RJC

RASĀYAN *J. Chem.*
Vol. 9 | No. 4 |812 - 824 | October - December | 2016
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

NON-CONVENTIONAL ADSORBENT PREPARED FROM *Wrightia tinctoria* FRUITS UNDER MICROWAVE HEATING FOR THE REMOVAL OF Ni(II) IONS

S. Saminathan[1,*], M. Asaithambi[2], V. Sivakumar[3] and P. Sivakumar[4]
[1]Department of Chemistry, Sakthi Polytechnic College, Sakthinagar, Erode, Tamilnadu, India
[2]Department of Chemistry, Erode Arts and Science College, Erode, Tamilnadu, India
[3]Department of Chemistry, Sri Vasavi College, Erode, Tamilnadu, India
[4]Department of Chemistry, A.A. Govt Arts College, Namakkal, Tamilnadu, India
*E-mail: ssaminathan91@gmail.com

ABSTRACT

A novel non-conventional activated carbon with good surface characteristics was synthesized using *Wrightia tinctoria* fruits as a precursor material under two stage microwave heating. The synthesized activated carbon has a BET surface area of 911m^2/g. The adsorptive capability of the prepared adsorbent (WAC) was tried using Ni(II) as an adsorbate. The adsorbent WAC removes 36.64 mg of Ni(II) per gram of adsorbent at an initial nickel concentration of 50 mg/L. On increasing the solution temperature from 30 to 45°C, the amount Ni(II) adsorbed by WAC increases from 24.17 to 25.81 mg/g, which substantiates the endothermic nature of adsorption. Freundlich model describes the adsorption with good correlation coefficient of $0.9971 < r^2 < 0.9997$, indicating the heterogeneous nature on the adsorbent surface. Thermodynamic studies indicates the endothermic (positive $\Delta H°$), spontaneous (negative $\Delta G°$) nature as well as the increased randomness (positive $\Delta S°$) at the solid liquid interface.

Keywords: Microwave heating, Surface area, Adsorption, Kinetics, Isotherm and Heavy metal.

© RASĀYAN. *All rights reserved*

INTRODUCTION

The increasing human population and industrial growth proportionally pollutes the fresh water resources and creates more deficiency in the fresh water availability. Among the various categories of pollutants discharged in the water streams, heavy metals create great impact on the human and animal health. The heavy metals such as chromium, copper, lead, cadmium, nickel and mercury are the most important constituents among toxic compounds in the effluents[1].The chemical manufacturing, battery manufacturing, metallurgical, tannery, fossil fuel processing industries etc., are the major sources of heavy metal release into the aquatic environment[2]. In the last few decades, the bioaccumulation, potential toxicity, and adverse health effects caused by the nickel ions was the matter of serious concern[3]. The heavy metals present in the water bodies interact with other compounds (either organic or inorganic), which results in altered bioavailability and toxicity[4]. As recommended by the World Health Organization (WHO), the maximum permissible level of Nickel (II) in drinking water is 0.07 mg/L[5]. When higher amount of Ni(II) fed into the animal as well as human bodies through polluted water was proved to cause severe damages to lungs and kidneys[6]. High intake of Ni(II) ions in human bodies may cause nausea, vomiting, pulmonary fibrosis, renal edema, gastrointestinal distress, diarrhea and skin dermatitis[6].

The effective removal of Ni(II) from wastewater was successfully achieved using the technologies like chemical precipitation, oxidation/reduction, ion exchange, reverse osmosis and adsorption using activated materials[7]. The applicability of these methods in the large scale industrial level is limited owing to their high operational cost or the complicated technology[8]. The adsorption using activated materials seems to be an attractive choice for the removal of Ni(II) ions from wastewater because of its removal efficiency and rapid adaptation to pollutant loading alteration[9]. Activated carbon is the best choice among the available adsorbents owing to its selectivity towards all categories of pollutants. However, commercially

available activated carbons are expensive and, for this reason, the production of low cost, disposable adsorbents for treatment of heavy metal bearing wastewater is worth considering.

The adsorbents prepared using agricultural by-products attracts the researchers all over the world due to their low-cost, renewable nature and wide prevalence. Among the agro by-products, the materials like cashew nut shell, orange peel, pomelo peel, Egyptian mandarin peel, rice husk, fruit juice residue, garden grass, garlic peel, mango peel, olive stone etc., were successfully used as a precursor material for the preparation of highly active carbon[10-14]. These prepared adsorbents were successfully demonstrated for their capability towards the effective removal of heavy metals from aqueous solutions.

Synthesis of activated carbon using Microwave heating is one of the versatile methodologies in terms of energy conservation and less by products. The energy conversion in microwave heating occurs by two mechanisms: ion conduction and dipole rotation inside particles[15]. In the microwave carbonization process, the efficiency is very close to 100, i.e. almost the all the carbon from biomass is converted into carbonized material, without generating CO and CO_2[16]. Microwave heating has been effectively used to prepare activated carbon using pine apple peel, tobacco stem, rice husk, mangosteen peel, cotton stalks, and orange peel precursors.

In the present work, unripe fruits of *Wrightia tinctoria* used as a precursor for the preparation of highly porous activated carbon. About the precursor, *Wrightia tinctoria* (Sweet Indrajao) is a small, deciduous tree with a light gray, scaly smooth bark. The juice from fresh unripe fruits is used for coagulating milk. The seeds are said to be aphrodisiac and anthelminthic[17]. Though, the fruits and seeds have some medicinal value, huge amount of fruits and seeds are left unused. The availability of fruits in large quantity without any cost makes *Wrightia tinctoria* fruits as good candidature for the preparation of a novel non-conventional activated carbon. The synthesized carbon with superior surface characteristics was be used for the adsorptive removal of Ni(II) ions from aqueous solutions.

EXPERIMENITAL

Preparation of Activated Carbon

The fresh unripe fruits were collected from the various regions of Erode District, Tamilnadu, India. The unripe fruits were cut into pieces of 2 to 3 cm size and dried in sunlight for about one week. The dried material was used for the preparation of activated carbon as per the following procedure.

Carbonization and activation using microwave oven

The dried precursor was carbonized in microwave oven at 600w for 10 minutes. The carbon was washed with plenty of water to remove all the washable contents. The washed carbon was activated in microwave oven in an N_2 atmosphere at 600w for a given period, washed again, dried in hot air oven at 110°C for 24 h, labeled as WAC and stored in tight lid container for further studies.

Characterization of the carbon

Physico-chemical characteristics of the activated carbon was studied as per the standard testing methods[18,19]. The N_2 adsorption-desorption isotherms of activated carbon were measured at 77K using N_2 gas sorption analyzer (Nova 1000, Quanta Chrome Corporation) in order to determine the surface area using the BET equation. The morphological characteristics of the activated carbon was studied using JSM–5610LV (Make: JEOL-JAPAN) Scanning Electron Microscope (SEM).

Adsorption experiments

A stock solution of 1000 mg/L of Ni(II) was prepared by dissolving AR 6.74 g of Nickel Ammonium Sulphate in double distilled water. Experimental solutions of desired concentrations are then obtained by successive dilutions. Batch adsorption studies were conducted in a 250ml tight lid Borosil glass bottles. For the kinetic studies, 100ml of the Ni(II) solution of specific concentration was agitated with 200mg of adsorbent (WAC) in a temperature controlled orbital shaker (Rivotek Model). The bottle is withdrawn at a particular time and centrifuged using (REMI make) centrifuge at 5000 rpm for 5min. About 1ml of the clear filtrate was added with 1mL Bromine water, 2 mL 1:1 NH_3 and 1 mL of 0.1% DMG to for a Ni-

DMG complex. The concentration of Ni(II) was estimated using UV-Vis spectrometers (Elico Make: Model SL-207) at a wavelength of 445 nm. The percentage of metal ion removed and the amount of metal ion adsorbed per gram of adsorbent was evaluated using the following equations.

Final Concentration = $C_i - \left[\frac{OD_i - OD_f}{OD_i} x C_i\right]$ (1)

Percentage Ni (II) removal = $\left[\frac{OD_i - OD_f}{OD_i} x100\right]$ (2)

Amount adsorbed (q_t) = $\left[\frac{OD_i - OD_f}{OD_i} x \frac{V}{M}\right]$ (3)

Where, OD_i and OD_t are the liquid phase concentration of the Ni(II) at initial and at time t (mg/L), respectively. M is the mass (g) of adsorbent and V is the volume of metal ion solution (mL).

The pH of solution was measured by using digital pH meter (Elico: Model LI-120). The conductivity was measured by using Digital Conductivity Meter (Deep vision model M-180). Temperature controlled orbital shaker (Rivotek Model) is used for the equilibrium studies. The effect of pH on Ni(II) adsorption was investigated in the initial pH range of 2-12. The initial pH of the solution was adjusted by using 0.1N HCl or 0.1N NaOH. Dried activated carbon (200 mg) was added to 100 mL of solution having 30 mg/L of Ni(II) ions for effect of pH and temperature studies. After adsorption, the solutions were centrifuged and the concentrations of the solutions were determined.

Kinetic models for adsorption

The kinetics of sorption describes the solute uptake rate, which in turn governs residence time of sorption process. It is one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of the nickel ion removal was carried out to understand the behavior of the prepared low cost adsorbent.

Pseudo-first order kinetic model

The adsorption kinetic data were described by the Lagergren (1898) pseudo first order model, which is the earliest known equation describing the adsorption rate based on the adsorption capacity[20]. The differential equation is generally expressed as follows

$$\frac{d_q}{d_t} = k_1(q_e - q_t) \quad (4)$$

Where, q_e and q_t are the amount of Ni(II) adsorbed at equilibrium and at time 't' respectively (mg/g), k_1 is the rate constant of first order adsorption (L/min). Integrating equation (4) for the boundary conditions t = 0 to t = t and q = 0 to q = q_t, gives

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303} t \quad (5)$$

Equation (5) can be rearranged to obtain the following linear form-

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

In order to obtain the rate constants, the values of log (q_e-q_t) were linearly correlated with t by plot of log (q_e-q_t) versus t to give a linear relationship; from which k_1 and predicted q_e can be determined from the slope and intercept of the plot respectively.

Pseudo-second order kinetic model

The adsorption may also be described by pseudo second order kinetic model[21]. The differential equation is generally given as follows

$$\frac{dq}{d_t} = k_2 (q_e - q_t)^2 \quad (7)$$

Where, k_2 (g/mg/min) is the second order constant for adsorption. Integrating equation (7) for the boundary conditions $q_t = 0$ to $q_t = q_e$ and $t = 0$ to $t = t$ is simplified as can be rearranged and linearized to obtain:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t \quad (8)$$

The second order rate constants were used to calculate the initial sorption rate, h (mg/g/min) given by the following equation.

$$h = k_2 q_e^{\,2} \quad (9)$$

A plot of "t/q_t" versus "t" should show a linear relationship. Values of k_2 and equilibrium adsorption capacity q_e can be calculated from the intercept and slope of the plot.

Intra particle diffusion model

In general the adsorption process is a diffusive mass transfer process where the rate can be expressed in terms of the square root of time (t). The intra particle diffusion model is expressed as follows[22].

$$q_t = k_i \, . \, t^{½} + I \quad (10)$$

Where, q_t is the fraction of Ni(II) uptake (mg/g) at time t, k_i is the intra particle-diffusion rate constant (mg/(g. $min^{0.5}$)) and I is the intercept (mg/g). The plot of q_t versus $t^{0.5}$ will give k_i as slope and I as intercept. The intercept I represents the effect of boundary layer thickness.

Adsorption Isotherm

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. Hence, the isotherm models selected for this study are Langmuir and Freundlich adsorption isotherm models.

Langmuir model

Langmuir Isotherm (1916) is valid for sorption of a solute from a liquid solution as monolayer adsorption on a surface containing finite number of identical sites[23]. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. The Langmuir isotherm can be expressed as-

$$q_e = \frac{Q_0 b_L C_e}{(1 + b_L . C_e)} \quad (11)$$

Where, b_L is the Langmuir constant, C_e is the equilibrium Ni(II) concentration in solution, C_e is the initial concentration (mg/L) and Q_0 is a constant related to monolayer adsorption capacity.

Linear form of the rearranged Langmuir model is-

$$\frac{C_e}{q_e} = \frac{1}{Q_0 . b_L} + \frac{C_e}{Q_0} \quad (12)$$

A plot of C_e/Q_e versus C_e should indicate a straight line of slope $1/Q_0$ and an intercept of $1/(b_L . Q_0)$. The essential characteristics of Langmuir Isotherm can also be described by a dimensionless separation factor R_L which is defined by the following equation-

$$R_L = 1/ (1+b_L . C_e) \quad (13)$$

The value of separation factor R_L indicates the nature of the adsorption process as given below.

$R_L > 1$ → Unfavorable
$R_L = 1$ → Linear
$0 < R_L < 1$ → Favorable
$R_L = 0$ → Irreversible

Freundlich model

The Freundlich (1906) isotherm model is an exponential equation that applies to the adsorption on heterogeneous surfaces with interaction between adsorbed molecules and is not restricted to the formation of a monolayer[24]. The well-known expression for the Freundlich model is given as-

$$q_e = k_f . C_e^{\frac{1}{n}} \quad (14)$$

Linear form of Freundlich equation is-

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (15)$$

Where, k_f[mg/g(L/g)$^{1/n}$] is the Freundlich constant, k_f is related to the binding energy and n is the heterogeneity factor (n is a measure of deviation from linearity of the adsorption). It indicates the degree of non-linearity between solution concentration and adsorption. The value of k_f and n were calculated from the linear plot of "log qe" versus "log Ce". When 1/n is > 1.0, the change in adsorbed Ni(II) concentration is greater than the change in the solute concentration.

Thermodynamics of adsorption

Thermodynamic parameters provide in-depth information of inherent energetic changes associated with adsorption; therefore, these parameters should be accurately evaluated. Changes to ΔG^0, ΔH^0 and ΔS^0 were calculated to elucidate the process of adsorption. The thermodynamic parameters were calculated via equations (16) and (17).

$$\ln k_c = \frac{\Delta S^O}{R} - \frac{\Delta H^O}{R} \frac{1}{T} \quad (16)$$

Where, k_c is a equilibrium constant (equilibrium concentration of solute between the solid surface and bulk of the liquid), R is the gas constant (8.314 x 10^{-3} kJ/K/mol) and T is temperature (K). Both ΔH^0 and ΔS^0 were determined from the slope and intercept of the Van't Hoff plot of "ln (k_c)" versus "1/T" [25].
The free energy of specific adsorption $\Delta G°$ (kJ/mol) is calculated from the following expression,

$$\Delta G° = \Delta H° - T\Delta S° \quad (17)$$

RESULTS AND DISCUSSION

Adsorbent characteristics

The characteristics of the activated carbon (WAC) prepared from unripe fruits of ***Wrightiatinctoria*** using microwave hydrothermal process is given in Table-1.
The pH of the WAC is near neutral and low conductivity values indicates that the carbon surface almost free from soluble ionic impurities. Less moisture content and very small amount of matter soluble in water and acid indicates that the microwave synthesis produces clean activated carbon when compared with other chemical activation methods. Rapid and uniform heating results the less amount of ash in

carbon synthesized by microwave heating. The carbon WAC is highly porous with a BET surface area of 911m^2/g.

Table-1: Physico-Chemical Properties of WAC

S.No	Properties	WAC
1	pH	7.34
2	Conductivity, mS cm^{-1}	0.08
3	$pH_{(ZPC)}$	6.81
4	Moisture content, %	8.91
5	Ashcontent, %	12.7
6	Matter soluble in water, %	0.28
7	Matter soluble in 0.25 N HCl, %	1.22
8	Bulk density, g/mL	0.45
9	Surface area (BET), m^2/g	911
10	Fixed carbon, %	65.5
11	Yield, %	53.7

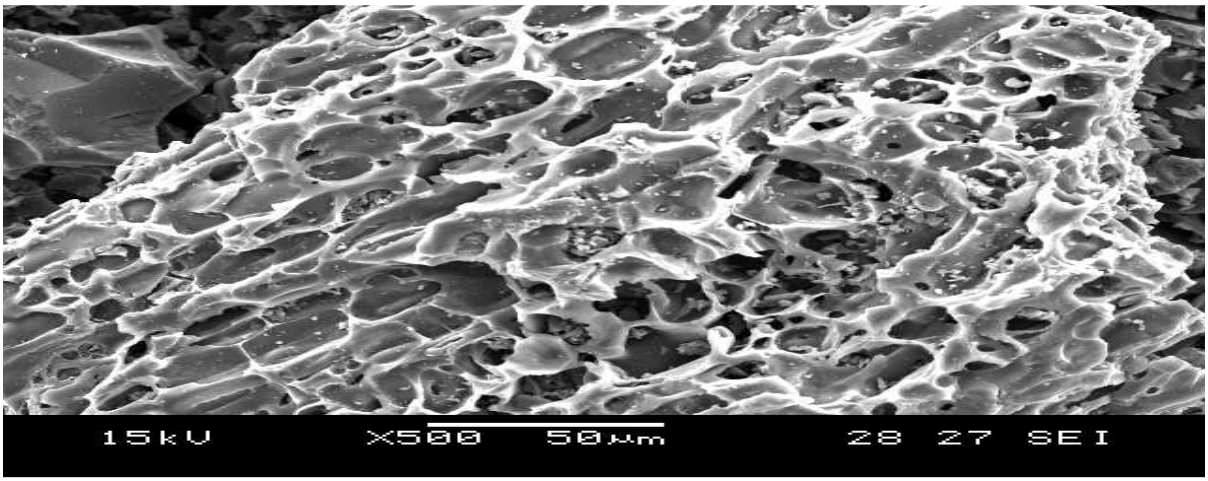

Fig.-1: SEM image of WAC

The electron microscope study reveals highly porous and branched particles. Small cavities, pores and more rough surfaces on the carbon sample indicate the presence interconnected porous network. The SEM image of Activated carbon WAC with 1000x magnification figure 1clearly shows the morphology of highly porous activated carbon sample. Most of the particles are having very fine pores of <1µm size.

Effect of pH

The adsorption of metal ion onto adsorbent surface is highly influenced by the solution pH. The adsorption capability of WAC against the solution pH is studied by varying the pH of the solution from 2.0 to 12.0 using dil. HCl and NaOH solutions for a fixed Ni(II) concentration of 30 mg/L. The surface properties of the activated carbon is also plays a significant role in the pH dependent adsorption of nickel species in solution[26].

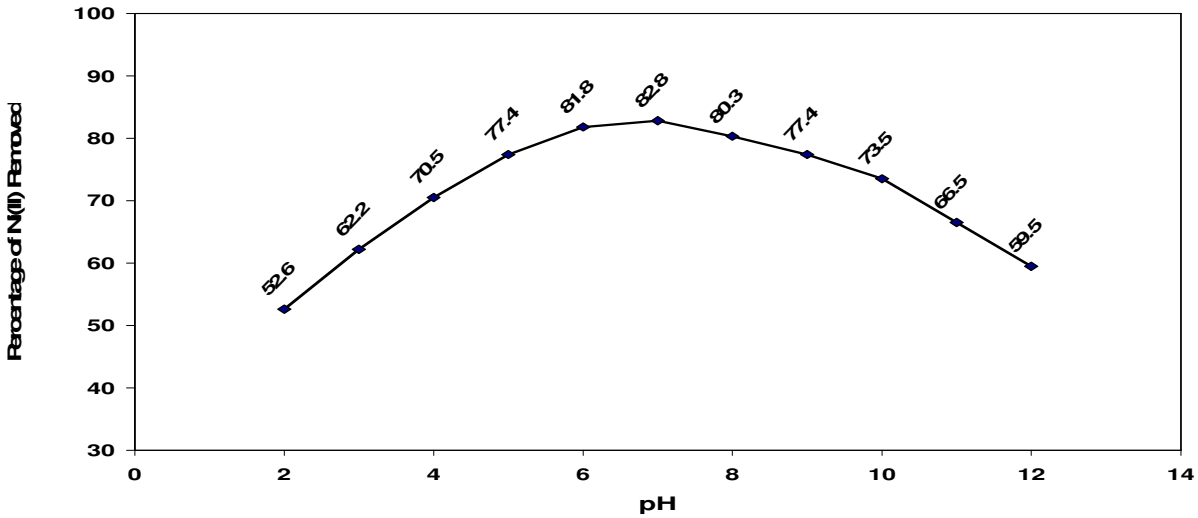

Fig.-2a: Effect pH for the adsorption of Ni(II) onto WAC

As observed from the figure 2a, the Ni(II) adsorption is very low (52.6 %) at a pH of 2.0 and it increases steadily to 82.8% at pH of 7.0. When the solution pH goes above 7.0 the Ni(II) adsorption decreases and it becomes 59.5% at a pH of 12.0. The decrease of adsorption at basic pH is due to the reduced solubility of metal ion and its precipitation. At lower pH (acidic pH) the H^+ ions compete with nickel ions for the adsorption sites which ultimately reduce the amount of nickel ion uptake. At highly acidic condition, adsorbent surface ligands would be closely associated with H_3O^+ that repulses the metal ions and drives the metal ions away from the sorbent surface[27]. As the pH of the solution increases, more and more negative surfaces are exposed for the positively charged metal ions and there by the adsorption increases[28]. When the pH goes above 7.0, the metal ions will start to precipitate which will ultimately reduce the availability of Ni(II) for the sorbent surface[27].

Effect of Initial metal ion concentration

The initial concentration of metal ion has good quantum of influence on the amount of Ni(II) adsorption onto the sorbent surface. The variation of Ni(II) adsorption at different nickel ion concentration is shown in figure 2b. On increasing the initial concentration of Ni (II) from 10 mg/L to 50 mg/L , the amount of Ni(II) adsorption increases from 8.75 to 36.64 mg/g. Whereas the percentage of Ni(II) adsorption decreases from 87.53% to 73.28%. On increasing the concentration of metal ion, the more number of metal ion on the solution side increases the driving force, which overcomes the mass transfer resistance and then more metal ions accumulates on the sorbent surface. Also, at higher Ni(II) concentrations, the number of metal ion competing for the sorption sites are more and there by more solute molecules are adsorbed on the sorption sites. As observed from the figure 2b, majority of the metal ions (more than 90 % of total adsorbed ions) are adsorbed within 60 minutes and the rate of adsorption slows down and finally reaches equilibrium at around 100 min.

Effect of temperature

The influence of temperature on the adsorption of Ni(II) by WAC is shown in figure 2c. The uptake of Ni(II) by WAC increases from 24.17 to 25.81 mg/g when solution temperature increased from 30 to 45°C. The enhanced adsorption at high temperature indicated the endothermic nature of Ni(II) adsorption onto the WAC surface. At high temperature, the pores of the adsorbent are widened, which can accommodate more solutes. Another fact is that, at high temperature, the mobility of the Ni^{2+} ion increases. An increasing number of nickel ions may also acquire sufficient energy to undergo an interaction with active sites at the surface.

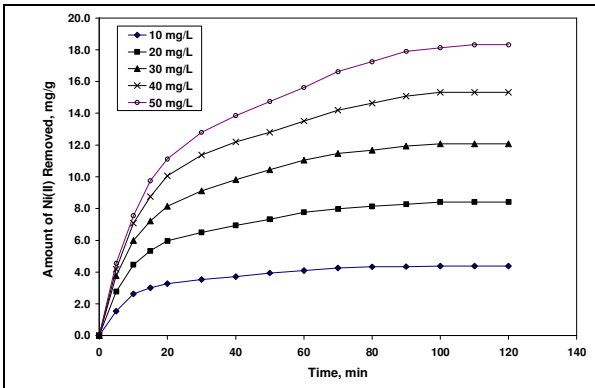

Fig.-2b: Effect of Initial concentration on the adsorption of Ni(II) by WAC

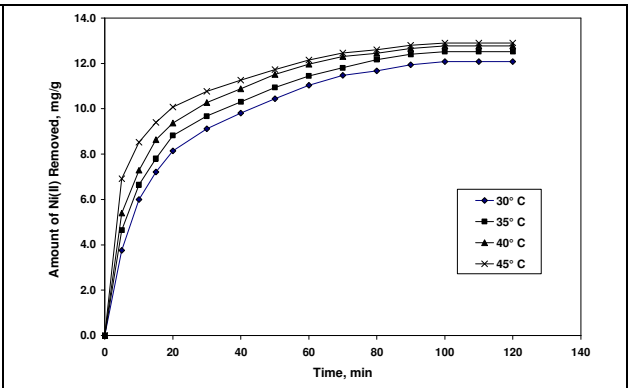

Fig.-2c: Effect of Temperature on the adsorption of Ni(II) by WAC

Kinetic studies

The results of kinetic studies are useful for the design and operation of an adsorption system in industrial scale. In-order to understand the kinetics of adsorption, already existing kinetic models like pseudo-first order and pseudo-second order kinetic models were used and intra-particle diffusion model was selected to analyze the mechanism of the adsorption Ni(II) on to WAC.

The pseudo-first order kinetics

The pseudo-first order plot of $\log(q_e-q_t)$ versus t for the adsorption of Ni(II) on the WAC at various initial metal ion concentration and temperature are shown in figure 3a, 3b and the results are presented in Table-2. The pseudo-first order rate constant decreases from 5.021 $x10^{-2}$ to 3.547$x10^{-2}$ sec^{-1} on increasing the metal ion concentration from 10 to 50 mg/L. As the concentration of the solution increases, the rate of backward reaction (i.e desorption) also increases, which leads to decrease of rate constant on increasing the concentration.

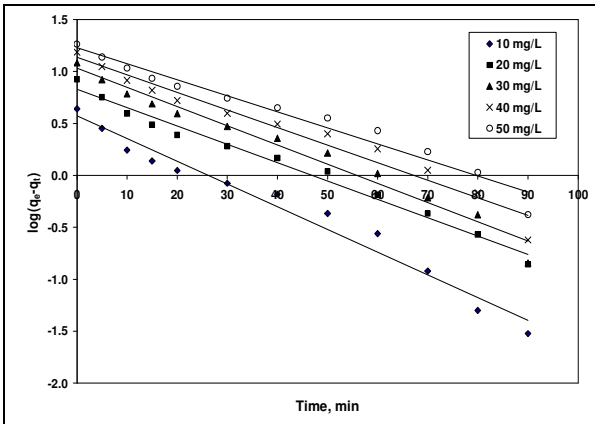

Fig.-3a: Pseudo-first order plot for the adsorption of Ni(II) by WAC

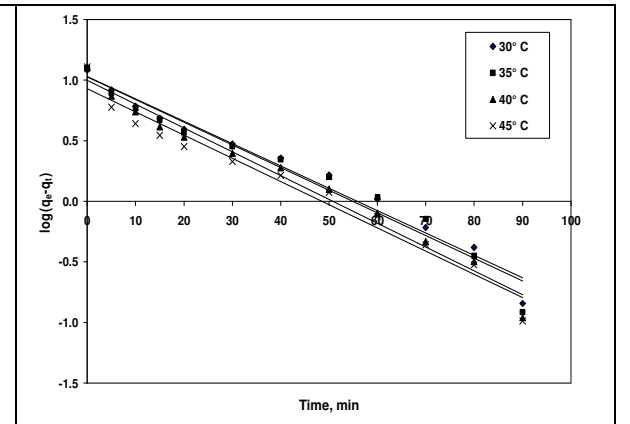

Fig.-3b: Pseudo-first order plot for the adsorption of Ni(II) by WAC

On increasing the solution temperature from 30 to 45°C, the pseudo-first order rate constant increases from 4.076 $x10^{-2}$ to 4.399 $x10^{-2}$ sec^{-1}. At high temperature the pores of the adsorbent are getting widened, there by the rate of adsorption increases which leads to increase of pseudo-first order rate constant. The q_e calculated from pseudo-first order kinetic model show large deviation from experimental q_e. The regression coefficient of the pseudo-first order plot for the adsorption of Ni(II) onto WAC for the range of concentration as well as temperature under investigation is varied between $0.9623 < r^2 < 0.9849$. This

suggests that the adsorption of Ni(II) by WAC does not follow the first order kinetics during the entire period of adsorption.

Table-2: Calculated kinetic parameters for the adsorption of Ni(II)

Parameters	Initial Ni(II) concentration, mg/L					Temperature °C			
	10	20	30	40	50	30	35	40	45
$q_e$exp.(mg/g)	8.75	16.82	24.17	30.64	36.64	24.17	25.04	25.54	25.81
Pseudo-first order kinetics									
k_1 x10^{-2}(min $^{-1}$)	5.021	4.261	4.076	3.892	3.547	4.076	4.307	4.537	4.399
$q_e$cal(mg/g)	3.73	6.75	10.75	13.70	16.91	10.75	10.65	9.97	8.47
r^2	0.9725	0.9849	0.9745	0.9627	0.9634	0.9745	0.9623	0.9774	0.9662
Pseudo-second order kinetics									
k_2 x10^{-2} (g/mg/min)	2.191	0.903	0.541	0.359	0.240	0.541	0.622	0.776	1.001
h	0.4984	0.78	1.00	1.10	1.101	0.998	1.19	1.49	1.98
$q_e$cal(mg/g)	4.77	9.30	13.59	17.48	21.41	13.59	13.81	13.85	14.06
r^2	0.9993	0.9994	0.9993	0.9989	0.9982	0.9993	0.9991	0.9995	0.9993
Intra particle diffusion model									
k_{id}(mg/g/min^{½})	3.121	1.493	0.951	0.747	0.598	0.951	0.998	1.038	1.322
r^2	0.9738	0.9699	0.9785	0.9618	0.9688	0.9785	0.9717	0.9695	0.9785

The pseudo-second order kinetics

The pseudo-second order plot of "t/q_t" versus "t" at various concentrations and temperatures are shown in figure 4a and 4b. The pseudo-second order constant calculated from the slope and intercept are given in table 2. The pseudo-second order rate constant decrease from 2.191 x10^{-2} to 0.240x10^{-2} (g/mg/min) on increasing the initial Ni(II) concentration from 10 to 50 mg/L and it increases from 0.541 x10^{-2} to 1.001 x10^{-2} (g/mg/min) on increasing the temperature from 30 to 45°C.

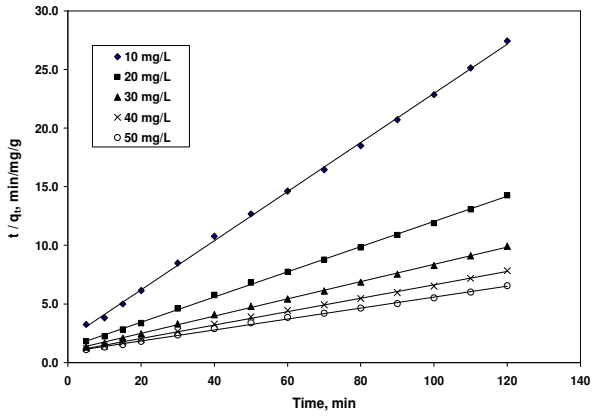

Fig.-4a: Pseudo-second order plot for the adsorption of Ni(II) (Concentration variation)

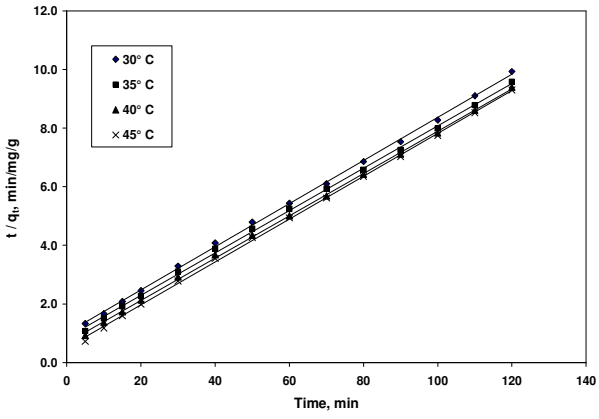

Fig.-4b:- Pseudo-second order plot for the adsorption of Ni(II) (Temperature variation)

The q_e calculated from pseudo-second order deviates from the experimental value but the deviation is small when compared with the value calculated from the pseudo-first order kinetic model. The correlation coefficient calculated from the pseudo-second order model ranged between $0.9982 < r^2 < 0.9995$.

The high correlation coefficient of pseudo-second order indicates that the adsorption of Ni(II) by WAC follows pseudo-second order kinetics. This proves that the overall rate of Ni(II) adsorption is controlled by chemical process via ion exchange and or complexation process[29].

Intra-particle diffusion model

The intra-particle diffusion plot of q_t vs $t^{0.5}$ at various initial Ni(II) concentration and temperature is shown in figures-5a and 5b. The results of intra-particle diffusion plots are presented in table 2. As observed from the intra-particle diffusion plot, the linear portion of the plot did not pass through the origin, which indicates that boundary layer diffusion also plays a significant role along with intra-particle diffusion. This is due to the difference in mass transfer between initial and final stages of adsorption.

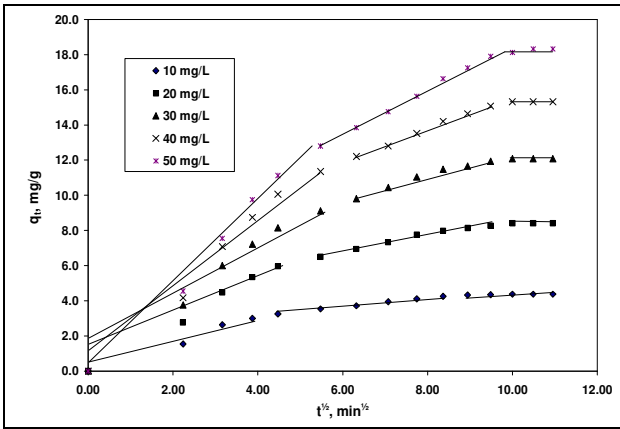

Fig.-5a: Intra-particle diffusion plot for the adsorption of Ni(II) (Concentration variation)

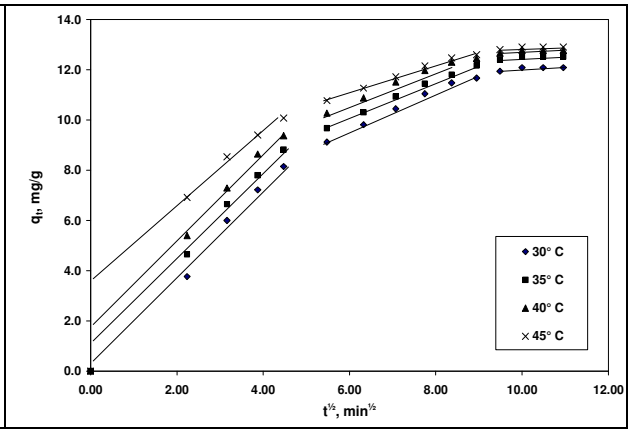

Fig.-5b: Intra-particle diffusion plot for the adsorption of Ni(II) (Temperature variation)

Isotherm Studies

Langmuir Model

The Langmuir plot of C_e/q_e versus C_e for the adsorption of Ni(II) onto WAC is shown in figure 6 and the results derived from the slope and intercept of this plot are presented in Table-3.

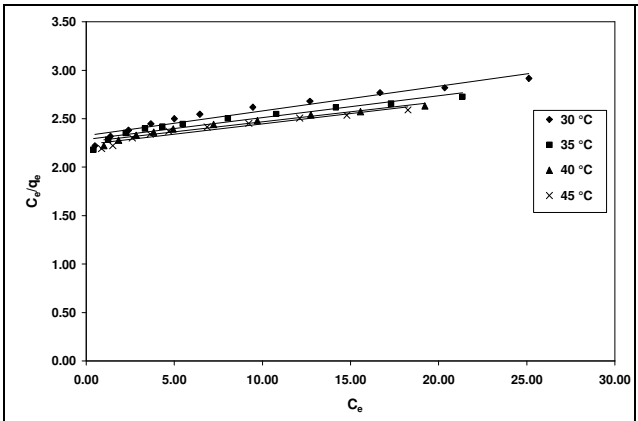

Fig.-6: Langmuir plot for the adsorption of Ni(II) by WAC

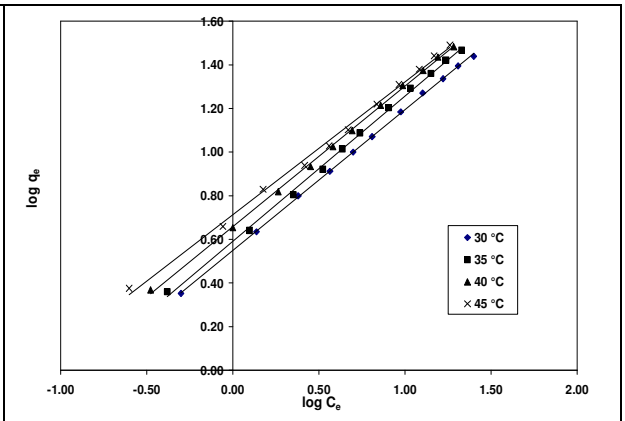

Fig.-7: Freundlich plot for the adsorption of Ni(II) by WAC

The Langmuir monolayer adsorption capacity increases from 39.22 to 48.31 mg/g, which is comparable with the results reported by the past researchers[30]. The dimensionless equilibrium parameter, R_L, also known as the separation factor ranged between 0 and 1 indicating the favorable adsorption of Ni(II) on WAC. The correlation coefficient r^2 ranged between 0.9187 to 0.9505 when the adsorption data for the adsorption of Ni(II) onto WAC is analyzed using Langmuir adsorption isotherm.

Freundlich Model

The Freundlich parameters k_f and n calculated from the slope and intercept of the plot log q_e versus log C_e(Figure-7) are given in Table-3.The Freundlich constant related to overall adsorption capacity k_f increases from 3.54 to 5.15 on increasing the temperature from 30 to 45°C. The value of a constant related to surface heterogeneity n is greater than 1.0 indicating that the adsorption of Ni(II) onto WAC is favorable. The correlation coefficient of Freundlich isotherm is varied between 0.9971 to 0.9997, which substantiates the surface heterogeneity and the exponential distribution of active sites and their energies. The applicability of Freundlich isotherm for the adsorption of Ni(II) by WAC indicates the surface is more heterogeneous during the Ni(II) adsorption.

Table-3: Results of isotherm studies for the adsorption of Ni(II) onto WAC

	Temperature °C			
Parameters	30	35	40	45
Langmuir isotherm				
Q_0 (mg/g)	39.22	44.44	46.73	48.31
b_L x10^{-3}(L/mg)	10.968	9.843	9.461	9.275
r^2	0.9392	0.9187	0.9505	0.9308
Freundlich isotherm				
n	1.55	1.50	1.55	1.64
k_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	3.54	3.90	4.55	5.15
r^2	0.9997	0.9984	0.9992	0.9971

Thermodynamics of Adsorption

The Van't Hoff plot of ln Kc versus 1/T is shown in figure-8 and the results are presented in Table-4. The magnitude of the enthalpy change (ΔH°) provides information about the type of sorption. The heat evolved during physisorption generally lies in the range of 2 to 40 kJ/mol, while the heat of chemisorptions generally falls in the range of 80 to 200 kJ/mol[31]. The enthalpy change for the adsorption Ni(II) by WAC is 25.36 kJ/mol, indicates the weak force of attraction between the sorbent surface and Ni(II) ion. Positive value of ΔS° indicated an increase in randomness at the solid/liquid interface during the sorption process while the obtained value of ΔS° (89.12 J/K/mol) indicated that there is a considerable change on entropy occurred during the adsorption of Ni(II) onto WAC surface[32].

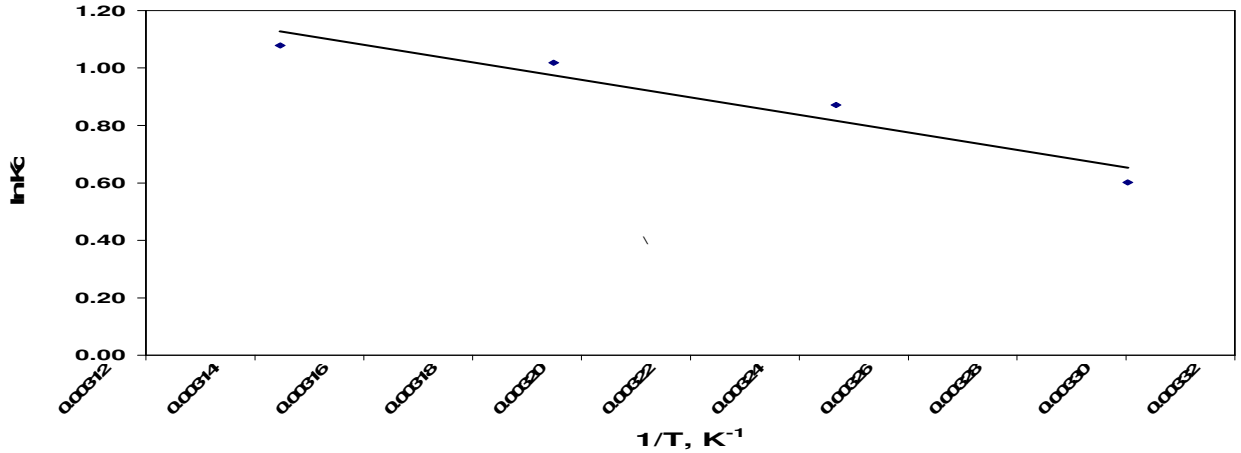

Fig.-8: Thermodynamic plot for the adsorption of Ni(II) by WAC

The free energy change ΔG° for the Ni(II) adsorption at all temperature is negative. The negative free energy change substantiate that the adsorption is favorable and spontaneous. The free energy is become

more negative when the temperature of the system is increased, substantiates that increase in the spontaneity of the process with temperature.

Desorption studies

Desorption studies were essential to evaluate the reusability of the spent adsorbent for further adsorption. If the spent adsorbent gives more number of cycles, will give more economic benefits for the industrial applications. The Ni(II) loaded WAC was agitated with aqueous solutions of varying pH from 2.0 to 12.0 and the percentage regeneration was estimated as shown in figure-9. The desorption of Ni(II) was 68.6 % at a pH of 2.0 and it was minimum around the pH of 7.0. At low pH the presence more H^+ creates a repulsive force between the metal ion and the protonated sorbent surface which leads to more desorption of Ni(II). Whereas at higher pH, the precipitation of the adsorbed metal ion leads to more desorption from the sorbent surface.

Table-4: Thermodynamic parameters

Temperature, °C	ΔG°, J/K/mol	ΔH°, kJ/mol	ΔS°, J/K/mol
30	- 1.516	25.36	89.12
35	- 2.231		
40	- 2.649		
45	- 2.851		

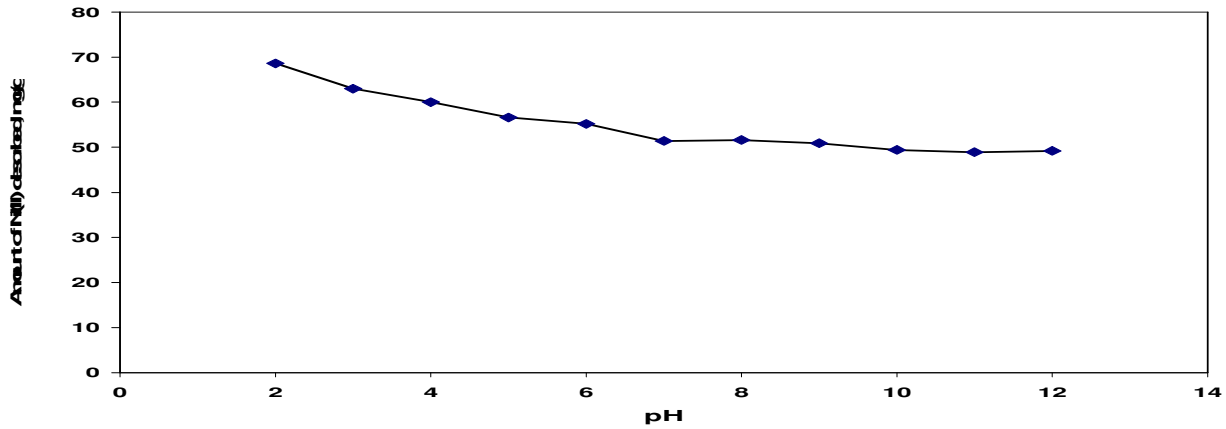

Fig.-9: Effect of pH on the desorption of Ni(II)

CONCLUSION

Activated carbon synthesized from the unripe fruits of *Wrightia tinctoria* seeds using microwave synthesis is a promising adsorbent with excellent surface characteristics. The surface characteristics of the adsorbent were comparable with that of commercial activated carbon. The Ni(II) ions showed a maximum adsorption at a pH of 5.0 to 7.0 and the adsorption decreased thereafter. The initial metal ion concentration has a great influence on the adsorption, the amount of Ni(II) adsorbed on the surface of WAC increased with increase of initial Ni(II) concentration. The pseudo-second order kinetic model is more appropriate describe the kinetics of Ni(II) adsorption than that of first order. The suitability of Freundlich model for the adsorption of Ni(II) onto WAC indicated the surface heterogeneity during the adsorption. The adsorption is more spontaneous at a given temperature as indicated by the negative free energy change. The positive ΔH° indicated the endothermic nature and positive ΔS° shows the increased randomness at the solid-solution interface.

REFERENCES

1. V.K. Gupta, D. Pathania, S. Sharma and P. Singh, *J. Colloid Interface Sci*., **401**, 125 (2013).
2. Y.P. Guo, D.A. and Rockstraw, *Carbon*, **44**, 1464 (2006).
3. H.Z. Mousavi, A. Hosseinifar and V. Jahed, *J. Serb. Chem. Soc*. **75**, 845 (2010).

4. Izidoro, C. Juliana, Fungaro, A. Denise, Abbott, E. Jennifer and S. Wang, *Fuel*,**103**, 827 (2013).
5. World Health Organisation, Guidelines for Drinking Water Quality. Recommendations, WHO, Geneva, 1984.
6. A.K. Meena, G.K. Mishra, P.K. Rai, Rajapopal, and P.N. Nagar, *J. Hazard. Mater.,* **122**, 161 (2005).
7. S. Tamilselvi, M. Asaithambi and P. Sivakumar, *Desalination and Water Treatment*, **1,** 8 (2015).
8. V. Sivakumar, M. Asaithambi and N. Gopal, *American Chem. Sci. J.* **4(40),** 424 (2014).
9. H. Hasar, *J. Hazard. Mater.,***B97**, 49 (2003).
10. P.S. Kumar, S. Ramalingam, S.D. Kirupha, A. Murugesan, T. Vidhyadevi, S. Sivanesan, *Chem. Eng. J.*, **167**, 122 (2011).
11. X. Li, Y. Tang, Z. Xuan, Y. Liu and F. Luo, *Sep. Purif. Technol*., **55**, 69 (2007).
12. P. Tasaso, *J. Clean Energy Technol*., **2**, 154 (2014).
13. D.Z. Husein, *Desalin. Water Treat.*,**51**, 6761 (2013).
14. D. Yadav, M. Kapur, P. Kumar, M.K.Mondal, *Saf. Environ*.,**94**, 402 (2015).
15. M.J. Ahmad and S.K. Thyodan, *Chem. Eng. J.*, **214**, 310 (2013).
16. M.M. Titirici, A. Thomas and M. Antonietti, New J. Chem., **31**, 787 (2007).
17. U.S. Khandekar, R.A. Ghongade and M.S. Mankar, *Int. J. Pharmacognosy and Phytochemical Res*., **5(1)**, 41(2013).
18. ISI, Activated Carbon, Powdered and Granular – Methods of sampling and its tests, (Bureau of Indian Standards, New Delhi), IS 877 (1989).
19. American Society for Testing Materials (ASTM), Standard test method for Determination of Iodine Number of Activated Carbon D4607-94, ASTM, (1980).
20. S. Lagergren, *Kung. Sven. Veten. Hand*., **24**, 1 (1898).
21. Y.S. Ho and G. McKay, *Process Biochem*.,**34**, 451 (1999).
22. W.J.Weber and J.C.Morris, *Proc. Int. Conf. Advances in Water Poll. Res*., **2**, 231–241 (1963).
23. I. Langmui, *J. Am. Chem. Soc*., **38**, 2221, (1918).
24. H. Freundlich, *Z. Phys. Chem*., **57**,387 (1906).
25. A.S.Ozcan, B.Erdem and A.Ozcan, *Colloid Surface A*, **266**, 73–81 (2005).
26. M. Jain, V.K. Garga and K. Kadirvelu, *J. Hazard. Mater*.,**162**, 365 (2009).
27. M. Bansal, D. Singh, V.K. Garg and P. Rose, *Int. J. Civil Environ. Eng*., **1(2)**, 108 (2009).
28. K.C. Sekher, S. Subramanian, J.M. Modak and K.A. Natarajan, *Int. J. Miner. Process*.,**53**, 107 (1998).
29. X.S. Wang, Z.Z. Li and S.R. Tao, *J. Environ. Manage*.,**90**, 721 (2009).
30. M. El-Sadaawy, O. Abdelwahab, *Alexandria Engg. J*., **53**, 399 (2014).
31. Y. Liu and Y.J. Liu, *Sep Purif Technol*., **61**, 229 (2008).
32. F.A. Dawodua and K.G. Akpomie, *J. Mater. Res. technol*., **3(2)**, 129 (2014).

[RJC-1523/2016]