

Removal of Ni (II) Ions on to Polymer Loaded Sawdust (PLSD) – Batch Adsorption Studies

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Abstract

Heavy metal ions are intensively polluting water is a major environmental problem and removal of those ions is highly important because of their toxic nature. In this present study, carbonized sawdust was impregnated with poly (sodium 4-styrene sulphonate) (PSSS) to enhance the metal affinity and selectivity via surface chelating ion-exchange as well as hydrogen bonding adsorption mechanism. An adsorbent characteristic was analyzed through Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and BET analysis. The process variables such as feed concentration, agitation speed, temperature effect and pH of the solution were optimized by adsorption studies for the analysis of Ni (II) ions removal. Various isotherm models were fixed with experimental data to explain the interaction of solute with adsorbent in batch studies. Kinetic behavior of different kinetic models and thermodynamic properties was also determined. The best isotherm in this study was selected by error analysis (χ^2 test) and the stability of adsorbents was also confirmed through desorption studies.

Keywords: Sawdust carbon; Polymer-ionomer; Morphology of adsorbent; Nickel (II); Ions and adsorption

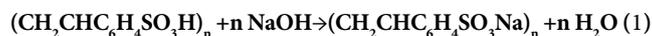
Introduction

Due to heaviness, bio-accumulating tendency and toxicity, heavy metal ions is contaminated water by industrial wastes is causes severe health defects to human life. Among various harmful industrial pollutants, pollution by heavy metal is the major problem. Nickel is one of the heavy metal and its exposure at higher concentration causes lungs cancer, nose and bone cancer, gastrointestinal distress, dermatitis etc. [1]. The main sources of heavy metals are mining and industrial wastes such as vehicle emission, batteries, fertilizers, metal finishing, paints, forging and treated woods, its concentration from these industries varies between 6 and 12 mg/L. The tolerable limit of Ni presence in drinking water level is 0.01 mg/L and the industrial discharge limit in wastewater is 2 mg/g reported by Worlds Health Organization (WHO) [2]. Agricultural and marine waste materials are converting into adsorbents was mainly concentrated from the past decade. Among those, sawdust and chitosan are the most promising adsorbent for removing these heavy metals from water and wastewater. Sawdust is one of the cheapest biomass having the constituents of cellulose (55-60%), hemicelluloses (20-25%), lignin (20-25%). The functional groups present in sawdust molecules are such as acetamido groups, phenol, carbonyl, sulphhydryl carboxyl groups, structural polysaccharides, amido groups, amino groups, esters and alcohols and these groups have the metal complexation affinity [3,4]. Different research workers have been reported the complexation behavior of various functional groups present in heavy metals during biosorption process using spectroscopic techniques. To enhance the capability and efficiency, pretreatment and surface modifications may be needed [5].

Due to its high surface area and easy availability, activated carbon is widely used as an adsorbent. Removal of Ni (II) ions from water and effluents using different forms of activated carbons as adsorbent are reported [6-10]. In recent years, several non-conventional and less expensive adsorbents are used for the removal of Ni (II) ions such as sphagnum peat, blast furnace slag, apple waste, soybean and cottonseed husk, peat nut husk carbon, straw, rice husk, treated saw dust and

activated alumina and silica gel [11-18]. Activated carbons are treated with acid, bases and oxidizing agents to enhance their surface activity. Enhancement of binding ability of the sawdust is modified with some other materials, such as dyestuff, hexamine, polyacrylamide, cross-linked polyethylenimine or other chemicals to introduce more extra active sites like -N, -S, and -P [19].

For example, divalent ions were effectively removed from an aqueous solution by using polysulfide treated sawdust have been reported. Surface modification of carbonized sawdust by impregnation of chelating polymer improves the metal affinity and selectivity for the adsorption of heavy metal through complexation mechanism. Poly-(Sodium 4-Styrene Sulphonate) (PSSS) is one of the metal-chelating biocompatible polymers. Polystyrene sulfonates polymers are combined structured of polystyrene and sulfonic acid or sulfonate functional groups. Polystyrene sulfonates are linear polymer, water soluble and white in colour when very pure. The cross-linked material (called a resin) typically appears amber in color because the sulfonic acid group (-SO₃H) is strongly acidic, this polymer neutralizes bases and produce various salts leading to Na and Ca.



These ion-containing polymers are called PSSS are widely used to remove ions from a solution in technical and medical applications [20]. PSSS is used to indicate potassium binders in acute and chronic

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kidney disease for patients suffering from hyperkalaemia (high blood serum potassium levels), which may result in weakness irregular heartbeat. Hence this present paper is intend the preparation and characterization of PSSS polymer impregnated carbonized sawdust which was used as an economic viable modified adsorbent, Polymer Loaded Saw Dust (PLSD) for the removal of Ni (II) ions from aqueous solutions. Adsorption isotherms and kinetic behavior analysis were studied to explain the solute interaction mechanism and predict the thermodynamic properties of adsorption process to assess the spontaneous nature. χ^2 Test statistics were used for the determination of best-fitting isotherm with the experimental data. Retaining of metal ions in non-labile forms is shown in regeneration studies.

Materials and Methods

Materials

Sawdust was purchased from the local saw mill. The polymer, Poly Sodium 4-Styrene Sulphonate (PSSS) was used for impregnation. Ni (II) stock solution was prepared by using Nickel sulphate hexahydrate and double distilled water. Addition of HCl and NaOH is maintained the pH level of the solution. Analytical grade reagents of dimethyl glyoxime, ammonium solution were used for analyzing the Ni (II) ions.

Preparation of polymer impregnated carbonized sawdust: A procedure similar to that followed for the preparation of sawdust - chitosan composite beads [21] was followed. Sawdust was sieved by sieve plate to obtain the uniform size (0.5 mm) of particles and was treated with concentrated sulphuric acid (50 mL per 10 g) for 2 h to get carbonized sawdust powder. And then treated with sodium carbonate (0.1 N) for neutralization till the effervescence stops and dried again in hot air oven at 100°C. The product obtained after carbonization was treated with 60% PSSS (1:1% wt/v of carbonized sawdust and PSSS stirred at room temperature in a rotary shaker for about 24 h at 200 rpm. Then, the mixture was washed thoroughly using distilled water until the pH of rinsed water was found to be neutral. Finally the samples were dried in a hot air oven at 100°C.

Characterization of adsorbents: Carbonized materials were analyzed by using GeminiV2.00 Micromeritics to determine the specific surface area. Hitachi S3000H Scanning Electron Microscope was used for analyze the surface morphological structure. Functional groups analysis was carried out using Perkin Elmer spectrum RXI FTIR spectrophotometer.

Batch Adsorption: To determine the equilibrium time and agitation speed for a known concentration of initial metal ion solution through adsorption studies. Batch adsorption studies were carried out to investigate the effect of initial metal ion concentration, adsorption dosage and pH of the solution at equilibrium time and agitation speed in rotary shaker. Whatmann filter paper was used for the filtration of supernatant and the concentrations of Ni (II) ions were determined using UV/visible spectrophotometer at a wavelength of 440 nm. The adsorption capacity (q_e mg/g) and % removal were calculated using Equations (2) and (3), respectively.

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

$$\text{Percentage Removal} = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \quad (3)$$

Where C_o : Concentration of Ni (II) ion at initial (mg/L)

C_e : Concentration of Ni (II) ion at any instant (mg/L)

V: Volume of the solution (L)

W: Mass of adsorbent (g)

Results and Discussion

The characterization of polymer treated carbonized sawdust is given in detail as follows.

BET Analysis

The specific surface area of untreated and polymer treated carbonized sawdust were found to be 13.6 m²/g and 114.3 m²/g, respectively. The increase in the surface area of polymer treated carbonized sawdust is due to the well impregnation of polymer into carbonized sawdust.

SEM analysis and FTIR spectrum

According to the image, sawdust particles were homogeneously dispersed and good adhesion between the particles and polymer matrix was evident. This is due to the presence of the hydrophilic, hydroxyl on the surface of lingo-cellulosic which resulted with aggregation of polymer matrix [22]. So this Morphological study shows better interfacial bonding between fiber and matrix. The image exhibits roughness, more crisp, cracked and many pores were clearly found on the surface (Table 1).

This table and FTIR spectrum show the presence of surface polar functional group such as amino, carbonyl, hydroxyl, aliphatic C-H, conjugated C=C, C-N, asymmetric -SO₃, etc. The shifts in the position of peaks before and after Ni (II) ions loading indicates that metal ion well associated with the binding centers of atom containing O, N, S and aromatic ring, etc [23-25]. The anionic surface modifications of PLSD is indicated by the observed change in position of peaks of asymmetric sulphites (ie., from 1197.21 cm⁻¹ to 1207.53 cm⁻¹), conjugated C=C in benzene (ie., from 1613.48 cm⁻¹ to 1712.60 cm⁻¹) and (C=S) stretching (ie., from 1028 cm⁻¹ to 1034 cm⁻¹). Stretching and bending frequencies are responsible for the incorporation of heteroatom in activated carbon matrix (PLSD) (Figures 1 and 2).

Effect of variables

Determination on the effect of pH, initial metal ion concentration, contact time and agitation speed on adsorption capacity of PLSD for the removal of Ni (II) ions from aqueous solution were analyzed by Batch adsorption studies and the results are illustrated in (Figures 3-6) respectively.

At pH=5, the sorption capacity is more and Ni (II) ions exist as Ni²⁺, Ni(OH)⁺, Ni(OH)₂. In adsorption process, the initial Ni (II) ions concentration acts as a driving force to overcome the mass transfer

Functional groups	PLSD	Ni- loaded PLSD
O-H (H bonded)and NH stretching	3412.95 cm ⁻¹	3364.37 cm ⁻¹
Aliphatic C-H stretching and N-H stretching	2923.51 cm ⁻¹	2930.13 cm ⁻¹
O-H & S-H stretching in acid group	2358.04 cm ⁻¹	2360.17 cm ⁻¹
Conjugated C=C in benzene& N-Hbending in amine	1613.48 cm ⁻¹	1712.60 cm ⁻¹
C-N stretching(or)asymmetric-SO3 group		
(C-O), (C=S)stretching, O-H bending	1197.21 cm ⁻¹	1207.53 cm ⁻¹
Aromatic ring	1027.67 cm ⁻¹	1034.87 cm ⁻¹
Wagging of -NH	669.62 cm ⁻¹	798.68 cm ⁻¹
	537.72 cm ⁻¹	638.25 cm ⁻¹

Table 1: Functional groups present in PLSD and Ni-loaded PLSD using FT-IR spectra.

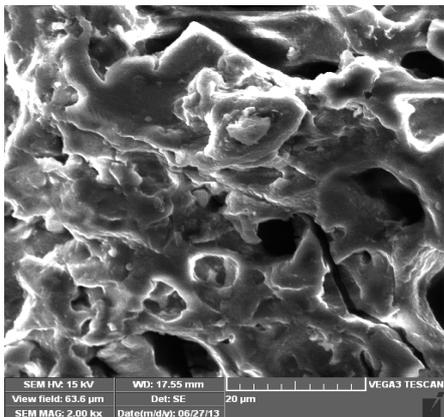


Figure 1: SEM image of PLSD.

The rate of adsorption initially increases and then gradually remains constant with increase in contact time and the equilibrium is reached nearly at 180 min for PLSD is shown in (Figure 5). At the initial stage, more number of surface sites is available for the adsorption and after a lapse of time, the occupation of remaining surface sites are difficult due to the repulsion between the solid and bulk phases of solute molecules [17,18]. Adsorption of Ni (II) ion is required 180 min to attain equilibrium. The equilibrium period does not change with the change of initial concentration of the metal ion solution is observed from the figure.

Figure 6 establishes that the rate of adsorption increases with agitation speed. The maximum 94% sorption is obtained at 200 rpm beyond which the increase is not significant. This is happened because of proper contact between the metal ion and active site is developed when increasing the agitation speed. Thus increase of the agitation speed improves the diffusion of Nickel ions towards the surface of the adsorbents. Hence the equilibrium agitation speed was fixed at 200 rpm.

The adsorption capacity of Ni (II) ions onto PLSD was determined at different temperatures and the results show that the uptake of Ni (II) ions onto PLSD increases with increasing temperature, implying that the adsorption capacity largely depend on the indirect interaction between the functional groups on the PLSD surface and adsorbate [26,27]. The increase in adsorption capacity may be due to the formation of some new adsorption sites, the enlargement of the pores during surface modification of adsorbent and also the significant role of increased rate

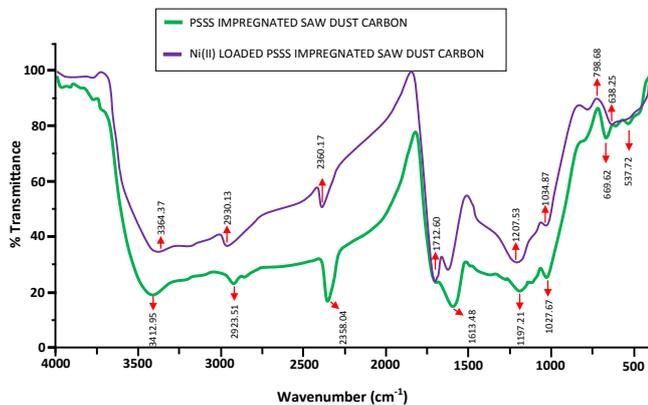


Figure 2: FTIR spectra of PLSD before and after loading of Ni (II) ions.

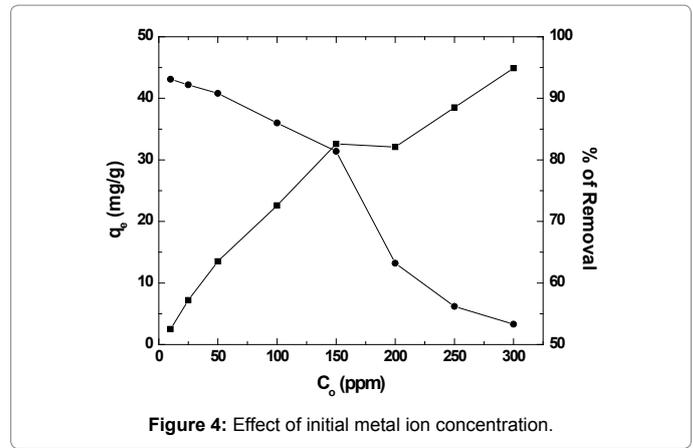


Figure 4: Effect of initial metal ion concentration.

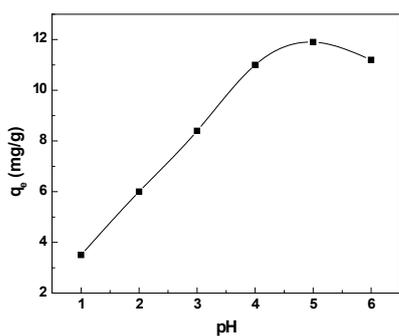


Figure 3: Effect of pH.

between the adsorbent and adsorbate. At pH=5, ionic and non-ionic active species of adsorbate may be adsorbed on the anionic surface with the formation of surface ion-exchange as well as hydrogen bonding ion pair complex between electron donating sites of PLSD and electron deficient nickel ions. The favorable removal of Ni (II) at higher pH is related with increasing negative charge density onto PLSD [19]. In the present study, the adsorption capacity increases from 2.5 mg/g to 43.7 mg/g and percentage removal decreases from 98.8% to 58.2% in the initial concentration ranging from 10 ppm to 300 ppm with same contact time and adsorption temperature (Figure 4).

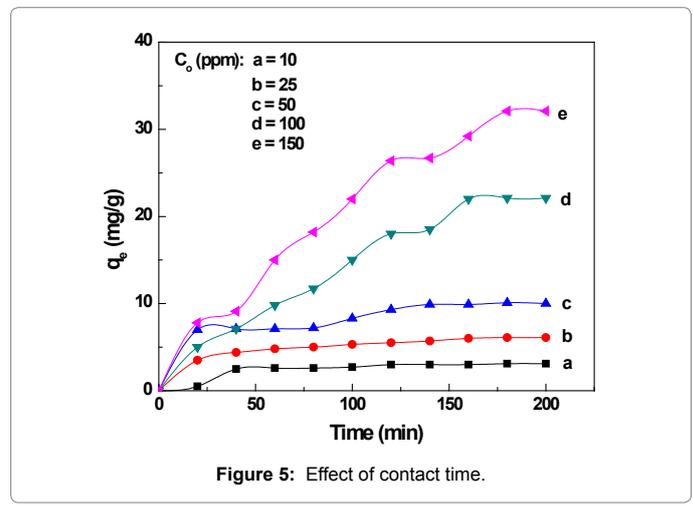


Figure 5: Effect of contact time.

of intraparticle diffusion in the initial stage of adsorption into the pores at higher temperature leading to the endothermic adsorption. The results are compiled in (Table 2).

The ΔG° , ΔH° and ΔS° values calculated at 303 K are -2.70 kJ/mol, 31.87 kJ/mol and 114.2 J/K/mol, respectively and the energy of activation ($E_a = \Delta H^\circ + RT$) is 34.39 kJ/mol. These thermodynamic parameters can be explained the interaction nature of the adsorbent-adsorbate. If the E_a value less than +42 kJ/mol points out that the adsorption process here is not a chemically-controlled one. ΔG° varies from -2.70 kJ/mol to -7.20 kJ/mol with temperature ranging from 303 K to 343 K, implying that ΔG° becomes more negative at higher temperatures. The negative ΔG° and positive ΔH° and ΔS° indicate that this is a feasible, spontaneous, endothermic, increased randomness of heterogeneous adsorption through physical phenomena.

Adsorption isotherm

The interaction of solute in the liquid phase and the adsorbent in solid phase is illustrated by adsorption isotherm. So many models of analyzing adsorption isotherm behavior [28] are available to fit the experimental data. Using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) adsorption isotherm models for quantify the adsorption capacity of adsorbents for the adsorption of Ni (II) from aqueous solution. Langmuir isotherm indicates surface homogeneity and monolayer adsorption by the separation factor, R_L which is between 0 and 1 for favorable adsorption. Surface heterogeneity and multilayer sorption determined by Freundlich isotherm. Temkin model considers the effects of adsorbent-adsorbate interaction. Dubinin-Radushkevich (D-R) Model is used to determine the adsorption occurred is physical or chemical in nature. The adsorption potential (ϵ) is depends on the nature of the adsorbent and adsorbate but independent of the temperature. The mean free energy of the adsorption E , which is the free energy for the transfer of one mole of metal ions from the infinity to the surface of the adsorbent, provide information about the nature

of adsorption either chemical ion exchange or physical ion exchange adsorption. The values of E lies between 8 and 16 kJ/mol depicts the adsorption process follows the chemical ion-exchange and if $E < 8$ kJ/mol, the adsorption process is of a physical ion-exchange via weak electrostatic nature [29,30]. The linearized form of these isotherms were applied to the adsorption of Ni (II) on to PLSD and the constants obtained from the slope and intercept of the plots have been compiled in Table 2.

Selection by error analysis

The linear regression and the non-linear χ^2 analysis gave different models as the best-fitting isotherm for the given data set, thus indicating a significant difference between the analytical methods. Non-linear χ^2 test provided a better determination for the experimental data [31]. In this analysis, correlation coefficient (r^2) and χ^2 test statistics were used for the determination of best-fitting isotherm with the experimental data.

The mathematical derivation was given by the equation (4).

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (4)$$

where, $q_{e,m}$: equilibrium capacity (mg/g) calculated from model

q_e : equilibrium capacity (mg/g) calculated from experimental data.

χ^2 Would be a small number and vice versa when the data from model are similar to the experimental data [31]. In linear analysis, the regression coefficient (r) and coefficient of determination (r^2) value will affect significantly of the final determination. It can be avoided by using nonlinear chi square test analysis.

Figure 7 shows the equilibrium adsorption of Ni (II) ions onto PLSD and the isotherms are plotted together with the experimental data. Both Temkin and Freundlich models show good fit with the experimental data. But Temkin has the lowest chi-square value (=3.14) and moderately high r^2 (=0.941) which indicates the favorable indirect interaction (larger B value) between ions and solid surface. Even though the Langmuir has the highest r^2 (=0.982) and chi-square value (=58.64) suggests that the adsorption is not homogeneous. Similar contradict observations were reported [32]. Chatterjee et al., (2009) through the application of correlation coefficients (r^2) and χ^2 error analysis. The mean free energy for adsorption ($=1.39$ kJ/mol) through DRK isotherm justifies weak forces are used in this ion-exchange adsorption. (if E is less than 8 kJ/mol the process is of physical nature.) So Temkin

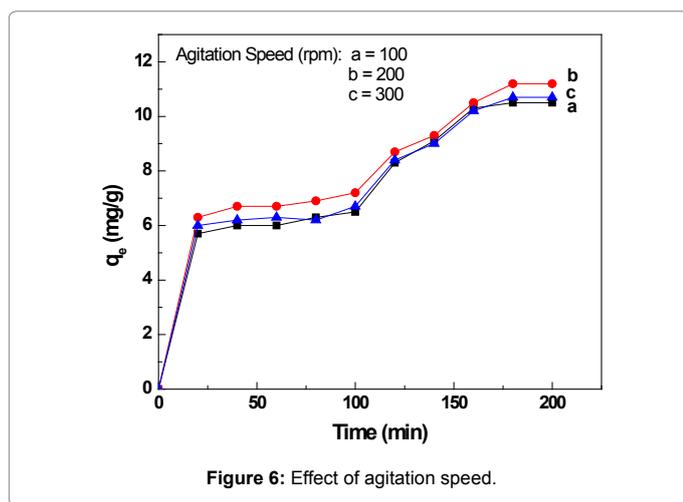


Figure 6: Effect of agitation speed.

T, K	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° J/K.mol	$T\Delta S^\circ$ kJ/mol	E_a kJ/mol	R^2
303	-2.70	31.87 ± 1.27	114.2 ± 4.0	34.59	34.39	0.990
313	-3.90			35.73		
323	-4.88			36.87		
333	-6.30			38.01		
343	-7.20			39.15		

Table 2: Activation parameters for Ni (II) adsorption on PLSD.

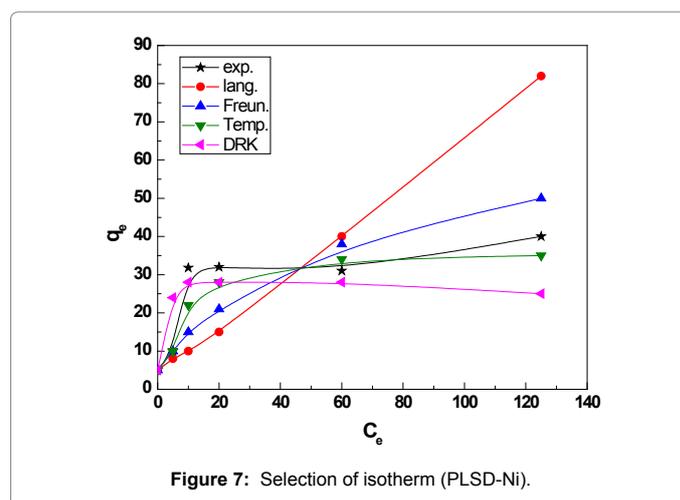


Figure 7: Selection of isotherm (PLSD-Ni).

S. No.	Isotherm Model	Equation	Constants for PLSD	r ²	x ²
1	Langmuir	$C_e/q_e = 1/b + C_e/\theta$ $K_L = (\theta/b)$ $R_L = 1/(1 + bC_0)$ (i.e. $C_0 = 50$ ppm)	$\theta = 44.1$ mg/g $b = 0.144$ Lmg ⁻¹ $K_L = 6.34$ Lg ⁻¹ $R_L = 0.122$	0.982	58.64
2	Freundlich	$\ln q_e = \ln K_{F+} + 1/n \ln C_e$	$n = 2.42$ $K_F = 7.33$ L g ⁻¹	0.960	5.7
3	Temkin	$q_t = B \ln K_T + B \ln C_e$	$B = 6.042$ $K_T = 6.25$ L g ⁻¹	0.941	3.14
4	Dubinin-Radushkevich isotherm	$\ln qe = \ln q_m - \epsilon t^2$ $\epsilon = RT \ln(1 + 1/C_e)$ $E = (2k)^{-0.5}$	$q_m = 27.58$ mg/g $K = 0.258$ mole ² /J ² $E = 1.39$ kJ/mol	0.715	18.26

Table 3: Summary of parameters for various isotherm models

S. No.	Kinetic model	Linear equation	Constant for PLSD (50 ppm)
1	Pseudo first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$k_1 = 1.34 \pm 0.22 \times 10^{-2}$ min $R^2 = 0.863$
2	Pseudo second order	$t/q_t = 1/k_2 q_e^2 + t/q_e$ $h = k_2 q_e^2$	$q_e = 14.1 \pm 1.2$ mg/g; $k_2 = 1.50 \pm 0.05 \times 10^{-3}$ g/mg.min; $h = 2.98$ mg/g.min; $R^2 = 0.951$
3	Simple Elovich	$q_t = \beta \ln \alpha + \beta \ln(\alpha \beta)$	$\alpha = 0.17$ mg/g.min $\beta = 2.52$ g/mg $R^2 = 0.844$
4	Intra particle diffusion	$q_t = k_{id} t^{0.5} + c$	$k_{id,1} = 0.34$ mg/g min ^{0.5} $c_1 = 4.931$ mg/g $R^2 = 0.924$ $k_{id,2} = 0.748$ mg/g min ^{0.5} $c_2 = 1.529$ mg/g $R^2 = 0.948$

Table 4: Summary of parameters for various kinetic models

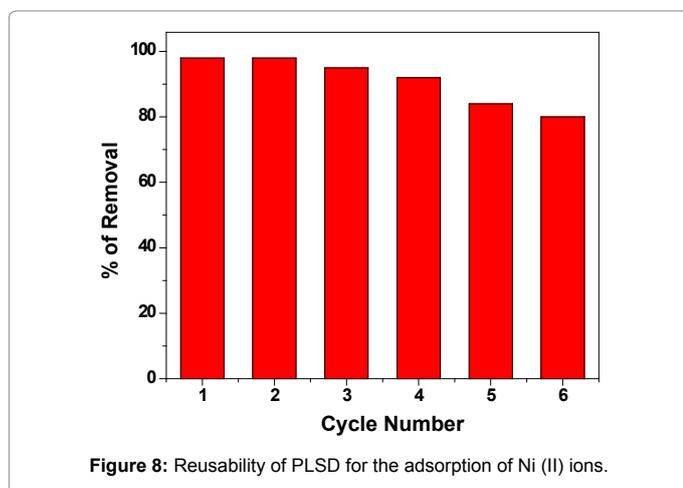


Figure 8: Reusability of PLSD for the adsorption of Ni (II) ions.

model shows a good fit with the experimental data and the values of the heterogeneity factor ($n > 1$) indicates the heterogeneous adsorption through physical phenomena.

Adsorption kinetics

Kinetic data showed better fit of pseudo second order but the rate is also influenced by intra particle diffusion [33]. But the gradual intra particle diffusion stage is not the rate controlling step, since the line does not pass through origin. The multi-linearity plot of intra particle diffusion model explained the initial linear portion indicates the boundary layer diffusion effects and the final linear portion is the result of intra particle diffusion effects. This can be attributed to the instantaneous utilization of the most readily available sites on the PLSD. The boundary layer thickness values indicate that the larger intercept and greater boundary layer effect. So, the intra particle diffusion

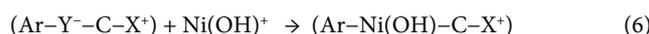
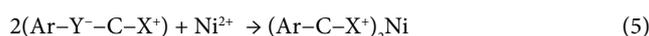
played significant role at the initial stage of adsorption process [34]. The Pseudo second order model indicates rapid adsorption initially due to ion-exchange and followed by slower adsorption because of diffusion of ions into pores for longer duration. The better-fit of intra particle diffusion method rather than simple Elovich indicates that the significance of acid-base as well as ion-pair sorption occurs between the Nickel ions and activation sites of PLSD.

Adsorption mechanism

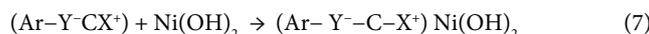
The adsorption of Ni (II) ions onto PLSD occurs as multistep process [19] involving (i) Initially ion-exchange rapidly because of weak electrostatic force of attraction between solid-solute interfaces and (ii) diffusion of ions then into the pores slowly by endothermic chemisorptions with active sites of adsorbent. So this chemisorption mechanism is evidenced by pseudo second order kinetics, intra particle diffusion and activation parameters. Finally the equilibrium is reached due to bonding with binding centers of surface functionality of the surface modified carbonized sawdust (PLSD).

The adsorption mechanisms are shown in the following equations (5-7):

For Ni (II) ions: (Ion exchange)



(And Hydrogen bonding)



Ar is the matrix of the PLSD with X⁺ & Y⁻ binding centres such as -O, -N, -S, (C-H), (-C=C), (C-O), (C-N), etc.

In aqueous solution at pH 5 the active forms of Ni (II) ions are Ni²⁺, Ni(OH)⁺, Ni(OH)₂ [19]. The positive charged active species of metal ions may be heterogeneously adsorbed with the formation of surface ion-exchange complex between electron donating sites of PLSD and electron accepting nature of Nickel ions through physical phenomena. Moreover, the metal ions may be neutral at this high pH (ie., Ni(OH)²) and also be adsorbed by hydrogen bonding mechanism along with ion-exchange.

Regeneration studies

Consecutive adsorption and desorption studies [23] were repeated six times by using the same adsorbent and is shown in Figure which indicate stability of the adsorbent. Metal ions are retained by the matrix in non-labile forms is evident by the multi-linearity plot of intra particle diffusion model and acid-base reactions are more effective for their displacement than complexation processes.

Conclusion

In this paper, the PLSD is derived through the impregnation of chelating biocompatible polymer PSSS on agricultural waste product of sawdust. The comparable performance of this low cost bio-sorbent is recommended since PLSD is relatively economically cheap, availability, regenerate, eco-friendly and shows high affinity of Ni (II) ions (ie.,) >90% removal at pH 5.0 evidenced by BET, SEM and FTIR results. Under experimental conditions, the existence of ionic and non-ionic forms of nickel ions (Ni^{2+} , $\text{Ni}(\text{OH})^+$, $\text{Ni}(\text{OH})_2$) are well adsorbed by ion-exchange as well as hydrogen bonding mechanism with the formation of surface complex. The increase in adsorption capacity may be due to the formation of some new adsorption sites on the surface, the enlargement of the pores on the adsorbent, specific surface area. The intra particle diffusion of Ni (II) ions into the pores of PLSD leads to the spontaneous endothermic chemisorption which is confirmed by the thermo dynamical parameters and the rate is also influenced by intra particle diffusion. Based on r^2 and χ^2 equilibrium isotherm for Ni (II) ions onto PLSD best represented by Temkin isotherm of multilayer ion exchange along with hydrogen bonding sorption via weak electrostatic forces.

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