ADSORPTION OF BIVALENT NICKEL ONTO ACTIVATED CARBON PREPARED FROM *CLERODENDRUM SERRATUM*

ANITHA M.[1], ARIVOLI S.[1,*] AND AJITHKUMAR M.[2]

[1]PG and Research Department of Chemistry, Raja Serfoji Government College (AU),
(Affiliated to Bharathidasan University), Thanjavur 613 005, Tamilnadu, India.
[1*,2]PG and Research Department of Chemistry, Poompuhar College(AU),
(Affiliated to Bharathidasan University),
Melaiyur 609 107, Tamilnadu, India

Abstract– This study shows that *Clerodendrum serratum* is an effective adsorbent for bivalent nickel(Ni(II)). Ni (II) sorption behavior onto the *Clerodendrum serratum* adsorbent was investigated in this study. Basic condition was favorable for Ni (II) adsorption to the adsorbent. The pseudo second order equation well described MG adsorption onto the wood adsorbent. The Langmuir Isotherm could describe the sorption data. The positive value of ΔH^0 showed that adsorption of Ni (II) onto the *Clerodendrum serratum* adsorbent was endothermic. The negative values of ΔG^0 at all temperatures indicate the spontaneous nature of the adsorption process.

INTRODUCTION

The quickness growth and development of industries on the worldcauses amplified concentration heavy metals ion in waterbodies, which is a most important environmental problem. Because of the toxicity of heavy metal ions it is expose human health when it was interred in to food chains (Ozer, 2007). The existence of heavy metals ion in water bodies is becoming the main environmental and public health problem (Hasas *et al.,* 2013). In addition, heavy metals are not bio-decomposable and have a tendency to accumulate in living beings, causing several diseases and disarrays. And so, their presence in the environs, in specifically in water, should be controlled. The removal of these toxic metals from aqueous solution has a significant responsiveness over the past decades to reduction their impact on the environment (Amuda, 2007; Errais, 2011). Several physical and chemical methods have been technologically advanced for the removal of toxic metals from aqueous solution. Physical methods, primarily adsorption on several supports were recognized to be a promising and in effect process to remove metal ionsfrom aqueous solution completely (Itodo, 2010; Arivoli, 2007; Arivoli and Venkatraman, 2007). The foremost benefits of adsorption are the reusability of material, low-cost, ease of process and short time of action so it is necessary to develop in effect adsorbents for the removal of heavy metalsfrom aqueous solution.

In the present investigation the adsorption of Ni (II) ion on activated carbon prepared from *Clerodendrum serratum* by carbonization with con. H_2SO_4. The kinetic and equilibrium adsorption data obtained were utilized to illustrate the sample systematized. The literature survey shows that no work has been done so for lift up the *Clerodendrum serratum* as an adsorbent by physical activation.

EXPERIMENTAL METHODS

All reagents used in the experiments were of analytical (AR) grade and were obtained from scientific equipment company, Trichy. Stock solutions prepared by dissolve 4.953 g of nickel nitrate (Ni $(NO_3)_2.6H_2O$) in 1000 ml of deionized water. All experimental solutions were prepared by diluting the stock solution to the required

concentration.

Preparation of adsorbent

The natural plant material of *Clerodendrum serratum* used in the present investigations was collected from nearby Poompuhar. The stem was washed with distilled water several times to remove the dirt and dust and was subsequently dried in a hot air oven at 110 °C. Afterward, carbonization of the stem was carried out by adding w/v ratio concentrated H_2SO_4 to get the primary carbon. The primary carbon was activated at muffle furnace above 900 °C for 360 minutes under optimized conditions to obtain the activated *Clerodendrum serratum* carbon (ACSC) (Arivoli, and Kalpana, 2007; Diaz, 2013).

Batch Method

The adsorption of Ni(II) on activated *Clerodendrum serratum* carbon adsorbent was studied by batch method (Boudrahem, 2009; El Nemr, 2007). A known volume of Ni(II) solutions with different initial concentrations (10-50 mg/l) was taken in a 50 ml conical flask and agitated in a mechanical shaker at 120 rpm with a known adsorbent dose for a specified interval. After equilibration, samples were filtered with Whatman 42 filter paper and the concentration of nickel were analyzed by UV-Visible spectrophotometer at 460 nm.. The amount of adsorption at time t, q_t(mg/g), can be determined using the following formula.

$$q_t = V \times \frac{(C_0 - C_t)}{w} \qquad .. (1)$$

Where, $q_{(t)}$ is the mass of adsorbed Ni (II) ion per unit mass of adsorbent (mg g^{-1}) (C_0) and (C_t) are the initial and actual concentration (g dm^{-3}) of Ni (II) ion at time, respectively V is the volume of the treated solution (ml), w is the mass of adsorbent (g). The removal percentage of Ni (II) ion can be calculated as following relationship

$$\% \text{ Removal} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \qquad .. (2)$$

RESULTS AND DISCUSSION

Batch experiment

The effect of contact time (Esmaeili, 2010; Gupta, 2009) on removal of Ni(II) onto ACSC was studied and is represented in Figure 1 also the equilibrium data are given in Table 1. The figure shows that the uptake rate was initially rapid with maximum of the adsorption was complete with in 30 min., equilibrium was achieved with in 50 min. therefore, an equilibration period of 60 min. was selected for all f urther experiments. The effect of adsorbent dose is very useful to find out the favorable amount of adsorbent necessary for the removal of Ni(II) ions. The figure 2 illustrated the effect of the adsorbent dose (Ong, 2007) on the sorption capacity of Ni(II) ions. The sorption efficiencies of Ni(II) were found to increase with the increase of adsorbent dose up to 25mg. This may be due to the increase in availability of surface active sites resulting from the increased dose of adsorbent. At all other higher dosages, sorptions were almost the same and at maximum, from now all studies were carried out each experiment work with 0.025g of adsorbent dosage. The effect pH (Gercel, 2007; Imamoglu, 2008) has a direct influence on the adsorption mechanism and this one shown in Figure 3. The function of pH in the range of 3 to 9 studied, and the maximum adsorption was reached at 6.9 pH that is pH_{ZPC}(Zero
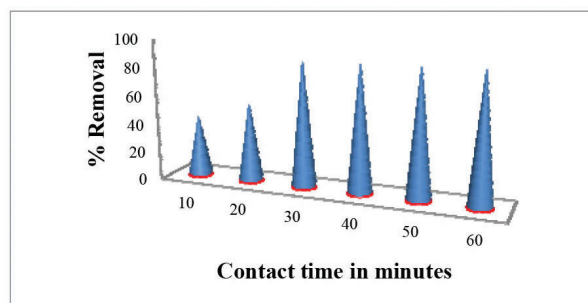

Fig. 2. Effect of Contact Time on the Removal of Ni (II) ion [Ni (II) ion]=10 mg/l; Temperature 30 °C; Adsorbent dose=0.025g/50 ml.

Table 1. Equilibrium Parameters for the Adsorption of Nickel (II) ION Onto ACSC

C_0	Ce (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	1.83	1.48	0.99	0.94	16.35	17.04	18.02	18.12	81.73	85.19	90.11	90.62
20	6.42	4.94	4.46	3.46	27.16	30.12	31.07	33.09	67.91	75.30	77.68	82.71
30	11.29	10.77	9.38	8.69	37.42	38.47	41.24	42.62	62.36	64.11	68.73	71.03
40	17.32	15.84	15.03	14.10	45.35	48.32	49.95	51.81	56.69	60.40	62.43	64.76
50	31.50	29.72	29.17	28.72	37.00	40.56	41.65	42.55	37.00	40.56	41.65	42.55

Point Charge), as the result initial pH value was optimized as pH 6.8. The effect of chlorine ions on the adsorption process studied (Mohanty, 2005) at different concentrations. The Figure 5 states that low concentration of chlorine ions does not affect the removal of Ni (II) ion from aqueous solution, for that reason competitive interaction was not so effective. While the concentration of chlorine ion increases, the interference of these ions at available surface sites of the sorbent through competitive sorption increases that, decreases the percentage removal of Ni(II) ion from aqueous solution.

Isotherm models
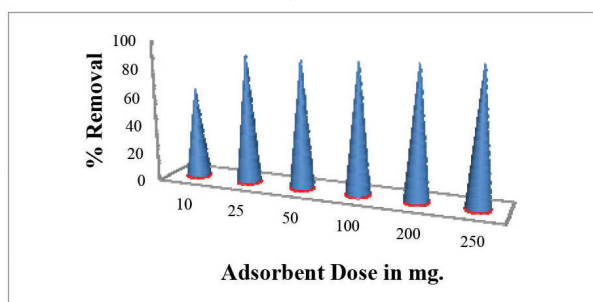
The Freundlich model (Nath, 2013; Arivoli, 2010)

Fig. 3. Effect of Adsorbent dose on the Removal of Ni (II) ion
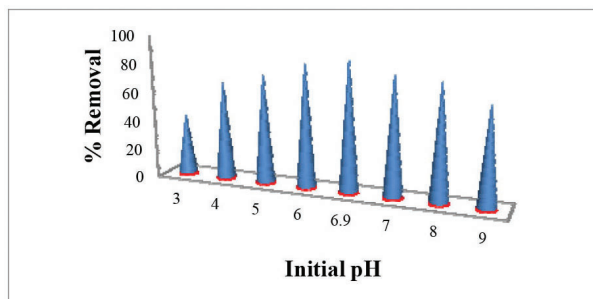[Ni (II) ion] =10 mg/l; Temperature 30 °C; Contact Time 60 min.

Fig. 4. Effect of Initial pH on the Removal of Ni (II) ion
[Ni (II) ion]=10 mg/l; Temperature 30°C; Adsorbent dose=0.025 g/50 ml.

which is an indicative of surface heterogeneity of the adsorbent is described by the following equation.

$$logq_e = logK_f + \frac{1}{n_f}logC_e \qquad ..(3)$$

Where, K_f and $1/n_f$ are Freundlich constants related with adsorption capacity and adsorption intensity respectively. The Freundlich plots dran between log q_e and log C_e for the adsorption of Ni (II) ion were shown Figure 5 and its make that correlation co-efficient (R^2) values these values listed in Table 2. The Langmuir adsorption isotherm (Arivoli, 2010) equation which is valid for monolayer adsorption on to a surface is given below.
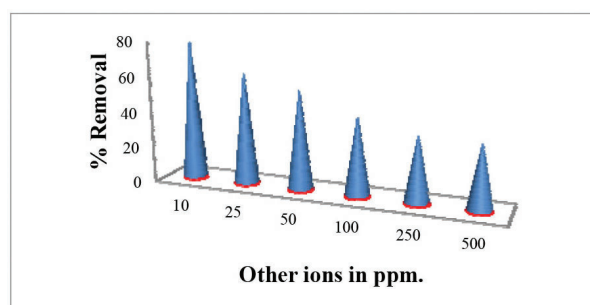

Fig. 5. Effect of other ionic strength on the removal of Ni (II) ion
[Ni (II) ion]=10 mg/l; Contact time=60 min.; Adsorbent dose=0.025 g/50 ml.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad ..(4)$$

Where, q_e (mgg^{-1}) is the amount adsorbed at the equilibrium concentration C_e (mol L^{-1}), q_m (mgg^{-1}) is the Langmuir constant representing the maximum monolayer adsorption capacity and K_L (L mol^{-1}) is the Langmuir constant related to energy of adsorption. The plots drawn between C_e/q_e and C_e for the adsorption of Ni (II) ionwas found linear and its shown in Figure 6. The correction coefficient (R^2) values confirm good agreement our experimental results the values of the monolayer capacity (q_m) and

Table 2. Langmuir and Freundlich Isotherm Parameter for the Adsorption of Nickel (II) Ion onto ACSC

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	K_f(mg/g) (L/mg)$^{1/n}$	14.53	16.64	19.65	21.09
	n_f	2.97	3.08	3.51	3.59
	R^2	0.83	0.86	0.86	0.82
Langmuir	q_m(mg/g)	41.33	44.67	44.71	45.14
	K_L (L/mg)	0.53	0.60	1.05	1.61
	R^2	0.97	0.98	0.98	0.98

equilibrium constant (K_L) have been evaluated from the intercept and slope of these plots and given in Table 2. These results suggest that Ni (II) ionis adsorbed in the form of monolayer coverage on the surface of the prepared adsorbent. In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L by the equation.

$$R_L = \frac{1}{1 + K_L C_0} \qquad \text{.. (5)}$$

Where, C_o (mg/l) is the highest initial concentration of Ni(II) ion and K_L (L/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of shape of the isotherm accordingly.

- ❖ $R_L > 1$ - Unfavorable adsorption
- ❖ $0 < R_L < 1$ - Favorable adsorption
- ❖ $R_L = 0$ - Irreversible adsorption
- ❖ $R_L = 1$ - Linear adsorption

The R_L values in the middle of 0 to 1 indicate favorable adsorption for all initial concentration (C_o) and temperatures studied. The calculated R_L values are given in Table 3.

Table 3. Dimensionless Seperation Factor (R_l) for the Adsorption of Nickel (II) Ion onto ACSC

C_0	Temperature °C			
	30°C	40°C	50°C	60°C
10	0.16	0.14	0.09	0.06
20	0.09	0.08	0.05	0.03
30	0.06	0.05	0.03	0.02
40	0.05	0.04	0.02	0.02
50	0.04	0.03	0.02	0.01

Thermodynamic study

Thermodynamic parameters (Arivoli, 2006) associated with the adsorption, via adsorption equilibrium constant K_0 is given by the equation:

$$\Delta G^0 = -RT \ln K_0 \qquad \text{.. (6)}$$

Where, DG^0 is the free energy of adsorption (kJ/mol), T is the temperature in Kelvin and R is the universal gas constant (8.314 J mol/K). The adsorption distribution coefficient may be expressed in terms of enthalpy change (DH^0) and entropy change (DS^0) as a function of temperature,

$$\ln K_o = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad \text{.. (7)}$$

These values of DH° and DS° can be obtained from the slope and intercept of plot of $\ln K_0$ against 1/T. The value of thermodynamic parameter calculated from equation 6 and 7 are shown in Table 4. The negative ΔG°values were confirming the spontaneous nature of adsorption Ni (II) ion onto ACSC. The lesser values of ΔG° suggest that adsorption is physical adsorption process. The positive value of ΔH° confirms the endothermic nature of adsorption process. The positive values of ΔS° in Table 4, showed increased randomness of the solid solution interface during the adsorption of Ni (II) iononto ACSC.

Kinetic models

In order to investigate the mechanism of adsorption kinetic models (Arivoli, 2006) are generally used to test experimental data. Pseudo-second-order (Namasivayam, 1995) equations can be used assuming that the measured concentrations are
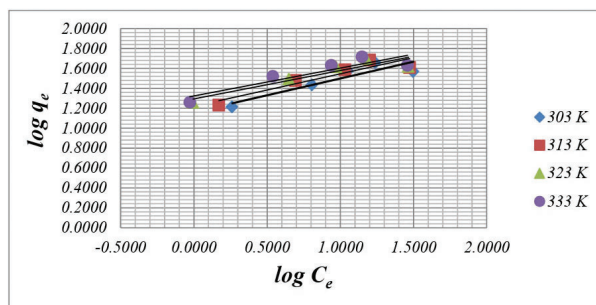

Fig. 6. Freundlich adsorption isotherm for the removal of Ni (II) ion

Table 4. Thermodynamic Parameter for the Adsorption of Nickel (II) Ion onto ACSC

C_0	ΔG°				DH°	DS°
	30°C	40°C	50°C	60°C		
10	-3774.29	-4552.39	-5934.41	-6278.63	23.32	89.47
20	-1888.01	-2900.86	-3348.65	-4333.92	21.66	77.91
30	-1271.78	-1510.13	-2114.70	-2482.47	11.57	42.19
40	-678.52	-1098.10	-1364.08	-1684.88	9.28	32.98
50	-1341.00	-994.94	-905.40	-830.79	6.28	16.55

equal to surface concentrations. The linearized form of pseudo second order equation becomes.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (9)$$

Where, q_t (mgg^{-1}) is the amount of adsorbed Ni (II) ionon the adsorbent at time t, q_e the equilibrium sorption uptake and k_2, (min^{-1}) is the rate constant of pseudo-second-order adsorption. The plot t/q_t versus t gives a straight line says second order kinetic model is applicable then q_e and k_2 are determined from the slope and intercept of the plot, respectively. The high regression value indicate the adsorption reaction exist a pseudo-second-order and these values shown Table 5.

The Elovich model (Arivoli, 2009) equation is generally expressed as

$$q_t = \frac{1}{\beta} \ln (\alpha\beta) + \frac{1}{\beta} lnt \quad .. (8)$$

Where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is desorption constant (g/mg) during any one experiment. If Ni (II) ion adsorption fits with the Elovich model, a plot of q_t Vsln(t) yields a linear relationship with a slope of (1/β) and an intercept of (1/β)ln($\alpha\beta$). The Elovich model parameters α, β, and correlation coefficient (R^2) are summarized in Table 5.

Kinetic data was further analyzed using the intraparticle diffusion model (Arivoli and Vijayakumaran, 2009) based on the following equation.

$$log\,R = log\,K_{id} + \alpha\,log\,t \quad .. (9)$$

Where, k_{id} is the intraparticle diffusion rate constant and it's related to the thickness of the boundary layer. According to above equation a plot of log R versus log tgivesa straight line that's says the adsorption mechanism follows the intra-particle diffusion process and the evidence of correlation co-efficient values are close to unity.
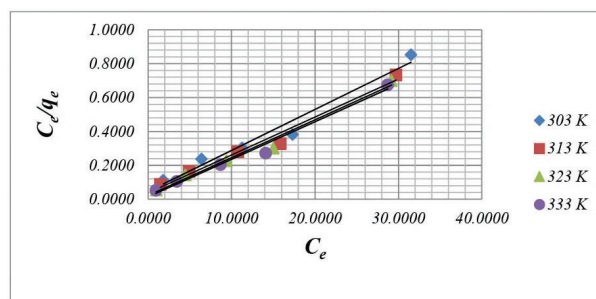

Fig. 7. Langmuir adsorption isotherm for the removal of Ni (II) ion

CONCLUSION

This study concluded that activated *Clerodendrum serratum* was an excellent adsorbent forheavy metal ions removal from aqueous solution. The Langmuir

Table 5. The Kinetic Parameters for Adsorption of Nickel (II) Ion Onto ACSC

C0	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q_e	k_2	R^2	H	α	β	R^2	K_{id}	α	R^2
10	30	22.41	1.77E-03	0.97	0.89	1.85	1.97E-01	0.96	14.26	4.19E-01	0.99
	40	20.73	3.18E-03	0.98	1.37	3.75	2.42E-01	0.96	24.19	3.01E-01	0.98
	50	19.88	6.75E-03	0.99	2.67	28.03	3.63E-01	0.96	43.45	1.74E-01	0.97
	60	19.84	7.32E-03	0.99	2.88	39.31	3.83E-01	0.96	5.26	1.63E-01	0.97
20	30	38.92	8.79E-04	0.96	1.33	2.72	1.12E-01	0.95	10.29	4.53E-01	0.99
	40	41.71	8.78E-04	0.94	1.53	3.21	1.06E-01	0.93	12.51	4.26E-01	0.97
	50	40.86	1.16E-03	0.98	1.94	4.29	1.11E-01	0.96	16.35	3.75E-01	0.98
	60	40.37	1.54E-03	0.98	2.52	6.70	1.23E-01	0.94	3.86	3.10E-01	0.97
30	30	50.67	7.21E-04	0.89	1.85	4.09	8.99E-02	0.86	11.00	4.04E-01	0.91
	40	49.89	1.10E-03	0.98	2.73	6.27	9.30E-02	0.94	15.32	3.50E-01	0.96
	50	55.40	8.60E-04	0.98	2.64	5.54	7.98E-02	0.97	13.94	3.92E-01	0.98
	60	51.58	1.58E-03	1.00	4.20	10.44	9.40E-02	0.99	3.75	3.05E-01	0.98
40	30	60.81	8.73E-04	0.99	3.23	6.17	6.89E-02	0.97	11.00	4.14E-01	0.96
	40	63.49	8.61E-04	1.00	3.47	6.88	6.76E-02	0.99	12.34	3.97E-01	0.97
	50	63.63	1.00E-03	1.00	4.05	8.33	6.93E-02	0.98	14.47	3.67E-01	0.96
	60	65.05	1.05E-03	1.00	4.44	9.50	6.94E-02	0.98	3.34	3.49E-01	0.97
50	30	44.99	1.64E-03	1.00	3.32	8.54	1.09E-01	1.00	10.67	3.06E-01	1.00
	40	50.19	1.26E-03	0.99	3.17	7.88	9.60E-02	0.98	10.72	3.22E-01	1.00
	50	47.92	1.97E-03	0.99	4.51	21.23	1.25E-01	0.94	16.11	2.26E-01	0.96
	60	50.31	1.76E-03	1.00	4.46	13.71	1.04E-01	1.00	3.17	2.70E-01	1.00

isotherm satisfactorily described the sorption data. The Ni(II) ions adsorption was a spontaneous endothermic process. The sorption kinetics followed the pseudo-second order equation, indicating that several processes were involved in Ni(II) ions sorption onto the activated *Clerodendrum serratum* can adsorbent. Basic condition was favorable for the removal of nickel using activated carbon adsorbent, in addition *Clerodendrum serratum* is widely available in the world, negligible economic values, and has excellent adsorption capacity for removal of heavy metals and feasibility of using this adsorbent for removal of other heavy metals and dyes for its possible industrial application are needed.

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