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Research Article

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Removal of Nickel (II) ion from aqueous solution onto H_2SO_4 Activated carbon prepared from *Erythrina Indica* Bark

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Abstract

The potential of economically cheaper natural materials like *Erythrina indica* Bark was assessed for nickel adsorption from aqueous solutions. The effects of pH, contact time, sorbent dose, initial metal ion concentration and temperature on the uptake of nickel were studied in batch process. The removal of nickel was dependent on the physico-chemical characteristics of the adsorbent, adsorbate concentration and other studied process parameters. The sorption data has been correlated with Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich adsorption models. It was found that Freundlich and Tempkin isotherms fitted well to the data. Maximum nickel removal was observed at pH 7.0. Under the chosen conditions, Experimental data obtained were fitted with linearised forms of Legergren and Ho kinetic models. The Sum of Error Squares Percentage (SSE%) for first order and second order kinetics were11.72& 0.44 respectively. Pseudo-second order model explains the nickel kinetics more effectively. The results revealed that nickel is considerably adsorbed on *Erythrina indica* Bark and it could be and economic method for the removal of nickel from aqueous solutions.

Keywords: Adsorption; *Erythrina indica* Bark Carbon (EIBC); Ni(II)ion removal; Kinetics models; Isotherm studies.

1. Introduction

Heavy metals are continuously released into the aquatic environment from natural processes like volcanic activity and weathering of rocks. Industrial processes have greatly enhanced the mobilization of heavy metals. The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentrations [1], [2]. They are highly toxic as ions or in compound forms; they are soluble in water and may be readily absorbed into living organisms. Nickel(II) ions containing wastewaters are common as it is used in a number of industries including electroplating, batteries manufacturing, mining, metal finishing and forging. Higher concentrations of nickel cause cancer of lungs, nose and bone. Dermatitis is the most frequent effect of exposure to Ni, such as coins and jewellery. The higher concentration of Ni(II) ion in an ingested water may cause severe damage to lungs, kidneys, gastrointestinal distress, e.g., nausea, vomiting, diarrhoea, pulmonary fibrosis, renal edema, and skin dermatitis[3]. A number of methods are available for the removal of metal ions from aqueous solutions. These are ion exchange, solvent extraction, reverse osmosis, electro dialysis, precipitation, flocculation and membrane separation processes [4]-[8]. However, these techniques have certain disadvantages, such as high capital and operational costs or the treatment and disposal of the residual metal sludge. Adsorption compared with other methods appears to be an attractive process due to its efficiency and the ease with which it can be applied in the treatment of heavy metal containing wastewater [9]. In recent years, a number of adsorptive materials, such as aquatic plants [10], agricultural by-products [11], industry by-product [4], sawdust[12], clay [13], zeolite [14], and microorganisms [15] were used in heavy metal removal from wastewaters.

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Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewablity, low cost and more efficiency seem to be a viable option for heavy metal remediation. Present investigation is devoted to study the removal of Ni(II) from synthetics aqueous wastewater by using *Erythrina indica* Bark. This agricultural byproducts is available in large amount in India and other countries. It is both used as fuel in brick kilns or packing material and available at negligible price. The effect of various process parameter, namely pH, adsorbent doe, initial metal ion concentration, contact time and temperature on the removal of Ni(II) have been investigated. The data may be used full for environmental engineer in designing of heavy metal containing waste water containing treatment systems.

Table: 1.0 Nomenclature

Nomenclature	
C_i	Liquid phase initial concentrations of the adsorbate (mg/L)
C_t	Liquid phase concentrations of the adsorbate at time "t" (mg/L)
C_e	Liquid phase concentrations of the adsorbate at equilibrium (mg/L)
V	Volume of the adsorbate solutions in liter (L)
W	Mass of the adsorbent (g)
q_e	Quantity adsorbed at equilibrium (mg/g)
q_t	Quantity adsorbed at time "t" (mg/g)
T	Time in minutes
Q_e	Amount of solute adsorbed per unit weight of adsorbent (mg/g)
C_e	Equilibrium concentration of solute in the bulk solution (mg/L)
Q_0	Langmuir adsorption efficiency
B	Langmuiradsorption energy
R_L	Langmuirseparation factor
C_0	Initial concentration of the adsorbate
K_f and n	Freundlich constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively
b_T	Tempkinconstant related to heat of sorption (J/mol)
a_T	Tempkin equilibrium binding constant
q_D	D-R isothermtheoretical saturation capacity (mg/g)
B	D-R isothermconstant related to the mean free energy
E	D-R isotherm polanyi potential
E	D-R isothermmean free energy of adsorption
R	Gas Constant
T	Temperature (K)
k_1	Rate constant of adsorption (l/min)
k_2	Second-order constants
h	Initial adsorption rate (mg/g min)
N	Number of data points

2. Materials and Methods

2.1 Materials:

All the chemicals used for these experiments are of analytical grade. Activated Carbon was prepared *from Erythrina indica* Bark. $(NH_4)_2$ Ni $(SO_4)_2$ $.6H_2O$, complexing reagent used as DMG purchased from Merck company.

2.2 Preparation of Stock solution:

Ni(II) ion was determined spectrophotometrically as Ni-DMG complex. To about 10 ml of the filtered sample solution containing Ni (II) ions, 0.5ml of 0.5N HCl, 0.2 mL of 0.25N Sodium citrate, 1drop of 0.05N iodine and 0.8ml of 0.5% DMG were added. The absorbance of rosy red Ni-DMG complex was measured at 445 nm.

2.3 Preparation of Adsorbent:

Activated carbon sorbent derived from the barks *Erythrina indica* (Indian coral tree) by sulphuric acid treatment. The barks of *Erythrina indica* were cut into smaller pieces, dried in sunlight for 8 hours and then soaked in concentrated H_2SO_4 acid at 1:1 ratio (W/V) for 48 hours and activated at 160°C in air oven for 6 hours. The activated carbon was repeatedly washed with distilled water until the pH of the wash water become neutral.

The carbon obtained was dried at 110 ± 0.5° C for nearly 2 hours to remove the moisture. The dried material was ground well to a fine powder and sieved using the sieves of desired particle size range. The particles in between the sizes of 0.106 and 0.212 mm were taken. The above prepared carbon was designated as *Erythrina indica* Bark Carbon (EIBC) and kept in a desiccator.

2.4 Physico - chemical characteristics of Adsorbent:

The activated carbon prepared from *Erythrina indica* barks was designated as *Erythrina indica* barks Carbon (EIBC). The various characteristics of the EIBC determined were collected in the Table: 2.0.

Table: 2.0 Physico - chemical characteristics of EIBC

S.No.	Properties	Values
1.	Surface area (BET), m^2/g	483.52
2.	Bulk density, g/mL	0.4210
3.	Particle size (mm)	0.106 -0.212
4.	Moisture content, %	3.98
5.	pH_{zpc}	6.42
6.	Pore volume, cm^3/g	0.448
7.	Fixed Carbon, %	76.32
8.	Pore size (Pore width), nm	2.436

2.5 Batch Adsorption procedure:

Batch adsorption studies were carried out in 250 mL iodine flasks with 50 mL of the working Ni(II) ion solution of different concentrations ranging from 8, 10 and 12 mg/L. Known amount of adsorbent was added to the solution. The flasks were agitated at a constant speed of 180 rpm. Samples were collected from the flasks at predetermined time intervals for analyzing the residual Ni(II) ion concentration in the solution. The amount of Ni(II) ions adsorbed in milligram per gram of adsorbent was determined by using the following mass balance equation:

$q_e = (C_i-C_e)V/W$

Where C_i and C_e are Ni(II) ion concentrations (mg/L) before and after adsorption, respectively, V is the volume of adsorbate in litre and m is the weight of the adsorbent in grams. The percentage of removal of Ni(II) ions was calculated using the following equation:

Removal (%) = $(C_i-C_e)/C_i$ x 100

3. Results and Discussion

3.1 Effect of Contact time and initial concentration:

The effect of contact time on percentage removal of Ni(II) ion for different initial concentration have been shown in figure 1. Adsorption of Ni(II) ion from the solution increases with the time and finally attains equilibrium at 60, 80 and 80 minutes for the initial concentrations 8,10 and 12 mg/L respectively. The percentage of removal increased with the increase in contact time and decreased with the increase of initial concentration of the Ni(II) ion. However the amount of metal ion adsorbed on the adsorbent increased with the increase of initial concentration of the Ni(II) ion solution [16],which is depicted in figure:1 and given in table: 3.

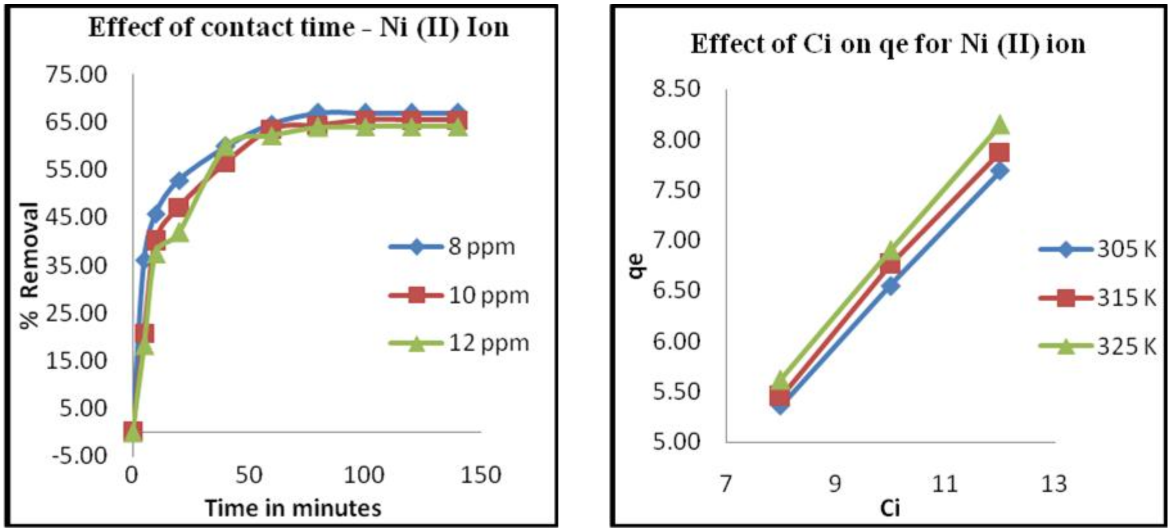

Figure: 1 Effect of Contact time and initial concentration

Table:3 Percentage of removal of metal ion and amount of metal ion adsorbed

C_i (mg/L)	% of Removal of metal ion at equilibrium	Adsorbed amount of Ni(II)ion at equilibrium (mg/g)
8	75.00	15.00
10	70.45	28.18
12	66.67	40.00

3.2 Effect of pH:

The pH of the adsorbate solutions has been identified as the most important parameter governing sorption of metal ion on different adsorbents. Adsorption of Ni(II) ion increased appreciably with an increase of pH from 2 to 7. The influence of pH on Ni(II) ion removal can be explained on the basis of an electrostatic interaction mode. pHzpcof the EIBC is 6.42. As the pH decreases below the pHzpc of the adsorbent, the surface of the carbon exhibits increasing positive characteristics. Since the species to be adsorbed, M^{2+}ions, were also positive, the adsorption is not favored. Besides this, H^+ ions present at a higher concentration in the reaction mixture compete with M^{2+}ions for the adsorption sites resulting in the reduction in the adsorption of M^{2+}ions. On the contrary, as pH increases, the positive charge accumulated on the surface of the adsorbent decreases and the adsorbent surface became more and more negatively charged and therefore the adsorption of positively charged Ni(II) ion, species were more favorable. The mechanism of adsorption of Ni(II) ions may also be explained based on ion exchange model because some carbon-oxygen complexes (CxO, COx and CxO_2) present in the surface of the activated carbon render it as polar[18].

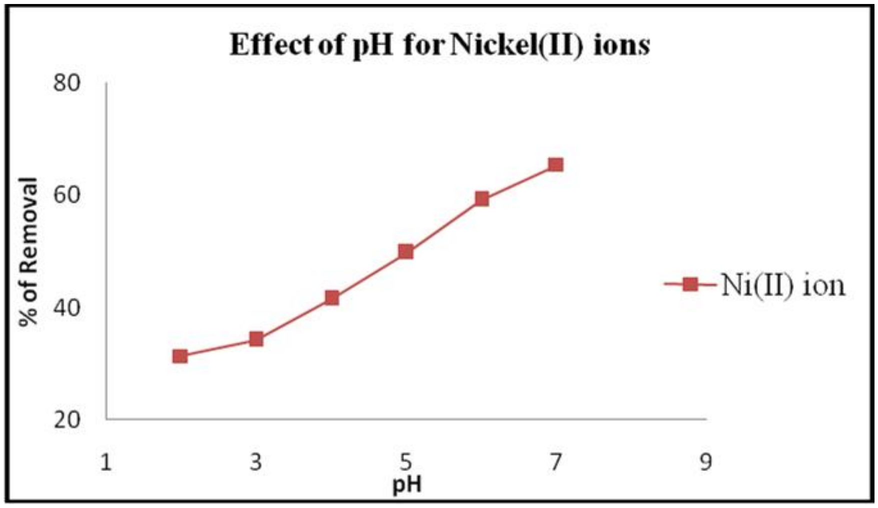

Figure: 2 Effect of pH for Ni(II) ion onto EIBC

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3.3 Effect of Temperature:

It is well known that temperature plays an important role in the adsorption process. The metal ions removal increase rapidly from 305K, 315K and 325K this result suggests that the experimental temperature had a greater effect on the adsorption process implying that the surface coverage increased at higher temperatures. This may be attributed to the increased penetration of metal ions inside micro pores or the creation of new active sites at higher temperatures. This indicates the endothermic nature of the controlled adsorption process. Similar result has been reported in the literature.

Table: 4 Data processing Tools

S. No.	Parameters		Formulae
1.	**Kinetic Models & SSE %**	Pseudo First order kinetics (Legergren equation)	$\log (q_e-q_t) = \log q_e - k_1/2.303 \times t$
		Pseudo Second order kinetics (Ho equation) The initial adsorption rate h	$t/q_t=1/k_2.q_e^2 +1/q_e\ t$ $h = k_2q_e^2$
		Sumoferror squares	$SSE (\%)= \surd\sum[(q_e)_{exp}-(q_e)_{cal}]^2/ N$
2.	**Isotherms**	Langmuir Separation factor	$C_e/Q_e = 1/Q_0b + C_e /Q_0$ $R_L = 1 / (1+ bC_0)$
		Freundlich	$\log Q_e = \log K_f + 1/n \log C_e$
		Tempkin	$q_e = b_T \ln a_T + b_T \ln C_e$
		Dubinin – Raduskevich, Polanyi potential Mean free energy of adsorption	$\ln q_e = \ln q_D - B\varepsilon^2$ $\varepsilon = RT \ln (1+1/C_e)$ $E = 1/ (2B)^{½}$

3.4 Adsorption Kinetics:

The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. Plots of different kinetic models applied were given in the Figure: 3 and the kinetic parameters calculated were given in the Table 5. Between the first order and second order, second order kinetic model seems to best describe the above adsorption system as its R^2 values were very close to unity. Moreover, difference between qe(cal) and qe(exp) values of second order is small when compared to first order kinetic model. Statistically it is tested with the tool Sum of error squares (SSE%) [16].The Δqe and SSE % values were given in the Table: 5 from which it was concluded that second order kinetic model was more appropriate rather than first order kinetic model.

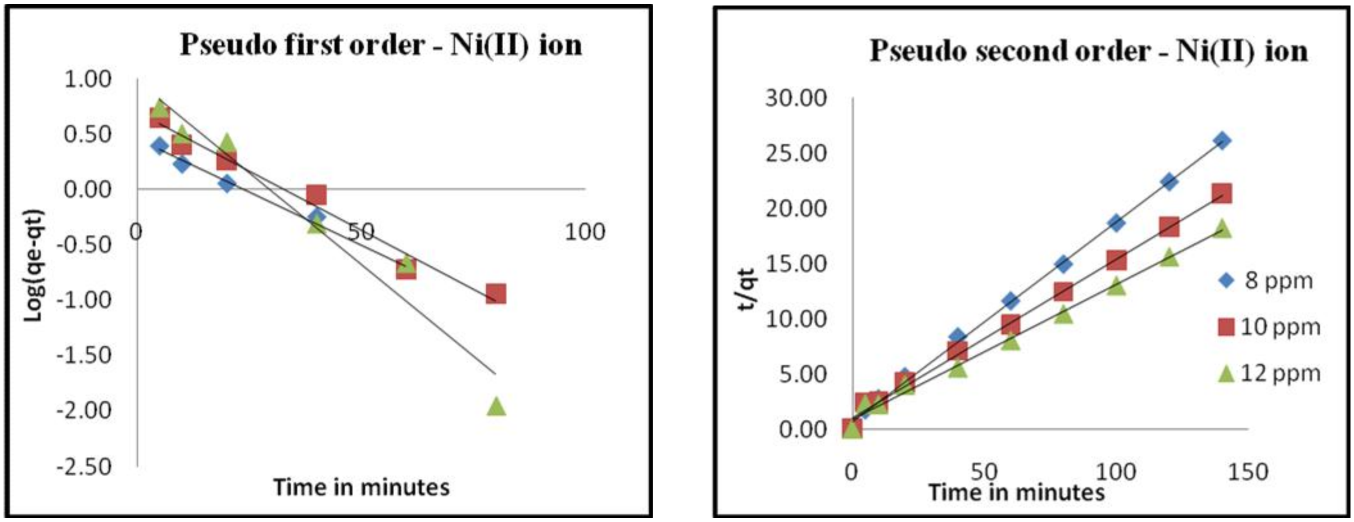

Figure: 3 Pseudo first and second order kinetics

Table:5 Kinetic parameters for Ni(II) ions onto EIBC

Ci mg/L	Rate constants		$q_{e(cal)}$ mg/g		$q_{e(exp)}$ mg/g		Δq_e		R^2		(SSE %)	
	k_1 (10^{-2}) (min^{-1})	k_2 (10^{-3}) $(gmg^{-1}$ $min^{-1})$	First Order	Second order	First order	Second Order	First order	Second Order	First order	Second order	First order	Second Order
8	4.08	4.5	16.63	5.5	5.3	5.3	2.5	0.2	0.99	0.99	11.72	0.44
10	3.52	2.1	24.32	6.9	6.5	6.5	1.6	0.4	0.97	0.99		
12	2.63	1.6	31.70	8.2	7.6	7.6	1.8	0.6	0.95	0.99		

3.5 Adsorption Isotherm Studies:

The existence of equilibrium between the liquid and solid phase is well described by adsorption isotherms. Equilibrium data collected at different temperatures were fitted in Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich adsorption isotherm models [17]. These isotherms are depicted in Figure: 4. The R^2 values of these isotherm plots reveal that Freundlich isotherm well describes the present system that is the possibility of multilayer adsorption. R^2 value of Dubinin-Raduskevich isotherm is very low. In Dubinin-Raduskevich isotherm, the very low value of the constant 'B' related to the mean free energy of adsorption per mole of the adsorbate and the adsorption is physical in nature. Results of various isotherms are presented in Table: 6.0.

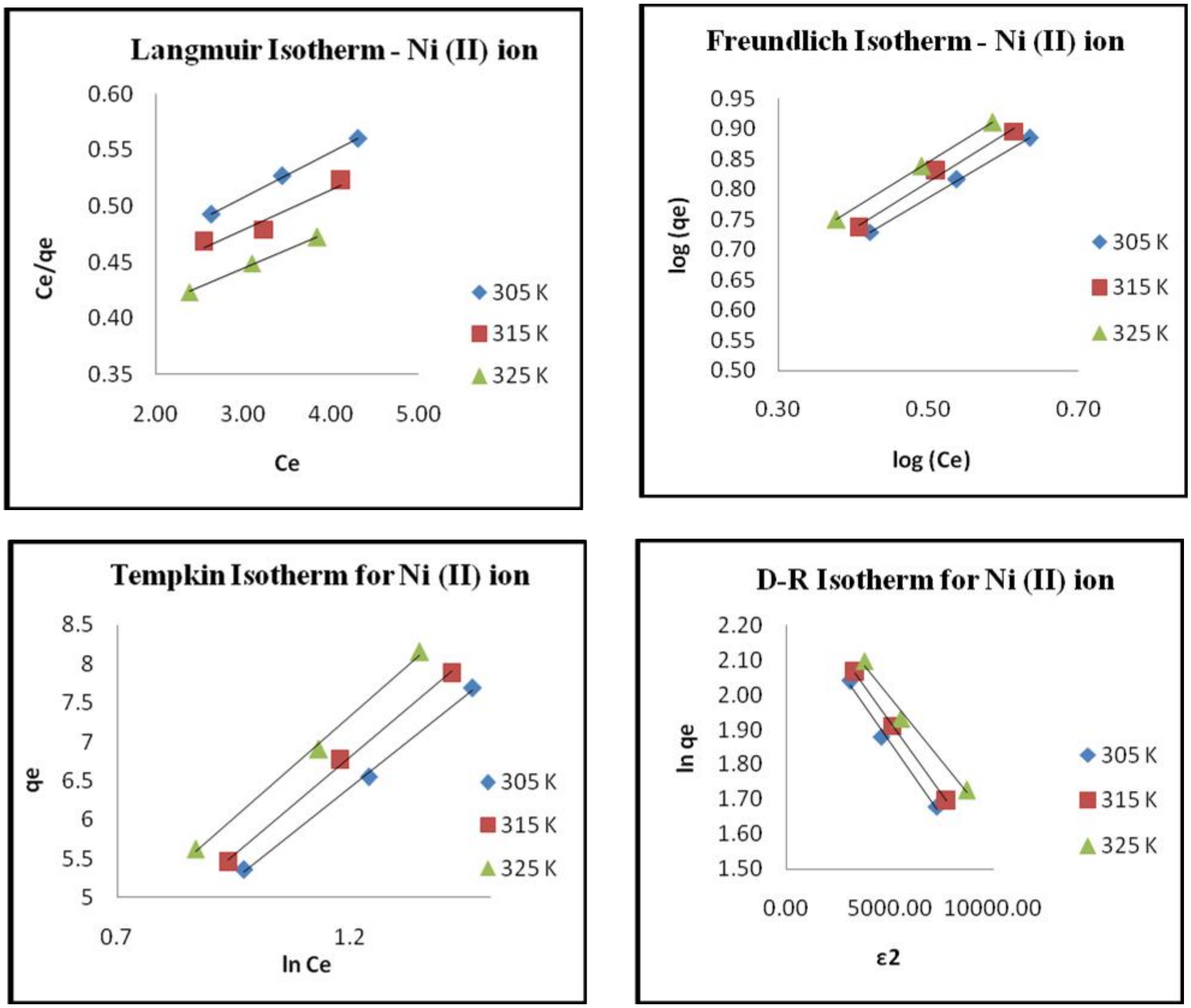

Figure: 4 Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich for the adsorption of Ni(II) ion onto EIBC

Table: 6 Results of various isotherms plots for the adsorption of Ni(II) ion onto EIBC

Isotherm Models	Temp (K)	Parameters and their results			
		Q_0 (mg/g)	b	R_L	R^2
Langmuir	305	25.51	0.23	0.45	0.9900
	315	23.81	0.15	0.40	0.9300
	325	58.82	0.04	0.35	0.9900
Freundlich		K_f (mg/g^{-1})	N		R^2
	305	4.70	1.80		0.9900
	315	3.30	1.40		0.9900
	325	2.20	1.10		1.0000
Tempkin		b_T (J/mol)	a_T (L/g)		R2
	305	534.972	2.2642		0.9900
	315	517.571	2.1746		0.9900
	325	515.265	2.8595		0.9900
DubininRaduskevich		q_D(mg/g)	E (kJ/mol)	B × 10^{-4} (mol^2/J^2)	R^2
	305	67.60	0.032	0.0013	0.9800
	315	77.70	0.027	0.0025	0.9900
	325	79.20	0.020	0.0038	0.9800

3.6 Analysis of Isotherm:

3.6.1 Langmuir isotherm:

In the present study Q_0 value ranges from 25.51 to 58.82, as the temperature increases the monolayer adsorption capacity also found to increase. This kind of results were obtained in various similar studies [18].The separation factor R_L values were in between 0 to 1 which indicates the favourable adsorption.R^2 values of isotherm ranged in between 0.9300 to 0.9900.

3.6.2 Frendlich isotherm:

The values of n were between 1 and 10 which indicates cooperative adsorption [19]**.**The R^2 values were close to unity which revealed the good fitting into frendlich isotherm.

3.6.3 Temkin Isotherm:

b_T-Temkin constant is related to the heat of adsorption. This b_T value increased from 515.265 to 534.972 as the temperature of adsorption increased. The temkin parameter a_T values give an idea about nature of adsorption [20],[22].In our present study the a_T values ranged from 2.2642 to 2.8595 which indicates that adsorption is physical nature. The R^2 value was low compared to frendlich isotherm.

3.6. 4 Dubinin-Raduskevich:

The activation energy E value ranges from 0.3535 to 0.4082 and B value from 0.020 to 0.032 indicates the physisorption[21]. The R^2 value was very low when compared to other three isotherms.

In general the fitting data in isotherm equation were in the following order: Frendlich>Temkin>Dubinin-Raduskevich>Langmuir.

7. Conclusion

The effect of various process parameters showed that percentage of adsorption decreased with increase in initial metal ion concentration while it increased with increase in adsorbent dose. Maximum nickel removal by adsorbent was at pH 7.0. Equilibrium adsorption showed that system followed Frendlich> Temkin> Dubinin-Raduskevich> Langmuir models. According to Dubinin Raduskevich model, the adsorption of nickel was physical in nature. The kinetics studies concluded that nickel removal followed pseudo second-order rate equation. Results in the present study showed that *Erythrina indica* Bark Carbon(EIBC) can be used for the removal of nickel from wastewater.

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