RJC

RASĀYAN *J. Chem.*
Vol. 12 | No. 3 |1315 - 1325| July - September | 2019
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

ADSORPTION ISOTHERM, KINETICS AND THERMODYNAMICS OF BIVALENT NICKEL SCAVENGING UTILISING SAWDUST CARBON

S. Rani[1,2,3], M. Bansal[4], K. Kaur[5] and S. Sharma[5,*]
[1]Department of YCoE, Punjabi University Guru Kashi Campus,
Talwandi Sabo-151302, (Punjab) India.
[2]Research Scholar, I.K. Gujral Punjab Technical University, Kapurthala-144603, (Punjab) India.
[3]Applied Chemistry and Polymer Science Laboratory, Department of Chemistry, Maharaja Ranjit Singh Punjab Technical University, Bathinda-151001, (Punjab) India.
[4]Department of Civil Engineering, Giani Zail Singh Campus College of Engineering and Technology, Bathinda-151001, (Punjab) India.
[5]Department of Chemistry, Maharaja Ranjit Singh Punjab Technical University,
Bathinda-151001, (Punjab) India.
*E-mail: paperpubseema@gmail.com

ABSTRACT

Batch mode studies were carried out for investigating the removal efficiency of sawdust carbon prepared by sulphuric acid treatment of Indian Rosewood sawdust for aqueous bivalent nickel ions. Experiments involved the study of influence of varying the parameters like pH, contact period, the initial strength of adsorbate, temperature, agitation speed and dosage of adsorbent on scavenging of adsorbate ions. Characterization of adsorbent has been done using FTIR, SEM-EDX, BET surface area and CHNSO elemental analysis. Adsorption isothermal studies are in good agreement with the Langmuir isotherm model. The highest calculated value of the correlation coefficient suggested Pseudo-second order reaction kinetics for adsorption of nickel bivalent ions on sawdust carbon. Exothermic nature and spontaneity of removal of nickel ions were shown by thermodynamic parameters. Desorption experiments were accomplished using HCl solutions of varying concentrations. High percentage adsorption of sawdust carbon adsorbent observed for Ni (II) ions indicated that it could be efficiently employed for scavenging of aqueous Ni (II) metal ions.

Keywords: Adsorption, Batch mode, Bivalent Nickel, Isotherm, Kinetics.

© RASĀYAN. *All rights reserved*

INTRODUCTION

Heavy metals present in effluents emanating from industries[1] discharged into water bodies are the most ubiquitous pollutants of utmost concern for the whole world[2]. Commonly employed metals in industries include Cu, Ni, Zn, Hg, Cd, Cr, As, Pb etc. Toxicity and persistency associated with these heavy metals demand their removal from effluent water[3]. Surprisingly, some of these metal ions could be highly hazardous at low concentration towards animals, plants and human beings. Serious health disorders are caused by ingestion of heavy metal ions beyond permissible limits[4]. Therefore, research in past decades is focused on the discovery of various alternative treatment processes for efficient eviction of these metallic pollutants from industrial emissions before their discharge into aquatic system[5].

Nickel in comparison to other metals is a more recalcitrant pollutant[6]. It is widely used in many industries such as electroplating, mining, smelting, aircraft, pigments and metal finishing etc.[7]. The high strength of metallic nickel in industrial effluents may result in various diseases and disorders in human beings like renal disorder, pulmonary fibrosis (excessive formation of connective tissue in lungs) and skin dermatitis[8]. In the metal-plating industry, continuous exposure to Ni has been known to cause

Rasayan J. Chem., 12(3), 1315-1325(2019)
http://dx.doi.org/10.31788/RJC.2019.1235279

occupational asthma in workers. Other respiratory problems associated with Ni uptake are chronic sinusitis, decreased pulmonary residual capacity, increased respiratory frequency, nasal septal erosions[9]. In this context, the scavenging of aqueous nickel ions is hugely desired.

The traditional nickel-metal ion removal techniques include ion-transfer, chemical precipitation, coagulation, solvent extraction, membrane filtration, electrochemical treatment[10] and reversal osmosis. But, certain demerits associated with these techniques including high operational cost, disposal of large quantities of generated toxic sludge and incomplete removal of metal ions further question the economic and technical feasibility of these processes. In contrast to these, the adsorption method has the inherent advantage of being without secondary pollution[11]. Several studies undertaken using natural agro-waste based adsorbents have been found to be cost-effective, environment-friendly and efficient. Their easy accessibility and abundant availability make them profitable alternative source of raw materials for natural adsorbents which can be employed for remediation of metallic pollutants[12]. The utilization of plant-based materials for the uptake of inorganic pollutants have been the focus of research in the past decade. In the same purview, sawdust, a timber industry based adsorbent has been proposed in the present study which could serve the purpose of being low cost, environment-friendly and having good adsorption efficiency. The efficacy of biomass depends upon several factors like a number of active sites on the adsorbent, their accessibility, affinity between active sites and metal ions[13].

Sawdust carbon prepared by treating sawdust of Indian Rosewood with concentrated sulphuric acid has been investigated in the present work for retrieval studies of divalent nickel. The adsorption ability of adsorbent in extracting metal ions was determined in batch mode. Mechanism and characteristics of the adsorption process were evaluated by using different adsorption isotherm and kinetic models.

EXPERIMENTAL

Material and Measurements

Analytical grade reagents were used in experimental studies. $Ni(NO_3)_2.6H_2O$ salt of nickel metal from Loba Chemie Pvt. Ltd, India was employed for preparing 1000 ppm stock solution of Ni (II) metal ions. pH adjustments of metal solutions were done using HCl and NaOH (0.1N) solutions. Sawdust of Indian Rosewood was procured from a local lumber mill of Bathinda, Punjab, INDIA and treated with concentrated H_2SO_4. The residual amount of Ni metal ions was obtained using AAS of Model GBC-932 plus. Orbital incubator shaker (Remi Scientific) was employed for performing batch experiments. pH meter (LT-49) was used for measurements of the pH of solutions.

Methods

Preparation of Sawdust Carbon

The raw sawdust, after sun drying, was freed from all aqueous impurities through washing. It was then carbonized on heating with concentrated H_2SO_4 in the proportion of 2:1 (volume of acid: the amount of solid). Removal of excess acid from carbonized sawdust was then carried out by soaking it in double distilled water followed by washing with 2% $NaHCO_3$ (w/v) solution. The adsorbent was dried in an oven at 70˚C for one day and one night followed by cooling, grinding and sieving through 300-micron size mesh[14].

Characterization

For characterization of sawdust carbon adsorbent, techniques like FTIR, SEM-EDX, CHNSO and BET surface area were employed. The functional group vibrational frequency changes of nickel loaded adsorbent were analyzed using Perkin Elmer Spectrum Two FTIR spectrometer (using KBr Pellet). The morphological characteristics of adsorbent surface and distribution of metal ions on it were analyzed from SEM images obtained using model JEOL-JSM-6510LV (Japan). Analysis of the elemental constitution of adsorbent (pre and post adsorption) was performed using EDX spectroscopic technique (INCAX-act, Model 51-ADD0076, Oxford Instruments). BET surface area and pore volume measurements were done on Quantachrome Instruments version 10.01 (Nova Station B) by N_2 adsorption-desorption technique. CHNS analyzer (Thermo Finnigan) was used for elemental analysis of adsorbent.

Batch Studies

Batch technique was employed for investigation of aqueous divalent nickel adsorption. In each experiment, 0.25 g of adsorbent was put into 100 ml aqueous nickel solution of concentration 25 ppm in conical flasks. The initial pH was adjusted in the range of 2 to 6, adsorbent weight was varied from 0.1 to 1.5 g/100 ml and temperature from 298 to 333 K. The effect of variation in adsorbate initial strength (10 – 250 mg/L), agitation time (30 – 240 minutes) and agitation speed (50–250 rpm) was determined at pH 6.0 and temperature 298 K. Adsorption isotherms were explored with initial adsorbate concentrations (10 – 250 ppm) at temperature 298 K. Kinetic study experiments were done by shaking 100 ml of metal ions solution of strength 25 ppm at different contact periods from 5 – 180 min.

The percentage retrieval and adsorption efficacy (q) of adsorbate were assessed with underwritten equations:

$$\%\ \text{Adsorption} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \tag{1}$$

$$\text{Adsorption capacity } (q) = V\left(\frac{C_o - C_e}{m}\right) \tag{2}$$

Where, C_o and C_e (mg/L) → initial & equilibrium concentration of bivalent nickel, q → quantity of metal ion adsorbed per unit mass of adsorbent (mg/g), m → adsorbent mass (g) and V → volume of metal solution in liters.

Desorption Studies

For desorption studies, 100 ml of 25 ppm of adsorbate solution was agitated employing orbital incubator shaker for 120 minutes at 200 rpm with 0.25 g of adsorbent in a conical flask. After 120 minutes, the metal loaded adsorbent was separated by filtration. It was then treated with 100 ml each of HCl (0.05 N, 0.1 N and 0.2 N) as desorbing solutions. The flasks were again subjected to shaking in a shaker for 1 hour. After filtration, filtrate Ni (II) concentration was determined by AAS. Desorption percentage (%) of metallic ions was obtained by the application of underwritten equation[15]:

$$\text{Desorption percentage } (\%) = \frac{C_d}{C_a} \times 100 \tag{3}$$

Where, C_a (mg/L) → concentration of metal ions on solid phase and C_d (mg/L) → metal ions concentration in solution after desorption.

RESULTS & DISCUSSION

Characterization of Adsorbents

Major functional groups of sawdust carbon and sawdust carbon loaded with Ni (II) metal ions were explored with the help of FTIR spectroscopy (Fig.-1). For sawdust carbon, a broad signal at 3403 cm^{-1} is attributed to hydrogen-bonded hydroxyl functional groups. Signals at 1707 and 1603 (cm^{-1}) indicates −C=O stretching vibrational modes of various functional groups i.e. ketonic, aldehydic and carboxylic acid etc. C−O stretching vibrations of an alcoholic functional group can be attributed to the peaks obtained at 1367 and 1402 cm^{-1}. Binding of metallic nickel ions on sawdust carbon is indicated by the considerable shift in the O−H stretching mode from 3403 to 3386 cm^{-1}. Also, the corresponding C−O stretching sharp signals at 1367 & 1402 (cm^{-1}) of alcoholic group merge to form a weak band, evidencing the interaction of Ni (II) ions through hydroxyl groups.

BET surface area and BJH pore volume measurements of prepared adsorbent obtained from BET analyzer were 514.996 m^2/g and 0.426 cm^3/g, respectively. The high surface area of sawdust carbon accounts for more number of active sites on its surface which may lead to high adsorption efficiency for the remediation of metal ions. The elemental analysis of sawdust carbon gave a percentage of C, H, O as 52.384, 2.919, 21.518, respectively.

SEM images indicated the variations in surface morphology due to the sulphuric acid treatment given to raw sawdust (Fig.-2a and b). EDX analysis reports the elements present in the sawdust carbon. EDX image of sawdust carbon showed the occurrence of carbon and oxygen in the biomass before adsorption while adsorption of nickel by the adsorbent was indicated by an additional signal in the spectrum for Ni (Fig.-2c and d).

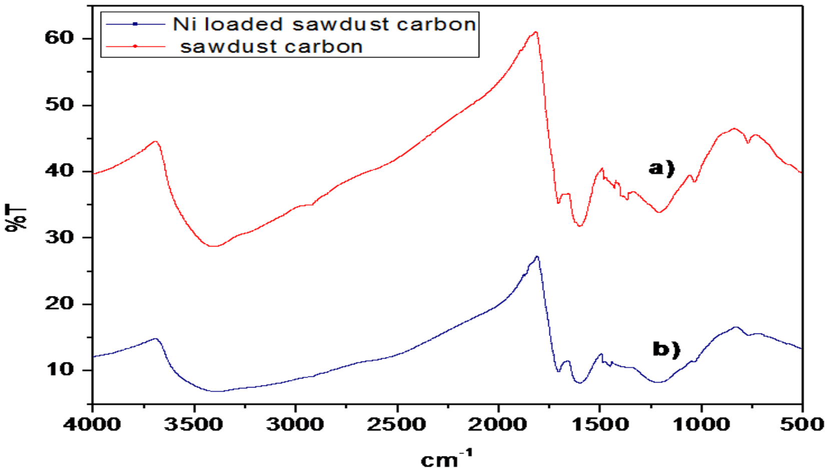

Fig.-1: FTIR of (a) Sawdust Carbon (b) Sawdust Carbon loaded with Nickel(II) Ions

Batch Experiments

Effect of Variation of pH

The effect of pH variation on adsorption performance of sawdust carbon towards bimetallic nickel was investigated in series of experiments using a metal solution of strength 25 ppm with different values of initial pH in the range 2.0 to 6.0. The removal efficiency of Ni (II) increased with increase in pH and the maximum value was noted at pH 6.0 (Fig.-3a) for sawdust carbon. At pH 2, lesser adsorption is a consequence of protonation of surface functional groups of sawdust carbon, thus repelling the positively charged metal ions. However, with increasing pH, deprotonation of the functional groups of adsorbent starts and its surface attains negative charge. It enhances the binding of metal ions, hence increasing the uptake efficiency of the adsorbent. Above pH 6.0, nickel-metal ions precipitate as nickel hydroxide.

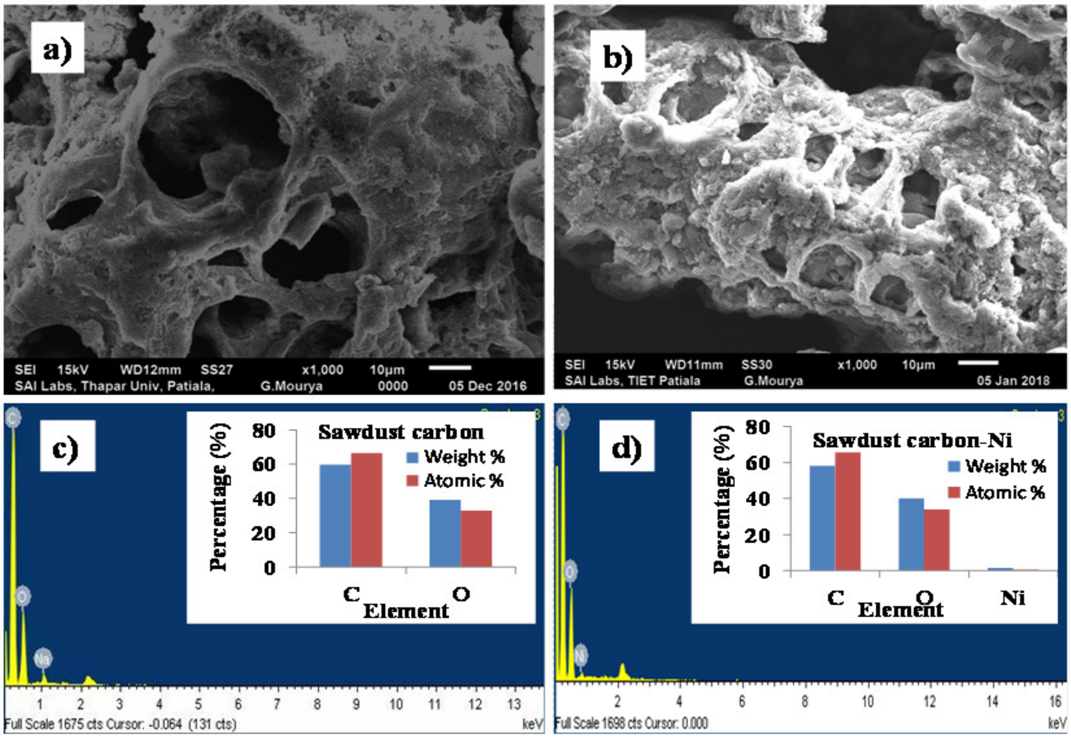

Fig.-2: SEM Pictures of (a) Sawdust Carbon (b) Ni(II) Laden Sawdust Carbon, EDX Images of (c) Sawdust carbon (d) Ni(II) loaded Sawdust Carbon

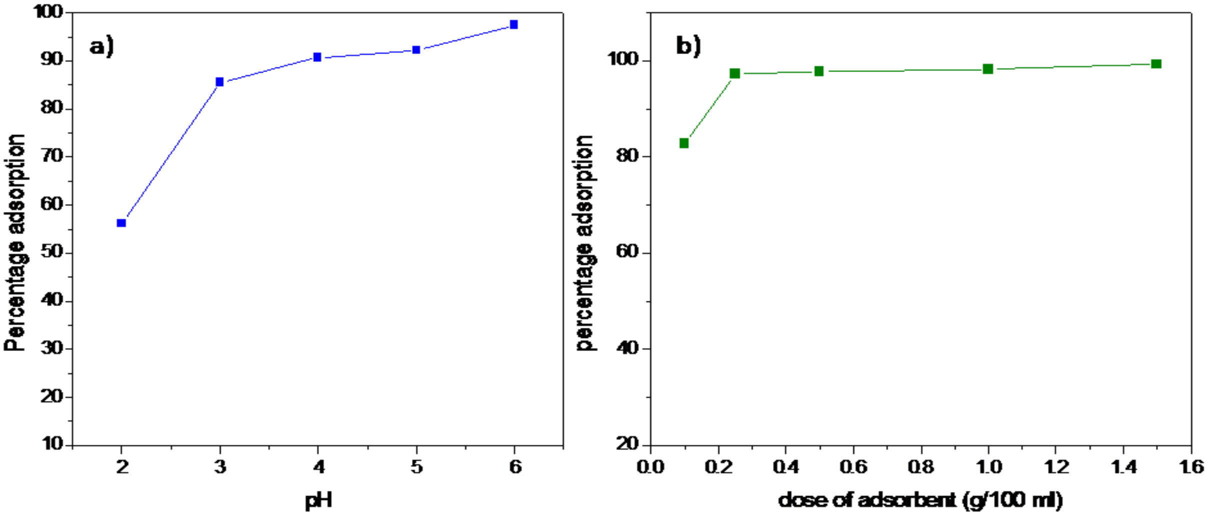

Fig.-3: Impact of (a) pH Variation (b) Dose of Adsorbent on Ni(II) Adsorption

Impact of Adsorbent Amount on Nickel Removal

The change in adsorption efficiency of sawdust carbon on increasing the adsorbent dosage from 0.1– 1.5 g was examined by shaking with 100 ml of adsorbate solution at 298 K. The percentage remediation of metal ions under consideration increases with enhancement in the dose of sawdust carbon, as inferred from Fig.-3b. This is because the increasing dose of adsorbent provides more vacant spaces for the uptake of adsorbate molecules from the liquid phase on to the surface of the adsorbent, resulting in a rise in adsorption efficiency. When sawdust carbon dose rises above 0.25 g, a slow increase in percentage adsorption which reaches to an almost constant value. This behavior could be due to reaching of equilibrium stage for both liquid and solid phases.

Effect of Variation of Contact Period

The contact time variation study for the biosorption of divalent nickel using sawdust carbon as adsorbent was undertaken from 30 to 240 minutes in the interval of 30 minutes. Graph (Fig.-4a), depicts the percentage increase in adsorption with an increase in the contact period and attainment of equilibrium in 120 minutes. After 120 minutes, there is a slight decrease in percentage adsorption up to 240 minutes. Initial elevation in percentage adsorption up to 120 minutes time is owed to the presence of more empty active positions on the adsorbent surface. After 120 minutes, these positions get saturated with adsorbate and metal ions diffuse slowly into pores from the adsorbent surface which account for a small decrease in percentage adsorption of metal ions from solution[16].

Influence of Adsorbate Initial Concentration

The impact of change in initial strength of nickel adsorbate on removal percentage using sawdust carbon was observed by taking its concentration (10 – 250 ppm), keeping other parameters constant (Fig.-4b). Percentage adsorption was observed to increase with concentration from 10 – 25 mg/L and thereafter decrease in percentage removal is noticed. This is because, for lesser strength of adsorbate, the vacant surface-active voids on the adsorbent surface are very high in number, so, all-metal ions can easily adsorb and percentage removal is high. But, at high initial strength of adsorbate, the vacant surface-active voids are available in less number for adsorption. So, the decrease in adsorption is observed at a high initial concentration of metallic nickel.

Influence of Temperature Variation

Metal ion adsorption efficiency of sawdust carbon for the uptake of divalent nickel with a change in temperature was investigated by varying it from 298 – 333 K, keeping other parameters constant. Fig.-5a, depicts decrease in removal percentage of nickel with rise in temperature from 298 – 323 K and further, increase in percentage adsorption for increase in temperature from 323 – 333 K. The initial decrease in value of removal percentage could be due to decrease in surface activity suggesting the adsorption process to be exothermic[17] and thereafter, the increase in percentage adsorption is attributed to elevated distribution of divalent nickel ions towards external surface and voids of sawdust carbon. Also, the decline in boundary layer width and resistance to metal ions transfer further adds to the increase in adsorption percentage with the rise in temperature (323 – 333 K)[15].

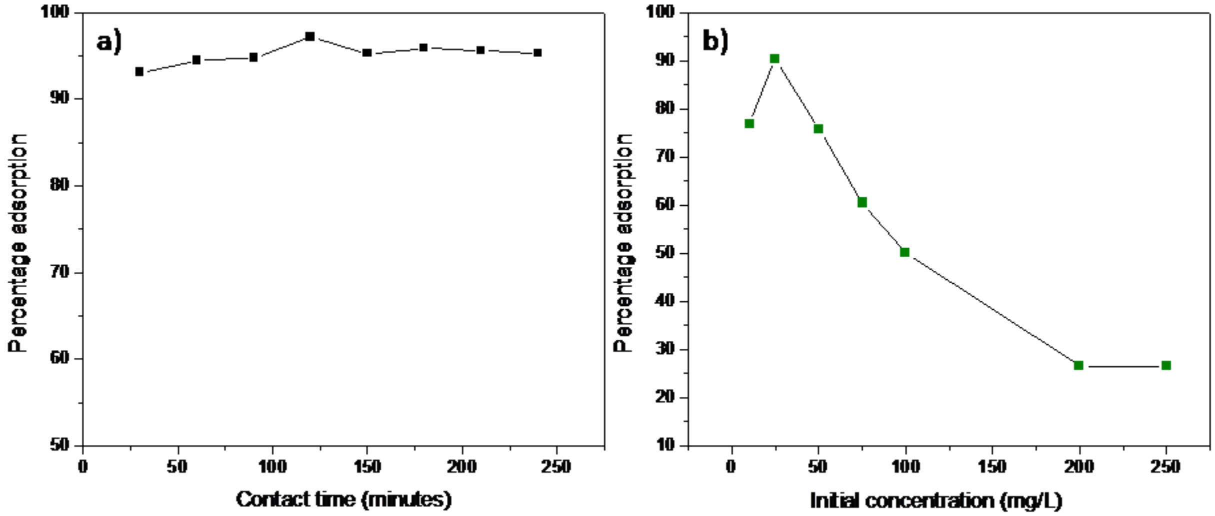

Fig.-4: Influence of Variation of (a) Contact Period (b) Initial Concentration of Bivalent Nickel

Influence of Agitation Speed

To investigate the variation in agitation speed on percentage uptake of divalent nickel, the shaking speed was varied from 50 – 250 rpm. Percentage adsorption of metal ions was observed to increase with the change in shaking speed, reaching a maximum at 200 rpm and then decreasing with increase in speed above 200 rpm (Fig.-5b).

On agitation, adsorption increases due to the vigorous movement of the solid adsorbent particles in the solution. It increases the concentration of divalent nickel near the solid adsorbent and hence its movement to the boundary layer of adsorbent is enhanced. Above 200 rpm, the decrease in adsorption may have resulted due to the breaking of interactive weak forces between the adsorbent and adsorbate[18,19].

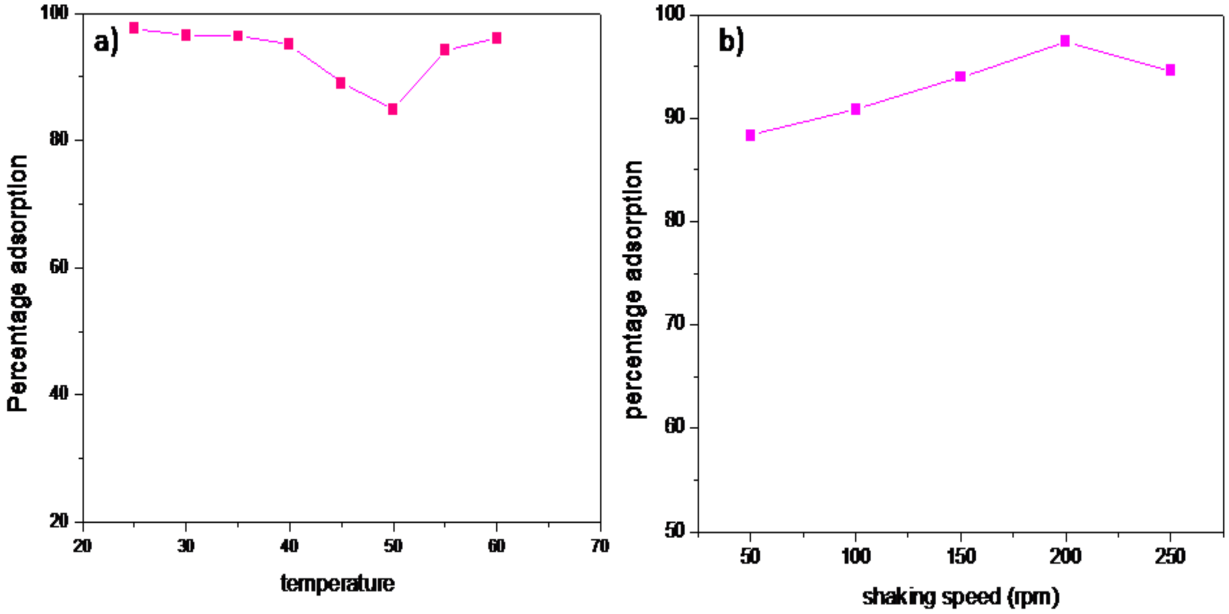

Fig.-5: Impact of Change in (a) Temperature (b) Shaking Speed on Adsorption of Ni(II) Ions

Adsorption Isotherm Studies

Langmuir Isotherm

The Langmuir isotherm and its linear form are expressed by underwritten equations[20]:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \tag{4}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \tag{5}$$

Where, C_e (mg/L) → concentration of metal ions in the liquid phase at equilibrium, q_e (mg/g) → concentration of adsorbate on adsorbent at equilibrium, q_m (mg/g) → maximum monolayer adsorption efficacy and K_L (L/mg) → Langmuir constant. The plot of C_e/q_e against C_e gives the values (given in Table-1) of constants q_m and K_L (Fig.-6a). The favorability of the adsorption phenomenon is determined from the value of R_L (separation factor), a dimensionless entity and necessary characteristics of Langmuir isotherm. The process can be either unfavourable (R_L>1), linear (R_L =1), favourable (0 < R_L < 1) or irreversible (R_L =0)[17]. R_L is described as:

$$R_L = \frac{1}{1+K_L C_o} \tag{6}$$

Where, C_o → initial strength of metal ions. The values of R_L in the present study involving various starting adsorbate concentrations for adsorption on sawdust carbon are found in the range 0 to1 indicating the process to be favorable.

Freundlich Isotherm Model

The empirical form of Freundlich isotherm is represented as [21]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{7}$$

Where, q_e (mg/g) and C_e (mg/L) → equilibrium concentration of adsorbate in solid and liquid phase respectively, K_f → constant related to uptake capacity and 1/n are Freundlich constants. Fig.- 6b represents the plot of log q_e vs. logC_e and K_f & n are obtained from this plot.

Dubinin-Radushkevich (D-R) Isotherm

The model is given by equation 8[22]:

$$q_e = q_D e^{-\lambda\varepsilon^2} \tag{8}$$

The linear form of isotherm is as underwritten:

$$\ln q_e = \ln q_D - \lambda\varepsilon^2 \tag{9}$$

where, q_e (mg/g) → adsorbate remediated / unit mass of solid material, q_D (mg/g) → maximum uptake efficiency of adsorbent, λ → related to mean free energy of adsorption (E),ε (polanyi potential) = RT ln (1+(1/C_e)), where R ($\mathrm{Jmol^{-1}K^{-1}}$) → universal gas constant and T (K) → absolute temperature. The value of E is obtained from the equation written below:

$$E = \frac{1}{\sqrt{2\lambda}} \tag{10}$$

The value of *E* enables the determination of kind of adsorption phenomenon. The value of *E* from 1 to 8 $\mathrm{kJmol^{-1}}$ corresponds to physical adsorption, from 8 to 16 $\mathrm{kJmol^{-1}}$ indicates ion-exchange adsorption while the value in the range 20 – 40 $\mathrm{kJmol^{-1}}$ points towards chemisorption.

The graph between ln q_e and ε^2 (Fig.-6c) gives the values of q_D and λ (Table-1).

Temkin Isotherm

The model is represented by the equation as written below[23]:

$$q_e = \frac{RT}{b} \ln (A_T C_e) \tag{11}$$

or

$$q_e = \frac{RT}{b} \ln A_T + \frac{RT}{b} \ln C_e \tag{12}$$

Where, A_T (L/g) → Temkin isotherm equilibrium binding constant, b ($\mathrm{Jmol^{-1}}$) →Temkin isotherm constant representing adsorption heat. The graph of q_e versus ln C_e (Fig.-6d) gives $\frac{RT}{b}$ and A_T.

The various calculated values and correlation coefficients (R^2) for all isotherms are given in the Table-1. For sawdust carbon, the decreasing order of value of correlation coefficient (R^2) for different isotherms is as Langmuir > Temkin > Freundlich > D-R. The value of R^2 for Langmuir isotherm indicates close relevance to experimental results. It indicates a uniform monolayer uptake process. The value of E from D-R isotherm suggests physisorption. From Temkin isotherm, it is observed that the value of A_T is high for adsorption of divalent nickel on biosorbent under study indicating very high adsorbate-adsorbent interactions. The maximum adsorption capacity of different adsorbents for nickel uptake is compared in Table-3. It indicates that sawdust carbon adsorbent under study has larger removal efficiency.

Table-1: Calculated Parameters of Isotherm Studies

Adsorbent	Langmuir				Freundlich			D-R			Temkin		
	q_m (mg/g)	K_L	R^2	R_L for 25 mg/L	K_f	n	R^2	q_D (mg/g)	E (kJ/mol)	R^2	b	A_T	R^2
Sawdust carbon	25.4	0.109	0.973	0.268	5.984	3.448	0.717	19.29	1.003	0.573	699.68	5.46	0.89

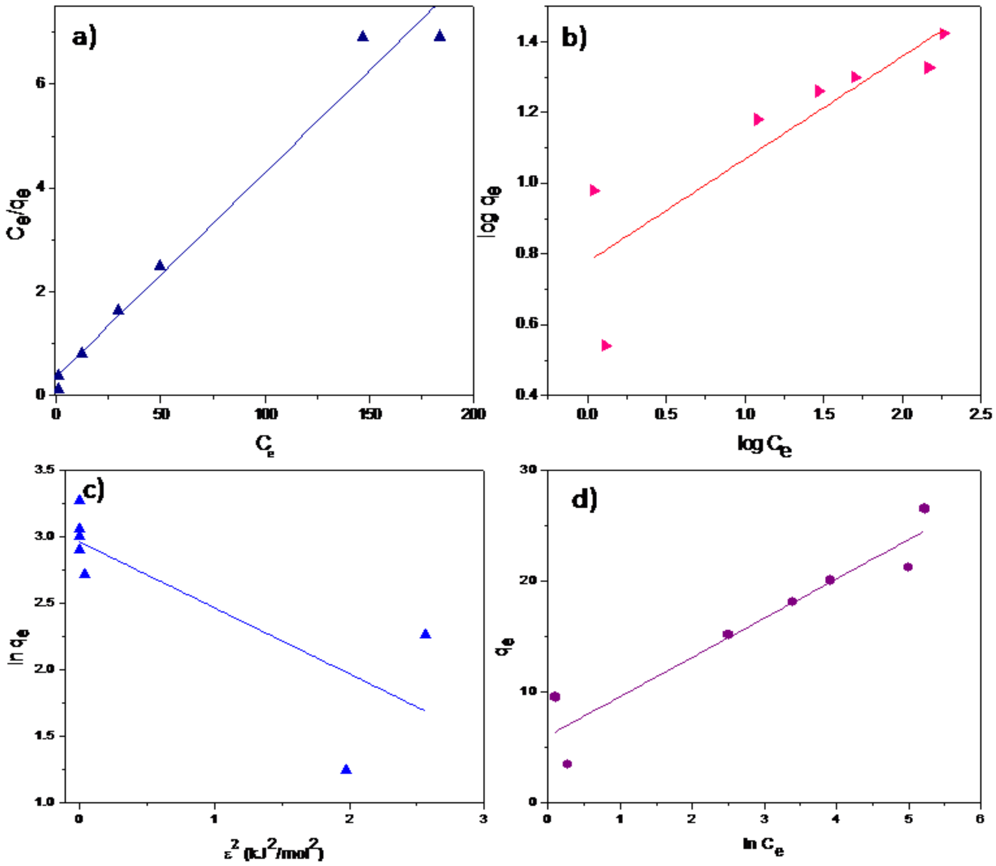

Fig.-6: Isotherm Models (a) Langmuir (b) Freundlich (c) Dubinin- Radushkevich (d) Temkin

Adsorption Kinetics

Adsorption kinetic parameters were obtained using Pseudo-first order (eq. 13)[24], pseudo-second-order (eq. 14)[25], Intraparticle diffusion (eq. 15)[26] and Elovich models (eq. 16)[27].

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (13)$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \qquad (14)$$

$$q = k_i\, t^{1/2} + C \qquad (15)$$

$$q_t = \frac{1}{\beta} \ln (\alpha\beta) + \frac{1}{\beta} \ln t \qquad (16)$$

Where q_t and q_e (mgg^{-1}) → mass of Ni (II) uptake at time t (minutes) and at equilibrium, respectively. k_1 (min^{-1}) and k_2 ($gmg^{-1}min^{-1}$) → first & second order rate constants. q (mgg^{-1}) → adsorbed metal quantity at t, C (mg g^{-1}) → relates to boundary layer thickness and k_i (mgg^{-1} $min^{-1/2}$) → intraparticle diffusion rate constant. α ($mgg^{-1}min^{-1}$) → relates initial rate of sorption and β (gmg^{-1}) → magnitude of surface covered. The graph of log (q_e - q_t) versus t (Fig.-7a) gives k_1 and q_e in pseudo-first order model. Values of k_2 and q_e in the pseudo-second order are obtained from the plot of t/q_t vs t (Fig.-7b). The parameters k_i, C (eq.15) and α, β in Elovich model are computed from plots of q versus $t^{1/2}$ and q_t versus ln t, respectively (Fig.-7c & d). The values obtained for kinetic model parameters are given in Table-2.

Table-2: Kinetic Study Parameters

Adsorbent	Pseudo-first order			Pseudo-second order			Intraparticle diffusion			Elovich model		
	k_1	q_e cal	R^2	k_2	q_e cal	R^2	k_i	C	R^2	α	β	R^2
Sawdust Carbon	$6.33x10^{-3}$	0.363	0.606	0.347	9.57	0.999	0.0348	9.155	0.528	$2.16x10^{29}$	7.782	0.703
Units →	min^{-1}	mg/g		gmg^{-1} min^{-1}	mg/g		mg g^{-1} $min^{-1/2}$			mgg^{-1} min^{-1}	g mg^{-1}	

The calculated R^2 values, infer that the adsorption of divalent nickel on sawdust carbon agrees well with pseudo-second order kinetics. The rate-determining step for scavenging of nickel metal involves both adsorbent as well as adsorbate species and the nature of interaction may be chemical.

Thermodynamic Studies

The values of ΔG°, ΔS° and ΔH° for adsorption of bivalent nickel from aqueous solution were computed by following equations[8] :

$$\Delta G^{\circ} = -RTlnK_d \tag{17}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{18}$$

$$K_d = \frac{C_a}{C_e} \tag{19}$$

$$ln\, K_d \; = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{20}$$

Where, R ($8.314Jmol^{-1}K^{-1}$) → gas constant, K_d → equilibrium constant, T (K) → temperature, C_a (mg/L) → adsorbate concentration on the adsorbent surface and C_e (mg/L) → equilibrium solution strength of adsorbate.

Values of ΔG° and ΔH° for the adsorbent showed the feasible, spontaneous and exothermic nature of adsorption phenomenon. The value of ΔS° showed a decrease in randomness indicating positive affinity between adsorbent and adsorbate during adsorption[9].

Desorption

Desorption of divalent nickel ions from metal loaded solid material was carried out with HCl of different strength. Increase in percentage desorption from 83.09 to 92.71% was observed with increase in HCl strength from 0.05 N – 0.2 N. With the increase in concentration, a number of H^+ ions are available for exchange with Ni (II) ions. Being more electronegative (electronegativity of H^+ & divalent nickel is 2.20 and 1.91, respectively) than Ni(II) ions, H^+ are able to elute Ni(II) ions from the adsorbent[28]. This resulted in an increase in percentage desorption of metal ions.

Table-3: Comparison of Adsorption Efficiency of Various Materials for Aqueous Nickel Remediation

Adsorbent	q_{max} (mg/g)	Adsorbent	q_{max} (mg/g)
Orange peel[4]	62.89	Beech sawdust[30]	4.0
Cassia fistula (Golden shower pods bark)[13]	188.4	Pigeon Pea Pod[31]	19.23
Cashew nut shell[17]	18.868	Black Carrot residue[32]	5.745
HCl treated oak sawdust[19]	3.29	Wheat straw[33]	2.5
Coir pith[28]	9.5	*Saccharomyces cerevisiae*[34]	46.3
NaOH treated coir pith[28]	38.9	Sawdust carbon (present study)	25.4
Alternanthera philoxeroides[29]	9.73		

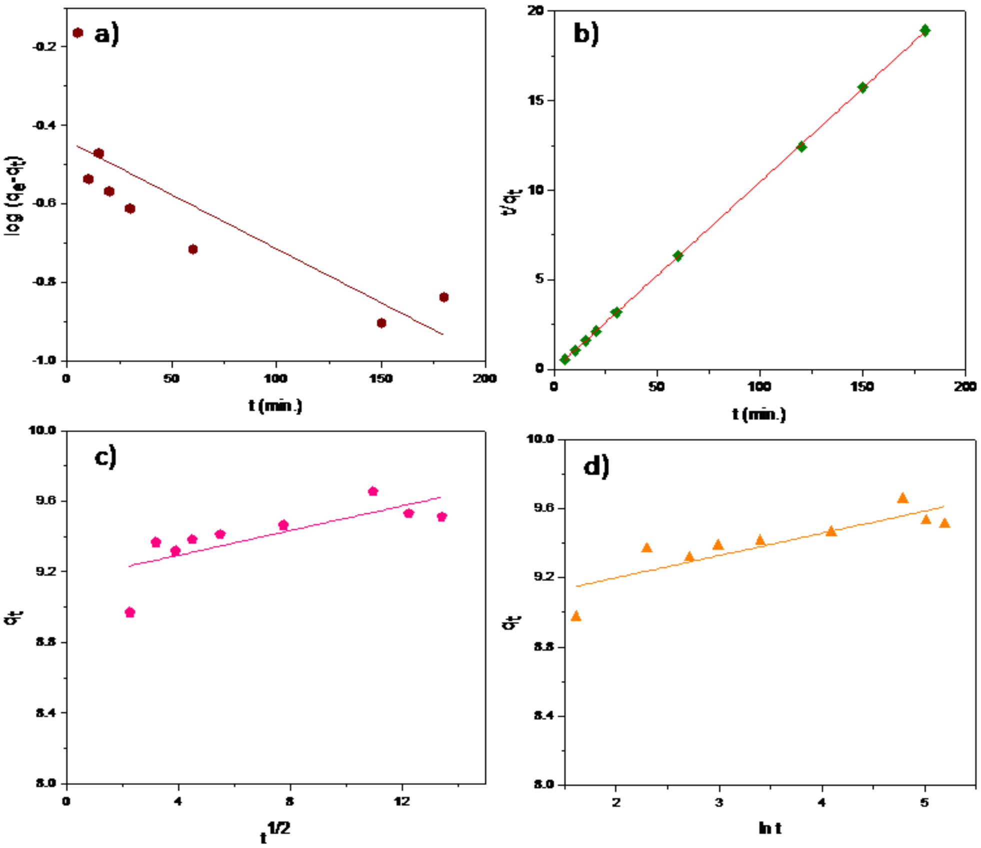

Fig.-7: Kinetic Studies (a) Pseudo-First Order (b) Pseudo-Second Order (c) Intraparticle Diffusion (d) Elovich Model

CONCLUSION

In the current study, sawdust carbon adsorbent prepared by sulphuric acid treatment of Indian Rosewood sawdust was employed for adsorption of bivalent nickel in batch mode experiments. The adsorbent is found to have notable percentage adsorption owing to the presence of large surface area as evidenced by BET surface area results. Langmuir isotherm model is found to indicate the best correlation between experimental and theoretical results pointing towards the monolayer formation and maximum monolayer adsorption efficiency is 25.4 mg/g. In kinetic studies, pseudo-second-order is best fitted to Ni (II) ions uptake. Thermodynamic parameters indicate Ni (II) biosorption to be feasible, exothermic and occurring with decreased randomness. Desorption studies with HCl (0.05-0.2N) implied that percentage desorption of nickel from metal loaded adsorbent elevates with an increase in strength of HCl. The results of percentage adsorption of processed adsorbent signify it to be economical and effective for the uptake of aqueous nickel. This study suggests that sawdust carbon can be employed for the remediation of bivalent nickel from wastewater.

ACKNOWLEDGMENT

The first author acknowledges I.K.G. Punjab Technical University, Kapurthala for facilitating research opportunity. Authors are highly thankful to Giani Zail Singh Campus College of Engineering and Technology, Bathinda for providing laboratories to do experimental work. Also, the first author is grateful to parent institution (Punjabi University, Patiala) for awarding teacher fellowship under FIP of University Grant Commission, New Delhi.

REFERENCES

1. R. Sharma and B. Singh, *Bioresour. Technol.,* **146**, 519(2013), **DOI:** 10.1016/j.biortech.2013. 07.146
2. M.H. Kalavathy and L.R. Miranda, *Chem. Eng. J.,* **158(2)**, 188(2010), **DOI:** 10.1016/j.cej.2009.12.039

3. F.A. Pavan, I.S. Lima, E.C. Lima, C. Airoldi and Y. Gushikem, *J. Hazard. Mater.,* **B137(1)**, 527(2006), **DOI:** 10.1016/j.jhazmat.2006.02.025
4. F. Gonen and D.S. Serin, *Afr. J. Biotechnol.,* **11(5)**, 1250(2012), **DOI:** 10.5897/AJ B11.1753
5. P. Thamilarasu, M. Mohan, V. Dharmalingam, R. Sharmila and K. Karunakaran, *Rasayan J. Chem.*, **7(4)**, 390(2014)
6. B. Alyuz and S. Veli, *J. Hazard. Mater.,* **167(1-3)**, 482(2009), **DOI:** 10.1016/j.jhazmat.200 9.01.006
7. U.K. Garg, M.P. Kaur, V.K. Garg and D. Sud, *Bioresour. Technol.,* **99(5)**, 1325(2008), **DOI:** 10.1016/j.biortech.2007.02.011
8. M.I. Din and M.L. Mirza, *Int. J. Biol. Macromol.,* **54**, 99(2013), **DOI:**10.1016/j.ijbiomac. 2012.11.010
9. K.G. Bhattacharyya, J. Sarma and A. Sarma, *J. Hazard. Mater.,* **165(1-3)**, 271(2009), **DOI:** 10.1016/j.jhazmat.2008.09.109
10. V.H. Waghmare and U.E. Chaudhari, *Rasayan J. Chem.*, **7(3),** 214(2014)
11. S. Xiuling, D. Huipu, L. Shijun and Q. Hui, *J. Chem.,* **2014**, 1(2014), **DOI:** 10.1155/2014/407146
12. M. Mustaqeem, M.S. Bagwan and P.R. Patil, *Rasayan J. Chem.*, **6(4)**, 307(2013).
13. M.A. Hanif, R. Nadeem, H.N. Bhatti, N.R. Ahmad amd T.M. Ansari, *J. Hazard. Mater.,* **B139(2)**, 345(2007), **DOI:** 10.1016/j.jhazmat.2006.06.040
14. M. Bansal, A. Mudhoo, V.K. Garg and D. Singh, *Int. J. Environ. Sci. Technol.,* **11(5)**, 1399(2014), **DOI:** 10.1007/s13762-013-0293-1
15. N. Kataria and V.K. Garg, *Chemosphere.,* **208**, 818(2018), **DOI:**10.1016/j.chemosphere .2018.06.022
16. D.H.K. Reddy, K. Seshaiah, A.V.R. Reddy, M.M. Rao and M.C. Wang, *J. Hazard. Mater.,* **174(1)**, 831(2010), **DOI:** 10.1016/j.jhazmat.2009.09.128
17. P.S. Kumar, S. Ramalingam, S.D. Kirupha, A. Murugesan, T. Vidhyadevi and S. Sivanesan, *Chem. Eng. J.,* **167(1)**, 122(2011), **DOI:** 10.1016/j.cej.2010.12.010
18. F. Ekmekyapar, A. Aslan, Y.K. Bayhan and A. Cakici, *J. Hazard. Mater.,***137(1)**, 293(2006), **DOI:** 10.1016/j.jhazmat.2006.02.003
19. M.E. Argun. S. Dursun, C. Ozdemir and M. Karatas, *J. Hazard. Mater.,* **141(1)**, 77(2007), **DOI:** 10.1016/j.jhazmat.2006.06.095
20. I. Langmuir, *J. Am. Chem. Soc.,* **40(9)**,1361(1918), **DOI:** 10.1021/ja02242a004
21. H.M.F. Freundlich, *J. Phys. Chem.*, **57**, 385(1906)
22. M.M. Dubinin and L.V. Radushkevich, *Chem. Zentr.*, **1**, 875(1947)
23. M.I. Temkin and V. Pyzhev, *Acta Phy. Chem, USSR*, **12**, 327(1940)
24. S. Lagergren, *K. Sven. Vetenskapsakademiens Handl.*, **24**, 1(1898)
25. Y.S. Ho and G. McKay, *Process Biochem.*, **34(5)**, 451(1999), **DOI:** 10.1016/S0032-9592(98)00112-5
26. W.J. Weber and J.C. Morris, *J. Saint. Eng. Div. Am. Soc. Civ. Eng.*, **89**, 31(1963)
27. H. Teng and C.T. Hsieh, *Ind. Eng. Chem. Res.*, **38(1)**, 292(1999), **DOI:** 10.1021/ie980107j
28. A. Ewecharoen, P. Thiravetyan and W. Nakbanpote, *Chem. Eng. J.,* **137(2)**, 181(2008), **DOI:** 10.1016/j.cej.2007.04.007
29. X.S. Wang and Y. Qin, *J. Hazard. Mater.,* **B138(3)**, 582(2006), **DOI:** 10.1016/j.jhazmat.2006.05.091
30. D. Bozic, M. Gorgievski, V. Stankovic, N. Strbac, S. Serbula and N. Petrovic, *Ecol. Eng.,* **58**, 202(2013), **DOI:** 10.1016/j.ecoleng.2013.06.033
31. J. Aravind, S. Muthusamy, S.H. Sunderraj, L. Chandran and K. Palanisamy, *Int. J. Ind. Chem.,* **4**, 25(2013), **DOI:** 10.1186/2228-5547-4-25
32. F. Guzel, H. Yakut and G. Topal, *J. Hazard. Mater.,* **153(3)**, 1275(2008), **DOI:** 10.1016/j.jhazmat.2007.09.087
33. M. Gorgievski, D. Božić, V. Stanković, N. Štrbac, and S. Šerbula, *Ecol. Eng.*, **58**, 113(2013), **DOI:** 10.1016/j.ecoleng.2013.06.025
34. A. Ozer and D. Ozer, *J. Hazard. Mater.,* **100(1-3)**, 219(2003), **DOI:** 10.1016/S0304-3894(03)00109-2

[RJC-5279/2019]