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Adsorption kinetics, equilibrium and thermodynamic studies of Nickel adsorption onto Thespesia Populnea bark as biosorbent from aqueous solutions

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ABSTRACT

The removal of selective metal ion like Ni^{2+} ion in aqueous solution were investigated by adsorption process on low cost activated carbon prepared from Thespesia Populnea bark(TPC).In this study, the effect of temperature, pH and initial concentration of metal ion on the biosorption capacities, Kinetics of adsorption and adsorption isotherms have been studied. Also various thermodynamic parameters such as ΔH°, ΔS° *and* ΔG° *were calculated. According to the results, Thespesia Populnea bark is recommended as cheapest and available bio adsorbent to removal of toxic metal ions from industrial waste water.*

Key words: adsorption, Freundlich, Langmuir, kinetic, Ni^{2+} ion

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INTRODUCTION

Industrial waste water may contain some toxic metals such as Cr, Ni, Co, Pb, etc. the release of toxic metals by electroplating, leather tanning, cement, dyeing, metal processing, textile and paint industries into the environment in quantities that pose risk to human health [1]. Nickel is well known toxic heavy metal pollutant which is present effluents of electroplating industries to the tune of 20- 200ppm [2]. Nickel is found in the environment as a result of various natural and industrial activities [3]. The higher concentration causes harmful effects like headache, dizziness, nausea, dry cough, tightness of the chest, vomiting, shortness of breath, cyanosis, chest pain and rapid respiration [4]. The aim of this study was to remove the metal ions from aqueous solution. The effect of various parameters such as adsorbent dose, solution of pH, initial metal ion concentration, contact time and temperature on metal ion adsorption were investigated. There are several types of adsorption process such as chemical separation, filtration, membrane separation, ion exchange and electrochemical treatment for separation of metal ions from waste water [5,6]. All these methods, with the omission of adsorption are very expensive, have low output and are incapable of removing trace level of toxic metals from waste water. Recently, a number of studies were carried out on low cost adsorbents from natural resources. The use of low cost adsorbent for heavy metals derived from natural resources has been reviewed by Baily, Olin, Bricka and Adrian[7]. In the present research work, Thespesia Populnea (TPC) as biosorbent to remove Ni (II) ion from aqueous solution, kinetics of adsorption, equilibrium and thermodynamic studies were studied.

MATERIAL AND METHODS

Adsorbent preparation

Adsorbent (Activated Carbon Fig 1) has been produced by using air-dried Thespesia Populnea bark with con. sulphuric acid in a weight ratio of 1:1. Then the product was heated in a furnace at 500°C for 12 hours and followed by washing with water until free from excess acid and dried at 150 ± 5°C. The dried material was ground well to fine powder and sieved.

Fig (1) Activated Carbon

Batch equilibrium method:

The experiments were done at various temparature such as 30, 40, 50 and 60ºC in batch process. The experiments were carried out in different 100 ml iodine flasks. Prior to each experiment, a predetermined amount of absorbent was added to each flask. The stirring was kept constant at 120 rpm. Each flask was filled with a known volume of sample before commencing stirring such as metal solutions with an initial concentration of 5 mg/L to25 mg/L. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered and the residual of the metal ion concentration has been measured.

Results and discussion

Characteristics of the adsorbent

The chemical nature and pore structure generally determines the sorption activity. The physico chemical properties of the adsorbent are listed in Table1.

Table 1-Characteristics of the Adsorbent

Sl. No	Properties	TPC
1	Particle size(mm)	0.041
2	Density (g/cc)	0.3243
3	Moisture content (%)	0.3255
4	Loss in ignition (%)	0.273
5	pH of aqueous solution	6.5

Effect of contact time and initial Ni (II) ion concentration

The effect of contact time on Nickel ion adsorption on TPC was investigated to study about the rate of removal of Nickel ion. The time is varies in parameter for the adsorption of nickel ion on TPC is shown in fig (1). It proves the percentage removal of Nickel ion for various values of initial Ni ion concentration ranging from 10 to 50mg/L. It is evident from figure 1 that, the percentage of nickel ions removed at 10, 20, 30, 40 and 50 mg/L levels are 27, 45, 61, 80 and 81 respectively. As the concentration of metal ion increases, more and more surface sites are covered and hence at higher concentrations of metal ions the capacity of the adsorbent get exhausted due to non- availability of the surface sites[8].It is therefore evident that at low concentration ranges the percentage of adsorption is high because of the availability of more active sites on the surface of the adsorbent. The experimental values for adsorption of nickel ion on TPC at different concentrations (5 to 25 mg/L) and contact times are shown in the following fig (1).

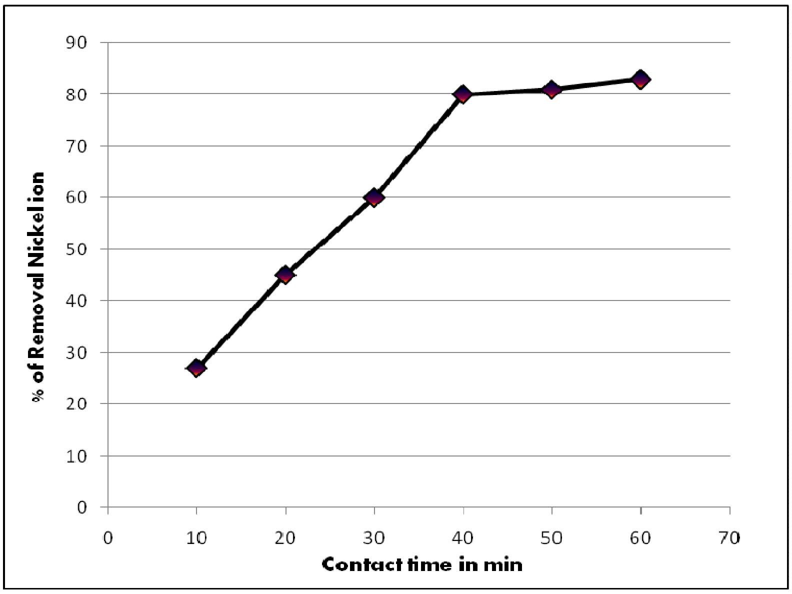

Fig. 1- Effect of contact time on the adsorption of Nickel ion onto TPC
[Nickel]= 50 mg/L: Adsorbent dose = 25mg/ 50ml: pH=6.5

Effect of adsorbent dose

The adsorption of Nickel ion on adsorbent has been studied by varying the carbon concentration from 10 to 50 mg/50 ml while keeping the Nickel ion concentration as 50mg /L. In fig (2), the increase in adsorbent dosage from 10 to 30 mg/50 ml resulted in an increase from 73 to 91% in adsorption of Nickel ion. It is due to the availability of high binding sites for complexation of Nickel ions[9]. The equilibrium values obtained from the studies are depicted in Table.2.

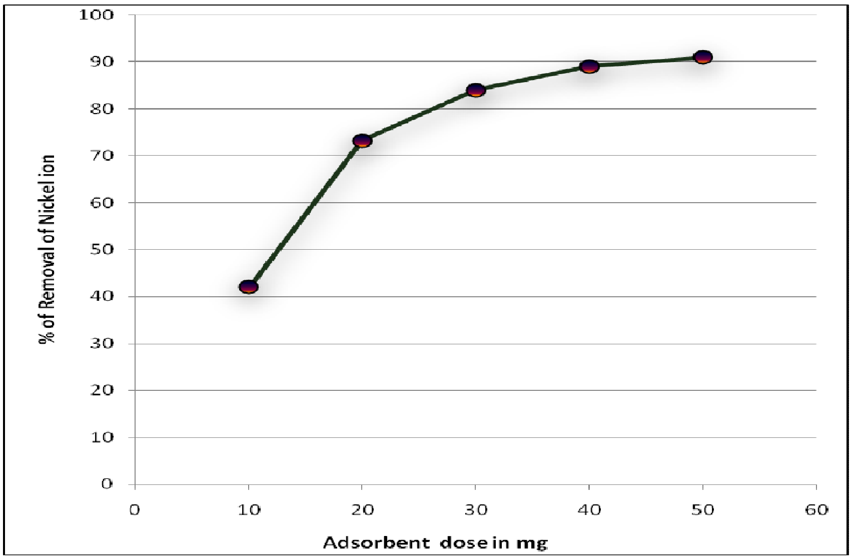

Fig. 2- Effect of adsorbent dose on the adsorption of Nickel ion onto TPC
[Nickel] = 50mg/L: contact time = 60min: pH=6.5

Adsorption isotherm

Adsorption isotherm study was carried out by four different temperatures which were are 30, 40, 50 and 60°C .Two most common isotherm models were employed for describing the adsorption data, which were Langmuir and Freundlich isotherm.

Langmuir equation is based on several assumptions they are: (i) the adsorbent surface is homogeneous, (ii) there is no interaction between adsorbates in the plane of the surface and (iii) monolayer type of adsorption. The Langmuir equation can be represented in the form of following equations.

$$C_{eq}/Q_{eq} = 1/Q_m b + Ceq/Q_m \qquad (1)$$

Where C_{eq} is the equilibrium concentration of nickel ion in solution (mg/L), Q_{eq} is the amount of nickel ion adsorbed; Q_m and b is Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of Ceq/ Q_{eq} vs. C_{eq} suggest the applicability of the Langmuir isotherms fig (3). The values of Q_m and *b* were calculated from slope and intercepts of the plots are listed in Table 3. From the results, it is clear that the value of adsorption efficiency Q_m and adsorption energy *b* of the carbon increases on increasing the temperature. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no diffusion of adsorbate in plane of the adsorbent surface. To confirm the favourability of the adsorption process, the separation factor (R_L) was determined and given in Table 2. The values were established to be between 0 and 1 and confirm that the ongoing adsorption process is favorable[10].The Freundlich isotherm is commonly expressed by the following equation.

$$\log Q_e = \log K_f + 1/n \log C_e \qquad (2)$$

Where Q_e is the amount of Nickel ion adsorbed (mg/g), C_e is the equilibrium concentration of Nickel ion in solution (mg/L), and K_f and n are constant integrates, the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of log Q_e versus log C_e shows that the adsorption of Nickel ion obeys the Freundlich adsorption isotherm. In figure (4), the Freundlich adsorption isotherm obtained by plotting C_e/ q_e versus C_e for the adsorption of Ni (II) on TPC at the different temperatures investigated, respectively. The K_f and *n* values are given in Table 3, which indicate that the increase of negative charges on the adsorbent surface makes electrostatic force like Vanderwaal's between the carbon surface and Nickel ion. The values clearly indicate the dominance in adsorption capacity. The intensity of adsorption is an indication of the bond energies between metal ion and adsorbent, and the possibility of slight chemisorptions rather than physisorption [11, 12]. However, the multilayer adsorption of nickel ion through the percolation process may be possible. The values of *n* are less than one, indicating the physisorption is much more possible [13].

Table 2 – Equilibrium parameters for the adsorption of metal ions onto activated carbon

Nickel ion, mg/L	**C_e (mg/L)**				**Q_e (mg/g)**				**Metal ions removed (%)**			
	Temperature ° C											
	30	40	50	60	30	40	50	60	30	40	50	60
10	1.941	1.640	1.450	1.301	16.11	16.71	17.09	17.39	80.58	83.59	85.49	86.98
20	4.754	4.516	4.309	4.115	30.49	30.96	31.38	31.76	76.22	77.41	78.45	79.42
30	9.241	9.001	8.801	8.601	41.51	41.99	42.39	42.79	69.19	69.99	70.66	71.32
40	16.58	16.01	15.51	15.01	46.83	47.97	48.96	49.96	58.54	59.96	61.20	62.45
50	28.40	27.51	26.61	25.79	43.18	44.96	46.76	48.41	43.18	44.96	46.76	48.41

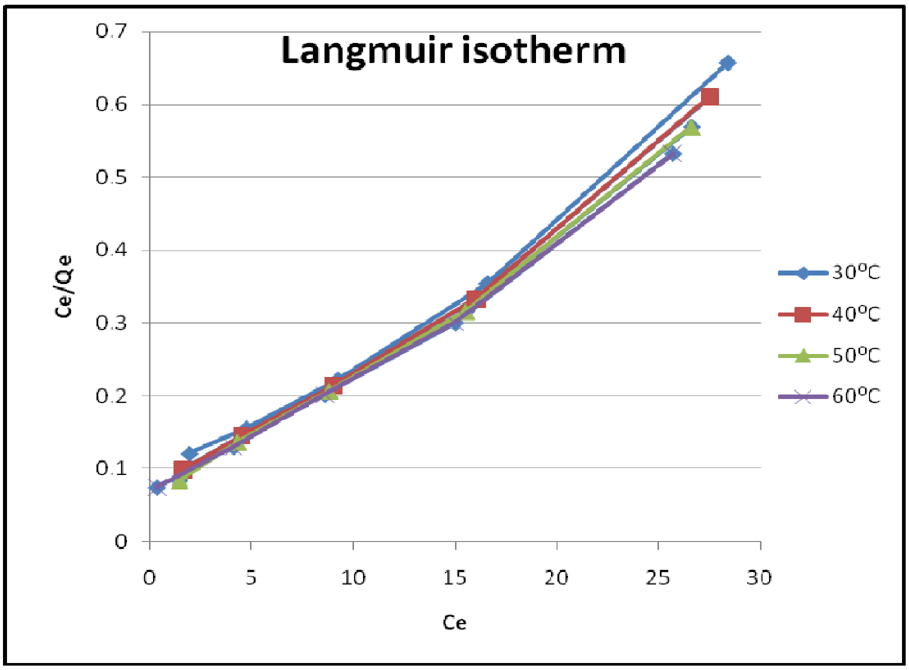

Fig. 3- Langmuir Isotherm for the adsorption of Nickel ion onto TPC

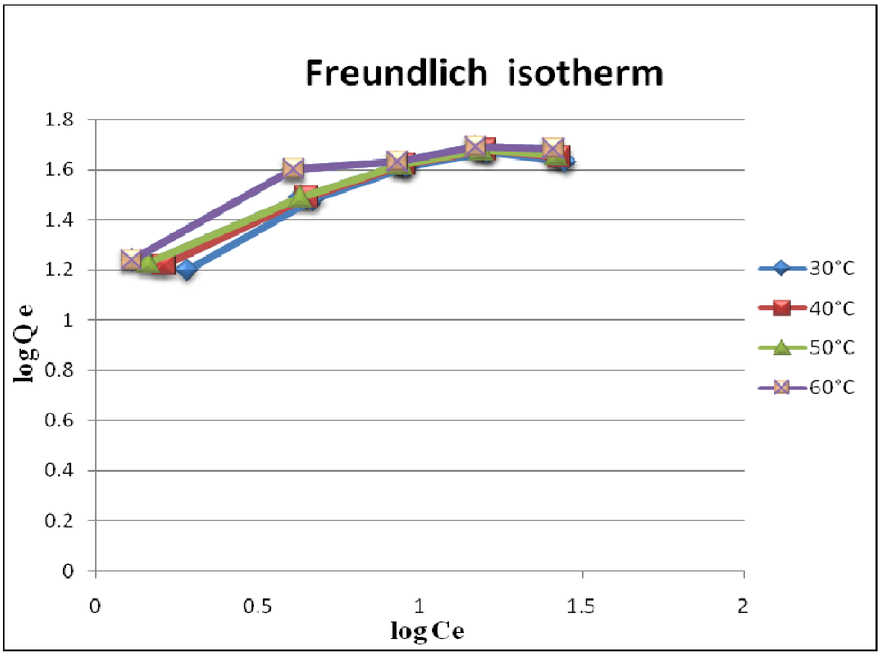

Fig 4- Freundlich Isotherm for the adsorption of Nickel ion onto TPC

Table.3 Langmuir Isotherm, Freundlich Isotherm results and Dimensionless separation factor (R_L)

Nickel ion, mg/L Copper ion **adsorption**	**Temperature C°**	**Langmuir Isotherm results**			**Freundlich Isotherm results**			**Dimensionless Separation Factor(R_L)**				
		Statistical parameters/constants			Statistical parameters/constants			[metal ion]。 (mg/L)				
		r^2	**Q_m**	**b**	**r^2**	**K_f**	**n**	**10**	**20**	**30**	**40**	**50**
	30	0.9909	49.261	0.3730	0.9111	3.231	2.629	0.2114	0.1179	0.081	0.062	0.050
	40	0.9911	50.761	0.3980	0.9171	3.336	2.716	0.2008	0.1116	0.077	0.059	0.047
	50	0.9917	52.631	0.3992	0.9143	3.407	2.748	0.2004	0.1113	0.077	0.058	0.047
	60	0.9944	54.347	0.4001	0.9132	3.459	2.770	0.2000	0.1111	0.079	0.058	0.050

Thermodynamic studies

the experiments were done at different temperatures of 30, 40, 50 and 60°. Thermodynamic parameters such as change in free energy ($\Delta G°$) (kJ/mol), enthalpy *($\Delta H°$)* (kJ/mol) and entropy ($\Delta S°$*)* (J/K/'mol) were determined by the following equations.

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$$K_0 = C_{solid}/C_{liquid}$$

$$\Delta G° = -RT \ln K_O$$

$$\log K_0 = \Delta S°/ (2.303R) - \Delta H°/(2.303RT)$$

Table 4 – Equilibrium constant and thermodynamic parameters for the adsorption of metal ions onto activated carbon

Nickel ion, mg/L	**$\Delta H°$**	**$\Delta S°$**	**$K_{\circ}$**				**$\Delta G°$**			
			Temperature (C)							
			30°	**40°**	**50°**	**60°**	**30°**	**40°**	**50°**	**60°**
10	13.24	55.67	4.150	5.096	5.894	6.683	-3585.4	-4238.1	-4763.8	-5259.2
20	5.171	26.75	3.306	3.428	3.641	3.859	-2935.2	-3206.3	-3470.4	-3739.0
30	2.840	16.10	2.246	2.332	2.408	2.487	-2038.6	-2204.4	-2360.5	-2523.3
40	4.554	17.90	1.412	1.497	1.577	1.663	-869.73	-1051.1	-1224.4	-1408.7
50	5.904	17.19	0.760	0.817	0.878	0.938	-690.6	-525.6	-348.2	-176.13

Where K_o is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant. The $\Delta H°$ and $\Delta S°$ values obtained from the slope and intercept of Van't Hoff plots are given in Table 4 .The values of $\Delta H°$ is in the range of 1 to 93 kJ/mol indicates the favorability of physisorption. It is very clear that from the results that physisorption is much more possible for the adsorption for nickel ion. The positive values of $\Delta H°$ indicate the endothermic nature of adsorption and it governs the possibility of physical adsorption[13, 14]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of metal ion adsorption increases, there is no possibility of chemical adsorption. The negative values of $\Delta G°$ are given in Table 4 indicate that the adsorption is greatly favorable for nickel ion. The positive values of $\Delta S°$ in Table 4 show the increased disorder and randomness at the solid solution interface of nickel ion with TPC adsorbent. The results indicate that more efficient physisorption[12, 15 and 16].

Adsorption kinetics

To find out the mechanism of nickel adsorption and the potential rate controlling steps, like diffusion mass transport and chemical reaction process, it is required to characterize the adsorption mechanism. In order to understand the kinetics of removal of Ni (II) using TPC as an adsorbent, pseudo first, pseudo second order are tested with the experimental data. The sorption of nickel ions on TPC may involve chemical sorption which can control the chemical reaction rate.

The removal of nickel ion from an aqueous solution obeys the reversible first order kinetics, when a single species considered on a heterogeneous surface. At equilibrium, the rate is the ratio of the concentration of adsorbate in adsorbent and concentration of adsorbate in aqueous solution given by K_0. The results indicate that K_0 values decreases with increase in the concentration of the nickel ion and increases with increase in temperature. The calculated values are listed given in the Table 4. The heterogeneous equilibrium between the nickel ion solution and the activated carbon are represented as

$$A \underset{k2}{\overset{k_1}{\rightleftharpoons}} B$$

Where k_1 is the forward rate constant and k_2 is the backward rate constant. A indicate the nickel ion remaining in the aqueous solution and B indicate that nickel ion adsorbed on the surface of activated carbon. The rate constants calculated as earlier [11, 12 and 17]. The data are specified in Table 5, shows that the forward rate constant is much higher than the backward rate constant suggesting that the rate of adsorption is clearly dominant.

Table 5- Rate constants for the adsorption of metal ions (k_{ad}, min $^{-1}$) and the constants for forward (k_1, min $^{-1}$) and reverse (k_2,min^{-1}) process.

Temperature (C)												
Nickel ion, mg/L	**k_{ad}**				**k_1**	**k_2**	**k_1**	**k_2**	**k_1**	**k_2**	**k_1**	**k_2**
	30°	**40°**	**50°**	**60°**	**30°**		**40°**		**50°**		**60°**	
10	0.019	0.021	0.020	0.026	0.015	0.003	0.018	0.003	0.017	0.003	0.022	0.003
20	0.016	0.017	0.018	0.020	0.012	0.003	0.013	0.003	0.014	0.003	0.016	0.004
30	0.013	0.011	0.013	0.014	0.009	0.004	0.008	0.003	0.009	0.004	0.010	0.004
40	0.010	0.009	0.010	0.010	0.006	0.004	0.005	0.003	0.006	0.004	0.006	0.004
50	0.007	0.008	0.008	0.009	0.003	0.004	0.003	0.004	0.003	0.004	0.004	0.004

A clear examination of the effect of nickel ion concentrations on the rate constant K_{ad} (Table 5), the values help to describe the mechanism of metal ion adsorption taking place .In cases of strict surface adsorption a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial nickel ion concentration and rate of reaction will not be linear. It shows that pore diffusion limits the overall rate of nickel ion adsorption[13, 18].

Effect of pH

The pH level of the aqueous solution is an important variable for the adsorption of metals on the adsorbent. The effect of pH on the removal of nickel ion using TPC as an adsorbent was studied with initial pH range from 3-11.The relation between the initial pH of the solution and percentage removal of nickel ion is depicted in figure 5.We have observed that the percentage adsorption nickel ions increased appreciably (1-2 times) with increase of pH from 3 to 6.5 and consistent with results obtained by others.

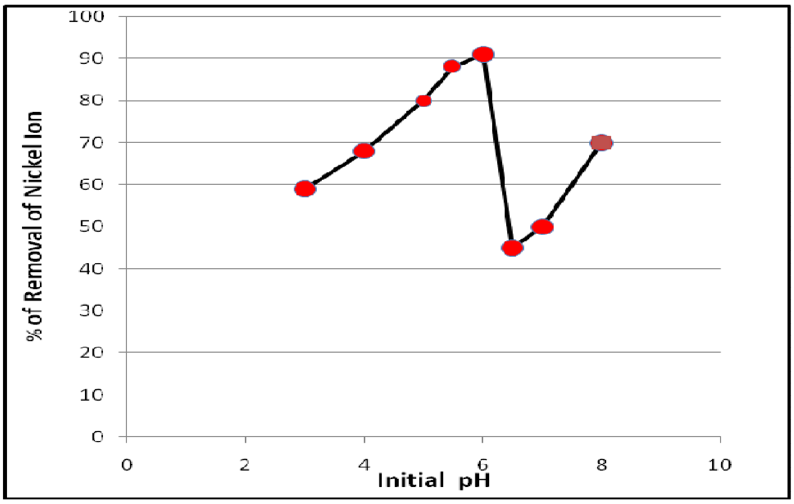

Fig. 5- Effect of pH on the adsorption of Nickel ion onto TPC
[Ni]= 20mg/L: adsorbent dose
= 25 mg / 50ml: contact time = 60min

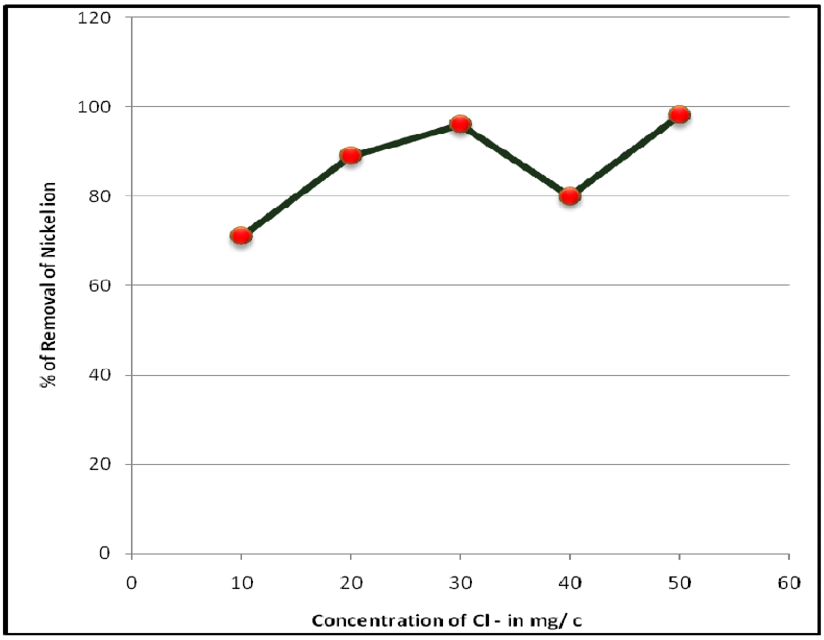

Fig. 6- Effect of other ions on the removal of Nickel ion onto TPC
[Ni]= 20mg/L: adsorbent dose
= 25 mg / 50ml: contact time = 60ml

Effect of the other ions

The effect of other ion like Cl^- on the adsorption process was studied at various concentrations. The effect of sodium chloride on the adsorption of nickel ion on TPC is shown in Figure 6. The low concentrate NaCl solutions have slight influence on the adsorption capacity. When the concentration of NaCl increases, the ionic strength is increased. At higher ionic strength, the adsorption of nickel ion will be high due to the partial neutralization of the positive charge on the carbon surface and a consequent compression of the electrical double layer by the Cl^- anion.

The chloride ion also enhances adsorption of nickel ion by pairing their charges, and hence reducing the repulsion between the removal of nickel ions on the surface. This initiates carbon to adsorb more positive nickel ions [19,20].

Desorption studies

Desorption studies helps to illuminate the nature of the adsorption process and the recovery of metal ion from TPC. Regeneration of the adsorbent material is of crucial importance in economic development. Regeneration must produce small volume of metal concentrates suitable for metal recovery process without damaging of the capacity of the adsorbent. The reuse of regenerated activated carbon was found to be efficient. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because more than 90% removal of adsorbed metal ion takes place. The reversibility of adsorbed metal ion in mineral acid or base is in agreement with the pH dependent results obtained. Desorption of metal ion by mineral acids and alkaline medium indicates that the metal ion was adsorbed onto the activated carbon through by physisorption mechanism[20].

CONCLUSION

This study confirmed that applicability of Thespesia Populnea bark were excellent low cost biosorbent for the removal of Nickel ions. The adsorption process was greatly based on solution of pH and effect of temperature. The kinetic study of Nickel (II) ion sorption on TPC was followed Pseudo- first –order kinetic model. The process of adsorption was best fitted by the Lanqmuir than Freundlich model. The thermodynamic parameters such as$\Delta H°$, $\Delta S°$ and $\Delta G°$ indicates the spontaneous and endothermic nature of the adsorption process. In this work, TPC has been found to be a good adsorbent for the removal of nickel ion from aqueous solutions.

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