto activated *Posidonia oceanica* nano 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) was prepared by dissolving the calculated quantity of ammonium ferrous sulphate decahydrate 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 *Posidonia oceanica* 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) 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 constant activated *Posidonia oceanica* nano 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, q_t(mg/g), can be determined using the following formula;

$$q_t = (C_0-C_t)V/ W \tag{1}$$

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 using the following equation

$$q_e = (C_0 – C_e) V/(W) \tag{2}$$

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:

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

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

Results and Discussion

Effect of contact time on Fe(II) ions adsorption

In batch adsorption process contact time is one of the potent factors. In the resultant process all of the parameters except contact time, temperature (30, 40, 50 and 60 ˚C), adsorbent dose and agitation speed (120 rpm), were kept constant. The maximum removal of Fe(II) by activated *Posidonia oceanica* nano carbon required contact time of 60 minutes, it is shown in Figure 2, It was revealed that the removal of Fe(II) increase with increase in contact time and the optimal removal efficiency was reached within 45 min. There is 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. Figure 2 indicates 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[11].
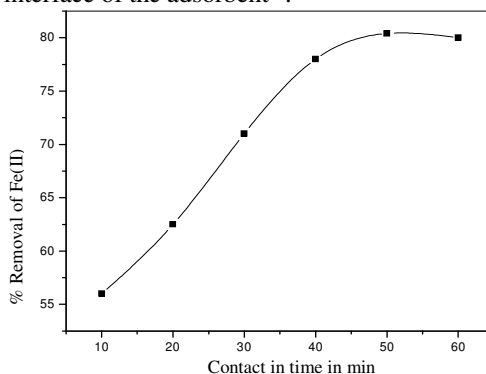
Figure 2. Effect of contact time on the removal of Fe(II) ion
[Fe(II)]=20 mg/L; Absorbent dose=25 mg/50 mL; Temp=30 ^{o}C

Effect of initial Fe(II) concentration

To study the effect of initial Fe(II) ions on the adsorption level by varying concentration (10, 20, 30, 40 and 50 mg/L) under the constant temperature (30, 40, 50 and 60 ˚C), pH 6.5 agitation speed (120 rpm) and 0.025 g of adsorbent dose. The removal efficiency by the effect of initial Fe(II) ions concentration was obtained from the experimental results were presented in Table 2. It shows that the increasing initial Fe(II) concentration results 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 becomes fewer and hence the percentage of Fe(II) ions which depends upon initial concentration.

Table 2. Equilibrium parameters for the adsorption of Fe(II) ion onto PONC

| 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	2.507	2.007	1.757	1.732	14.99	15.99	16.49	16.54	74.93	79.93	82.43	82.68
20	4.007	3.758	3.517	3.007	31.99	32.48	32.97	33.99	79.97	81.21	82.41	84.96
30	7.277	6.708	6.007	5.658	45.45	46.58	47.99	48.68	75.74	77.64	79.98	81.14
40	10.03	9.278	8.865	8.394	59.94	61.44	62.27	63.21	74.93	76.81	77.84	79.02
50	14.26	13.81	13.53	12.80	71.49	72.39	72.94	74.40	71.49	72.39	72.94	74.40

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 data are tabulated in Table 2. The adsorbent dosages have impact on the adsorption of Fe(II) ions by PONC are represented in Figure 3, It is revealed that the increased adsorbent doses with increase the Fe(II) ions removal. This is because the contact surface areas of adsorbent have increased. It would be more probable for Fe(II) ions on to be adsorbed on adsorption sites and the adsorption efficiency increased. Hence the entire studies were carried out with the adsorbent dosage of 25 mg 50 mL of adsorbate solution.
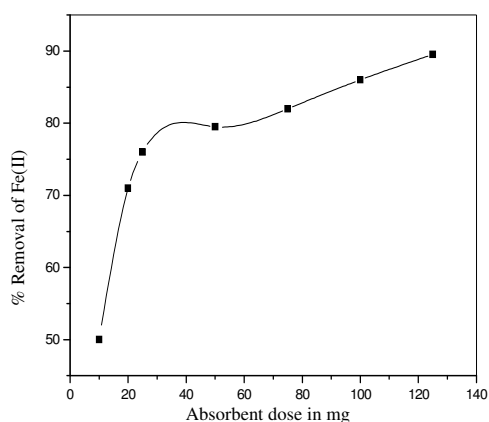
Figure 3. Effect of absorbent dose on the removal of Fe(II) ion
[Fe(II)]=20 mg/L; Contact time=50 min; Absorbent dose=25 mg/50 mL; Temp=30 ^{o}C
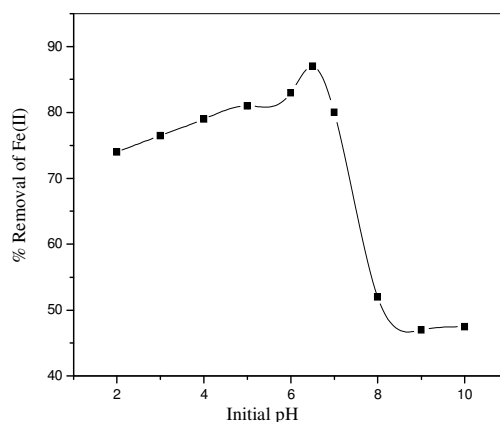
Figure 4. Effect of initial pH on the removal of Fe(II) ion
[Fe(II)]=20 mg/L;   Contact   time=50   min; Absorbent dose=25 mg/50 mL; Temp=30 ^{o}C

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 may be attributed to the chemical form of heavy Fe(II) ion in the solution at 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 the effect 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 This increases may be due to the presence of negative charge on the surface of the adsorbent that may be responds for the Fe(II) binding. 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 hinds the binding of positively charged Fe(II) ions. On other hand, decrease in the adsorption under pH >6.5 may be due to occupation of the adsorption sites by OH^- ions which retard the approach of such ions further toward the adsorbent surface. From the experimental results, the optimum pH range for the adsorption of the Fe(III) ions is 2.0 to 6.5 shown in Figure 4.

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 20 mg/L with 0.025 g of activated nano carbon at 30 ^{0}C with a constant agitation. Agitation was provided for 1.0 h, which is more than sufficient time to reach equilibrium.

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[12,18]. The adsorption isotherm is expressed by the following equation

$$q_e = K_F C_e^{1/nF} \tag{4}$$

Which, can be linearized as

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

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 Freundlich parameters are shown in Table 3. The magnitude of K_F showed that PONC had a high capacity for Fe(II) 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[9]. A $1/n_F$ value of less than 1 indicated that Fe(II) is favorably adsorbed by PONC. The Freundlich isotherm did not show a good fit to the experimental data as indicated by SSE and Chi-square statistics.

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:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{6}$$

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 and the data so obtained were also presented in Table 3. The model predicted a maximum value that could not be reached in the experiments. The value of K_L decreases with an increase in the temperature[13,19]. A high K_L value indicates a high adsorption affinity. Weber[22] expressed the Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter (R_L) defined in the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{7}$$

Where, C_0 is the initial Fe(II) concentration (ppm).

Table 3. Isotherms parameter for the adsorption of Fe(II) ion onto PONC

Model	Constant	Temperature (^{o}C)			
		30	40	50	60
Freundlich	K_f (mg/g) (L/mg)$^{1/n}$	7.9621	10.264	11.982	12.890
	n	1.1599	1.2811	1.3610	1.3683
Langmuir	Q_m (mg/g)	242.54	168.18	144.36	145.64
	K_L (L/mg)	0.0311	0.0577	0.0800	0.0864
Temkin	b_T (J/mol)	31.779	29.429	28.203	28.737
	K_T (L/mg)	0.8376	0.9357	0.9910	1.0108
Hurkins-Jura	A_H (g^2/L)	-199.90	-239.16	-266.59	-278.24
	B_H (mg^2/L)	-1.0592	-1.0386	-1.0219	-0.9992
Halsay	K_{Ha} (mg/L)	11.095	19.752	29.371	33.047
	n_{Ha}	1.1599	1.2811	1.3610	1.3683
Radlich-Peterson	g	0.1379	0.2194	0.2653	0.2692
	K_R (L/g)	0.1256	0.0974	0.0835	0.0776
Dubinin-Radushkevich	q_s (mg/g)	66.045	63.182	62.989	66.749
	$K_D \times 10^{-4}$ mol^2 kJ^{-2}	1.5073	1.4925	1.4882	1.4976
Jovanovic	K_J (L/g)	0.1190	0.1175	0.1149	0.1198
	q_{max} (mg/g)	15.865	17.518	18.988	19.644
BET	C_{BET} (L/mg)	7.9326	3.6465	4.6859	6.0441
	qs (mg/g)	0.1261	0.2742	0.2134	0.1655

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 4, at all concentrations and temperatures tested the values of R_L for Fe(II) adsorptions on the PONC 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 PONC surface, since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.

Table 4. Dimensionless seperation factor (R_L) for the adsorption of Fe(II) ion onto PONC

(C_i)	Dimensionless seperation factor, R_L			
	30 °C	40 °C	50 °C	60 °C
10	0.5624	0.4095	0.3334	0.3165
20	0.3912	0.2575	0.2000	0.1880
30	0.2999	0.1878	0.1429	0.1337
40	0.2432	0.1478	0.1111	0.1037
50	0.2045	0.1218	0.0909	0.0847

Temkin adsorption isotherm

The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent-adsorbate interactions[14]. The Temkin isotherm equation is given as:

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

Which, can be represented in the following linear form

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \tag{9}$$

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. The model parameters are listed in Table 3. 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 PONC can be described reasonably well by the Temkin isotherm.

Hurkins-Jura adsorption isotherm

The Hurkins-Jura[12] adsorption isotherm can be expressed as:

$$q_e = \sqrt{\frac{A_H}{B_H + \log C_e}} \tag{10}$$

This can rearranged as follows:

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

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[15].

Halsay adsorption isotherm

The Halsay[13] adsorption isotherm can be given as

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

(12)

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

$$\ln q_e = \frac{\ln K_{Ha}}{n_{Ha}} - \frac{\ln C_e}{n_{Ha}}$$

(13)

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

A plot of $\ln q_e$ *vs.* $\ln C_e$ 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 based on the non-linear form of the Halsay models. The model parameters are listed in Table 3. This result also shows that the adsorption of Fe(II) on PONC was not based on significant multilayer adsorption. The Halsay model is also not suitable to describe the adsorption of Fe(II) on PONC, because this model also assumes a multilayer behavior for the adsorption of adsorbate onto adsorbent.

Redlich-Peterson adsorption isotherm

The Redlich-Peterson[16] 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:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g}.$$

(14)

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

$$\ln \frac{C_e}{q_e} = g \ln C_e - \ln K_R .$$

(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 3, indicate that the adsorption capacity of the PONC 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[15] adsorption isotherm is another isotherm equation[17]. 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:

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

(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.

Jovanovich 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[18]:

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

(17)

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

$$\ln q_e = \ln q_{max} - K_J C_e$$

(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, Their related parameters are listed in Table 3. By comparing the values of the error functions, it was found the Langmuir and Temkin models are best to fit the Fe(II) adsorption on the PONC. Both models show a high degree of correlation. This is clearly confirming the good fit of Langmuir and Temkin models with the experimental data for removal of Fe(II) from the solution.

The Brunauer-Emmett-Teller (BET) isotherm model

Brunauer–Emmett–Teller (BET)[19] isotherm is a theoretical equation, most widely applied in the gas–solid equilibrium systems. It was developed to derive multilayer adsorption systems with relative concentration ranges from 10 to 50 mg/L corresponding to a monolayer coverage lying between 20 and 30 mg/L. Its extinction model related to liquid–solid interface is exhibited as:

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

(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

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

(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.

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 them equations presented in below.

Model	Nonlinear Form	Linear Form	
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)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 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 γ(0.999) related to the pseudo-second order model revealed that Fe(II) adsorption followed this model, nevertheless, pseudo-first order and pseudo-second order kinetic models cannot identify the mechanism of diffusion of Fe(II) into the adsorbent pores[20].

Table 5. The kinetic parameters for the adsorption of Fe(II) ion onto PONC

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	15.20	0.0158	0.9901	3.653	64.00	0.5615	0.9939	0.0181	0.9889	1.863
	40	17.31	0.0096	0.9902	2.862	94.40	0.4787	0.9866	0.1456	0.9881	1.637
	50	17.27	0.0163	0.9959	4.876	97.82	0.7172	0.9868	0.0905	0.9909	1.751
	60	17.28	0.0174	0.9929	5.203	51.83	0.7557	0.9879	0.0853	0.9920	1.761
20	30	35.39	0.0034	0.9963	4.250	40.85	0.2003	0.9922	0.1791	0.9942	1.570
	40	35.63	0.0038	0.9909	4.807	60.29	0.2097	0.9877	0.1666	0.9909	1.602
	50	35.98	0.0043	0.9943	5.597	96.13	0.2200	0.9872	0.1541	0.9935	1.636
	60	36.47	0.0049	0.9904	6.489	222.4	0.2427	0.9889	0.1344	0.9952	1.682
30	30	48.48	0.0037	0.9912	8.685	557.2	0.1997	0.9926	0.1213	0.9892	1.651
	40	50.21	0.0040	0.9970	10.165	461.3	0.1837	0.9867	0.1271	0.9883	1.663
	50	52.24	0.0034	0.9955	9.299	200.7	0.1576	0.9890	0.1458	0.9875	1.644
	60	51.84	0.0050	0.9971	13.32	809.2	0.1856	0.9868	0.1200	0.9877	1.700
40	30	64.42	0.0037	0.9945	15.21	480.4	0.1362	0.9906	0.1335	0.9896	1.644
	40	65.91	0.0034	0.9904	14.95	486.4	0.1336	0.9883	0.1334	0.9905	1.652
	50	66.56	0.0037	0.9934	16.30	666.2	0.1369	0.9930	0.1278	0.9926	1.669
	60	67.52	0.0037	0.9965	16.79	762.2	0.1370	0.9886	0.1256	0.9937	1.680
50	30	76.44	0.0022	0.9912	12.60	442.5	0.1162	0.9888	0.1342	0.9924	1.601
	40	77.49	0.0021	0.9972	12.71	440.9	0.1145	0.9881	0.1345	0.9945	1.606
	50	77.66	0.0023	0.9906	13.73	719.7	0.1212	0.9888	0.1252	0.9892	1.626
	60	79.41	0.0021	0.9930	13.16	503.2	0.1133	0.9917	0.1322	0.9892	1.621

Simple Elovich model

The simple Elovich model[21] is expressed in the form,

$$q_t = \alpha + \beta \ln t \tag{23}$$

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.* lnt should give a linear relationship for the applicability of the simple Elovich kinetic. The Elovich kinetics of Fe(II) on to PONC 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 6.5.

The intra-particle diffusion model

The Weber and Morris[22] 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

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

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 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[21].

$$\Delta G^0 = -RT \, \ln Ko \tag{25}$$

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

$$\Delta G^0 = \Delta H - T\Delta S \tag{26}$$

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

$$\ln K_0 = \Delta H^0 / RT + \Delta S^0 / R \tag{27}$$

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) ions on activated *Posidonia oceanica* nano carbon and the values are tabulated in Table 6. The negative values of free energy changes confirm the spontaneous nature of sorption of Fe(II) on activated *Posidonia oceanica* 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) ions on the activated *Posidonia oceanica* nano carbon.

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:

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

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

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[23]. The values of Ea and S^* can be calculated from slope and intercept of the plot of $\ln(1-\theta)$ *versus* $1/T$ respectively and are listed in Table 6.

Table 6. Thermodynamic parameter for the adsorption of Fe(II) ion onto PONC

(C_0)	ΔG^o, kJ/mol				ΔH°, kJ/mol	ΔS°, J/Kmol	E_a, kJ/mol	S^*
	30 ^{o}C	40 ^{o}C	50 ^{o}C	60 ^{o}C				
10	-2758.4	-3596.5	-4150.3	-4327.9	13.289	53.450	10523.4	0.0037
20	-3486.9	-3809.0	-4148.0	-4794.3	9.3628	42.208	7722.77	0.0095
30	-2868.3	-3239.4	-3719.0	-4039.8	9.2532	40.000	7267.69	0.0136
40	-2758.2	-3115.8	-3373.3	-3670.8	6.3198	30.030	4867.65	0.0361
50	-2315.4	-2508.1	-2663.1	-2953.6	3.9333	20.577	2868.56	0.0917

From Table 6 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). The result as shown in Table 6 indicate that the probability of the Fe(II) to stick on surface of biomass is very high as $S^* << 1$, these values confirm that, the sorption process is physisorption[24].

Conclusion

The adsorption of Fe(II) on to activated *Posidonia oceanica* 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 PONC can be effectively employed for the adsorption of Fe(II) ions. Thermodynamic results show that adsorption of Fe(II) ions on to PONC was spontaneous and physical adsorption.

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