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Removal and recovery of Ni(II) ions from synthetic wastewater using surface modified *Strychnos potatorum* seeds: experimental optimization and mechanism

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ABSTRACT

Strychnos potatorum seeds have been utilized for the preparation of adsorbent, surface modified *S. potatorum* seeds (SMSP), by sulfuric acid treatment with 1:2 ratios of precursor to sulfuric acid. The adsorption process depends on the solution pH, adsorbent dose, contact time, initial Ni(II) ions concentration, and temperature. The adsorption kinetics of Ni(II) ions removal by the SMSP was relatively fast and it reaches the equilibrium at 30 min. The maximum removal of Ni(II) ions was observed at an optimum conditions: pH of 5.0, adsorbent dose of 5 g/L, contact time of 30 min, and at temperature of 30°C for an initial Ni(II) ions concentration of 100 mg/L. In order to investigate the adsorption kinetics for the removal of Ni(II) ions by SMSP, pseudo-first-order and pseudo-second-order kinetic models were studied. It was observed that the pseudo-second-order kinetic model fits the experimental data better than the pseudo-first-order kinetic model with good coefficient of determination values. Adsorption mechanism was discussed with different models such as intraparticle diffusion, Boyd kinetic, and shrinking core models. It was observed that the adsorption process was controlled by both film and particle diffusion. The effective diffusivity and diffusivity values were estimated from the Boyd kinetic and shrinking core models, respectively. Adsorption isotherm data were tested with the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich models. It was observed that the Freundlich model fits the isotherm data better than other isotherm models with good coefficient of determination values. The Freundlich constant "*n*" was found to be of 3.888 g/L which indicates that the adsorption of Ni(II) ions onto the SMSP followed the physical process. The thermodynamic parameters such as change in free energy, enthalpy, and entropy were also calculated. It was found that the adsorption process was spontaneous and exothermic in nature.

Keywords: Adsorption; Isotherms; Kinetics; Mechanism; Ni(II) ions; Thermodynamics

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1. Introduction

The pollution of aquatic system has been increased mainly because of the presence of the heavy metal ions, particularly, nickel, in the wastewater which is generated from the electroplating and vegetable fat producing industries, metal mining, and processing as well as other industrial, urban, and agricultural activities. The excess amount of nickel in water causes adverse health effects such as cancer, skin allergy, and lung fibrosis to the human beings. According to the Bureau of Indian Standards, the permissible limit of nickel in drinking water is 0.02 mg/L [1]. Hence, the removal and recovery of nickel from water and wastewater is highly important to protect the living environment. For the separation of nickel from aqueous solution, treatment methods like chemical precipitation, coagulation, solvent extraction, reverse osmosis, distillation, complexations, ion exchange, and adsorption have been found to be effective [2–4]. However, these treatment methods have several disadvantages which include incomplete metal ions removal, higher amount of reagent and energy requirements, and the generation of secondary waste i.e. toxic sludge which requires proper treatment and further disposal facilities. Generally, at low metal ions concentrations, the removal of metal ions is more effective by ion exchange process or adsorption onto activated carbon process [2]. However, the huge capital and regeneration cost of the activated carbon and also the ion exchange resins have resulted in the search of new low-cost adsorbents for the removal of metal ions from the aqueous solution.

The different low-cost adsorbents that were already reported for the removal of nickel ions from the aqueous solutions are as follows: sulfuric acid-treated cashew nut shell [3], orange peel [5], H_3PO_4 treated rice bran [6], mango peel [7], modified coir pith [8], coir pith [8], meranti sawdust [9], barely straw untreated [10], cashew nut shell [11], tea factory waste [12], *Parthenium hysterophorus* L. activated carbon [13], Irish peat moss [14], corncobs [15], dye-loaded sawdust [16], dye groundnut shells [16], *Moringa oleifera* seeds [17], etc.

The objective of this study is to prepare the surface modified *Strychnos potatorum* seeds (SMSP) by sulfuric acid treatment and to investigate its adsorption potential towards the removal of Ni(II) ions from the aqueous solution. The removal of Ni(II) ions from aqueous solution by the SMSP was measured as a function of initial solution pH, adsorbent dose, contact time, initial Ni(II) ions concentration, and temperature. The adsorption kinetic data were analyzed by the pseudo-first-order and pseudo-second-order kinetic models. These kinetic data were further applied to the different adsorption models such as intraparticle diffusion, Boyd kinetic, and shrinking core models to check the adsorption mechanism. The adsorption equilibrium data were analyzed by the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich adsorption isotherm models. Scanning electron microscopic (SEM) analysis was also employed to understand the surface morphology of the prepared SMSP for the removal of Ni(II) ions. The thermodynamics of the adsorption process was also investigated.

2. Experimental

2.1. Materials

$NiSO_4 \cdot 6H_2O$ salts was supplied by Merck Chemicals, India. All the chemicals were of analytical reagent grade. Ni(II) stock solutions of 500 mg/L were prepared by dissolving measured quantity of salt (2.239 g) in one liter of double distilled water. The Ni (II) ions with different concentrations were obtained by dilution of the stock solutions.

2.2. Preparation of SMSP seeds

Collected *S. potatorum* seeds (Pudukkottai District, Tamilnadu, India) were washed several times with water and allowed to dry in sun light and then made into powder. About 40 g of dried powdered seeds was treated with the required quantity of concentrated sulfuric acid of 16 mol/L (1:2 ratio of powder to acid) to form a mixture and keep the mixture for about 24 h. The excess acid present in the mixture was removed by adding double distilled water to the mixture until the pH of supernatants reached the constant pH value of 7.0. This wet solid material was dried at 80˚C till the moisture content was completely removed from the solid material. Finally, the dried solid material was grounded and then sieved to obtain the average particle size of 0.354 mm. This prepared material was called as SMSP seeds and it was applied for the removal of Ni(II) ions from the aqueous solution.

2.3. Analysis methods

The surface morphology of the synthesized adsorbent, SMSP, was characterized by SEM analysis using a Quanta 200 FEG SEM at an accelerating voltage of 20 kV, and with a working distance of 50 μm. The concentration of Ni(II) ions in the solution, before and after treatment, was analyzed by using atomic absorption spectrometer (AAS, SL176 Model, Elico Limited, Chennai, India; Lamp details: Hollow cathode lamp, analytical lines = 232 nm, operating current = 10 mA, flame type = air-acetylene). The solution pH was measured with a pH meter (Li 617 Model, Elico Limited, Chennai, India).

2.4. Batch adsorption experiments

All batch adsorption experiments were carried out in an incubation shaker at 180 rpm (Orbital incubation shaker, Royal Testing Equipment, Chennai, India). The known quantity and quality of Ni(II) ions solutions were taken in a 100 mL stoppered conical flasks. The pH of the solution was adjusted using 0.1 mol/L HCl or 0.1 mol/L NaOH. The measured quantity of adsorbent is added to the Ni(II) ions solution in conical flasks. After the adsorption process, the spent SMSP was separated from the solutions by using centrifugation operation and the final concentration of Ni(II) ions in the supernatant was determined by using an AAS. The percentage removal of Ni(II) ions was estimated by the following equation:

$$\%\ \mathrm{Ni(II)\ removal} = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where C_i and C_f are the initial and final Ni(II) ion concentrations in the solution (mg/L), respectively.

2.4.1. Adsorption kinetics and mechanism

Batch adsorption kinetic studies were performed by mixing 0.5 g of SMSP with 100 mL of Ni(II) ions solution with the concentrations of 100–500 mg/L at a pH of 5.0 in 100 mL stoppered conical flasks. Then, the conical flasks were kept in an incubation shaker. The samples were withdrawn at preselected time intervals ranging from 10 to 60 min and the residual Ni(II) ions concentrations were determined after the centrifugation operation. The amount of Ni(II) ions adsorbed onto the SMSP at time t, q_t (mg/g), was estimated by the following equation:

$$q_t = \frac{(C_i - C_t)V}{m} \tag{2}$$

where C_t is the concentration of Ni(II) ions in the solution at time t (mg/L), V is the volume of Ni(II) ions solution (L), and m is the mass of the adsorbent (g). The adsorption kinetic data were applied to the pseudo-first-order [18] and pseudo-second-order [19] kinetic models to explain the adsorption process. The kinetic models are given as follows:

Pseudo-first-order kinetic model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

Pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{4}$$

where q_e is the adsorption capacity at equilibrium (mg/g), q_t is the adsorption capacity at any time t (mg/g), k_1 is the pseudo-first-order rate constant (min^{-1}), t is the time (min), k_2 is the pseudo-second-order rate constant (g/mg.min), and $h = k_2.q_e{}^2$, is the initial adsorption rate (mg/g.min). The adsorption mechanism was explained by applying the kinetic data to the different models such as intraparticle diffusion [20], Boyd kinetic [21], and shrinking core models [22,23]. The models explaining the adsorption mechanism are given as follows:

Weber and Morris intraparticle diffusion model:

$$q_t = k_p t^{1/2} + C \tag{5}$$

The Boyd kinetic model:

$$-0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) = \mathrm{Bt} \tag{6}$$

The effective diffusion coefficient, D_i (m^2/s) values were calculated by using the following equation:

$$B = \frac{\pi^2 D_i}{r^2} \tag{7}$$

k_p is the intraparticle diffusion rate constant (mg/g min$^{0.5}$), t is the time (min), C is a constant related to the thickness of the boundary layer, and r is the radius of the SMSP. The shrinking core model was successfully applied to fluid particle chemical reactions by Levenspiel [23]. For the film diffusion control, the extent of the adsorption process as a function of time is given by the following equation:

$$X = \frac{3D}{\delta r C} \alpha \tag{8}$$

If the film, diffusion is controlled in the adsorption process, then the plot of X vs. α yields a straight-line relationship. If the adsorption process is controlled by the diffusion through reacted shell (particle diffusion control), then the model can be represented by the following expression:

$$F(X) = 1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X) = \frac{6D}{r^2 C^{\mathrm{o}}}\alpha \tag{9}$$

In case of particle diffusion control, a plot of $F(X)$ vs. α gives a straight-line relationship and the diffusivity of the Ni(II) ions in adsorbent can be calculated from the slope of the plots. It is given as follows:

$$D = (\mathrm{Slope})\frac{C^{\mathrm{o}} r^2}{6} \tag{10}$$

where

$$X \text{ is the extent of reaction} = \frac{(C_{\mathrm{o}} - C)}{(C_{\mathrm{o}} - C_{\mathrm{eq}})} \tag{11}$$

$$\alpha = \int_0^t C\mathrm{d}t \tag{12}$$

C_{o} is the initial Ni(II) ions concentration (mg/L), C_{o} is the average Ni(II) ions binding site density of the SMSP (mg/L), C is the final Ni(II) ions concentration (mg/L), C_{eq} is the concentration of Ni(II) ions at equilibrium (mg/L), D is the diffusion coefficient (m^2/s), and r is the radius of the adsorbent particles (m).

2.4.2. Adsorption equilibrium study

Adsorption equilibrium study were performed by mixing 0.5 g of SMSP with 100 mL of Ni(II) ions solution with the different initial Ni(II) ions concentrations ranging from 100 to 500 mg/L at a solution pH of 5.0. Then the flasks were kept in an incubation shaker at an equilibrium time and at 30˚C. After the adsorption process and subsequent separation of spent SMSP, the final Ni(II) ions concentrations in the supernatant were measured by using AAS. The adsorption equilibrium data were fitted to the different adsorption isotherm models such as Langmuir [24], Freundlich [25], Temkin [26], and Dubinin–Radushkevich [27] models. The nonlinear form of adsorption isotherm models is given as follows:

Langmuir adsorption isotherm model is given as follows:

$$q_{\mathrm{e}} = \frac{q_{\mathrm{m}} K_{\mathrm{L}} C_{\mathrm{e}}}{1 + K_{\mathrm{L}} C_{\mathrm{e}}} \tag{13}$$

and the separation parameter from the Langmuir model is given as follows:

$$R_{\mathrm{L}} = \frac{1}{1 + K_{\mathrm{L}} C_{\mathrm{o}}} \tag{14}$$

Freundlich adsorption isotherm model is given as follows:

$$q_{\mathrm{e}} = K_{\mathrm{F}} C_{\mathrm{e}}^{1/n} \tag{15}$$

Temkin adsorption isotherm model is given as follows:

$$q_{\mathrm{e}} = B\ln(AC_{\mathrm{e}}) \tag{16}$$

Dubinin–Radushkevich adsorption isotherm model is given as follows:

$$q_{\mathrm{e}} = q_{\mathrm{m,D}} \exp\left(-\beta(\mathrm{RT}\ln(1 + 1/C_{\mathrm{e}}))^2\right) \tag{17}$$

where q_{e} is the adsorption capacity at equilibrium (mg/g), q_{m} is the maximum monolayer adsorption capacity (mg/g), K_{L} is the Langmuir constant related to the affinity of Ni(II) ions to the adsorbent (L/mg), C_{e} is the concentration of Ni(II) ions solution at equilibrium (mg/L), K_{F} is the Freundlich constant ($(\mathrm{mg/g})(\mathrm{L/mg})^{(1/n)}$) related to the bonding energy, n is a measure of the deviation from linearity of adsorption (g/L), $B = \mathrm{RT}/b$, is the constant related to the heat of adsorption, b is the heat of adsorption (kJ/mol), R is the gas constant (8.314 J/mol.K), T is the temperature (K), A is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy, $q_{\mathrm{m,D}}$ is the Dubinin–Radushkevich monolayer adsorption capacity (mg/g), and β is a constant related to adsorption energy.

2.4.3. Adsorption thermodynamic study

Adsorption thermodynamic study were performed by mixing 0.5 g of SMSP with 100 mL of Ni(II) ions solution with the different initial Ni(II) ions concentrations ranging from 100 to 500 mg/L at a solution pH of 5.0. Then, the flasks were kept in an incubation shaker with various temperatures (303–333 K) and at an equilibrium time. After the adsorption process and subsequent separation of spent SMSP, the final Ni(II) ions concentrations in the supernatant were measured. In order to study the thermodynamics of the adsorption process, the thermodynamic parameters such as change in free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) were calculated from the following equations:

$$\Delta G^{\circ} = -\mathrm{RT}\ln\left(\frac{C_{\mathrm{Ae}}}{C_{\mathrm{e}}}\right) \tag{18}$$

$$\log\left(\frac{C_{\mathrm{Ae}}}{C_{\mathrm{e}}}\right) = \frac{\Delta S^{\circ}}{2.303\,R} - \frac{\Delta H^{\circ}}{2.303\,\mathrm{RT}} \tag{19}$$

where R is the gas constant (8.314 J/mol/K), T is the temperature (K), C_{Ae} is the amount of Ni(II) ions adsorbed onto the SMSP per liter of solution at equilibrium (mg/L), and C_{e} is the concentration of Ni(II) ions in the solution at equilibrium (mg/L).

2.5. Batch desorption study

Batch desorption experiments were performed by mixing 0.5 g of spent SMSP with 100 mL of HCl solutions with the different initial HCl concentrations ranging from 0.2 to 0.35 M at an equilibrium time. Then, the flasks were kept in an incubation shaker at 30˚C. After the desorption process and subsequent separation of SMSP, the final Ni(II) ions concentrations in the supernatant were measured.

3. Results and discussion

3.1. Characterization of adsorbent

The SEM analysis of the SMSP is shown in Fig. 1 which reveals the texture and porosity of the adsorbent. The presence of the pores and internal surface are the important requirement for an effective adsorbent which is clearly observed in the SEM image of the SMSP. From the SEM image, it was further observed that the SMSP possesses irregular shape of the porous surface. Based on the results observed, it can be concluded that the SMSP has an adequate morphology for Ni(II) ion adsorption.

3.2. Effect of operating parameters

The solution pH is an important operating parameter in the adsorption process. Metal species in water is in the forms of M^{2+}, $M(OH)^{+}$, and $M(OH)_{2(S)}$ [28]. If the pH value of the solution is up to 5.0 then the solubility of the $M(OH)_{2(S)}$ is appreciable which indicates M^{2+} is the main adsorbate species in the aqueous solution [28]. If the solution pH is increased then the solubility of the $M(OH)_{2(S)}$ decreased. At solution pH 10.0, the solubility of the $M(OH)_{2(S)}$ is very small. At this higher pH, the main species in the solution is $M(OH)_{2(S)}$ [29]. To avoid the precipitation of metal ions at higher pH, all the adsorption experiments were conducted slightly at acidic condition (pH 5.0). The effect of solution pH on the removal of Ni(II) ions from its aqueous solution by the SMSP is shown in Fig. 2. The percentage removal of Ni(II) ions was found to be increased with an increase in solution pH from 2.0 to 5.0. The maximum removal of Ni(II) ions was observed at pH 5.0. At lower pH, the less removal of Ni(II) ions by SMSP was observed may be due to the higher concentration of the hydronium ions and also its high mobility which are preferentially adsorbed at the SMSP surface than the Ni(II) ions in the solution. At higher pH, the less number of hydronium ions in the solution along with the more negative charge ligands on the SMSP surface resulted in maximum removal of Ni(II) ions. The pH effect on the removal of Ni(II) ions by the SMSP can also be explained with the Fourier Transform Infrared Spectroscopic analysis. SMSP primarily contains weak acidic and basic functional groups and carboxyl groups (−COOH) as discussed in our previous research work [30]. At a pH higher than 3.0, the carboxylic groups available in the SMSP was deprotonated and which acquires the negative charge over the adsorbent surface which aids in strong attraction with positively charged Ni(II) ions. The pH effects on the removal of Ni(II) ions may also be explained with the help of point of zero charge (PZC) of the adsorbent. The surface of the adsorbent is positive when the pH of the solution was below PZC of the adsorbent. The increase in pH of the solution above the PZC of the adsorbent will show a slight increase in the removal of Ni(II) ions by the SMSP.

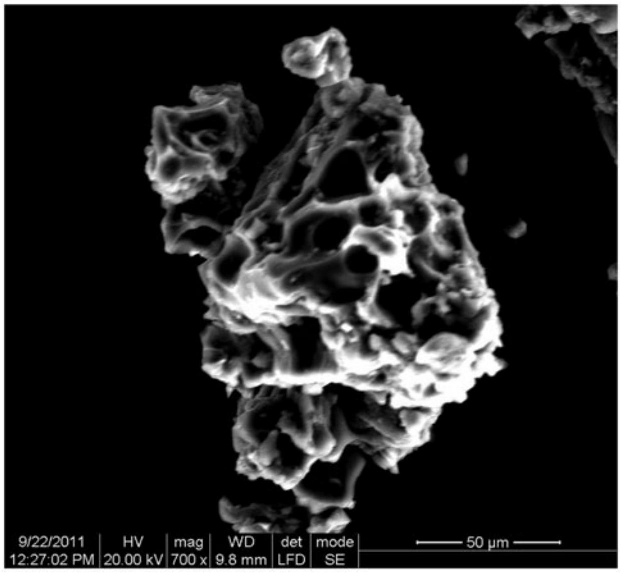

Fig. 1. SEM image of SMSP.

The effect of adsorbent dose on the percentage removal of Ni(II) ions was investigated in the range of

1–8 g/L, while the solution pH was fixed at 5.0 and the contact time was fixed at 30 min and at 30˚C. The observed experimental results were shown in Fig. 3. From Fig. 3, it was observed that the percentage removal of Ni(II) ions increased with the increase in adsorbent dose up to a certain value, and then approximately remained constant above an adsorbent dosage of 5 g/L. The reason may be due the reduction in the Ni(II) ions concentrations in the solution or concentration gradient of Ni(II) ions. The maximum removal of Ni(II) ions was observed as 99.152% at an optimum condition.

The proper residence time is needed for the adsorption process to reach equilibrium for the maximum removal of Ni(II) ions by the SMSP. With a selected adsorbent dosage of 5 g/L and a solution pH of 5.0, the effect of contact time on the removal of Ni(II) ions was investigated in the range from 10 to 60 min at 30˚C. The result of the present investigation is shown in Fig. 4. It can be seen from Fig. 4 that the percentage removal of Ni(II) ions increased with the increase in contact time and it reaches the maximum value at the time of 30 min. The results indicated that the equilibrium time for Ni(II) ions adsorption on SMSP is about 30 min. At an initial stage, the Ni(II) ions are adsorbed by the exterior surface of the adsorbent, the percentage removal of Ni(II) ions is fast. When the exterior surface of the adsorbent reaches the saturation value, the Ni(II) ions enters into the pores of the adsorbent which is adsorbed by the interior surface of the adsorbent. This process takes relatively long contact time.

The effect of initial Ni(II) ions concentration on the removal of Ni(II) ions from the aqueous solution by SMSP is shown in Fig. 5. It was observed that the percentage removal of Ni(II) ions decreased with the increase in initial Ni(II) ions concentration as is generally expected in the adsorption equilibrium process. The percentage removal of Ni(II) ions decreased from 99.152 to 71.57% when the initial Ni(II) ions concentration increased from 100 to 500 mg/L. This may be due to that the fixed amount of adsorbent dose was used for the present experimental study. The fixed dose of adsorbent can able to remove only a particular amount of Ni(II) ions from the aqueous solution. At lower Ni(II) ions concentration, the higher removal of Ni(II) ions was observed which may be due to the ratio of the number of Ni(II) ions to the number of active sites is less. At higher Ni(II) ions concentration, the less removal of Ni(II) ions was observed which may be due to the ratio of the number of Ni(II) ions to the number of active sites is high.

The temperature is an important operating parameter in the adsorption process. In the present study, the effect of temperature on the percentage removal of Ni(II) ions was investigated in the range from 303 to 333 K for the various initial Ni(II) ions concentration and keep the other parameters constant based on the above experimental studies. The results of the present experimental studies were shown in Fig. 6. It was observed from Fig. 6 that the percentage removal of Ni(II) ions decreased with the increase in temperature. The reason may be due to that the weakening of bonds between Ni(II) ions and active sites of the adsorbent at higher temperatures. It was indicated that the present adsorption system is independent of the temperature. The maximum removal of Ni(II) ions was observed at the temperature of 30˚C. The above results were also showed that the adsorption process was exothermic in nature.

3.3. Adsorption kinetics

The adsorption kinetic data were applied to the pseudo-first-order and pseudo-second-order kinetic

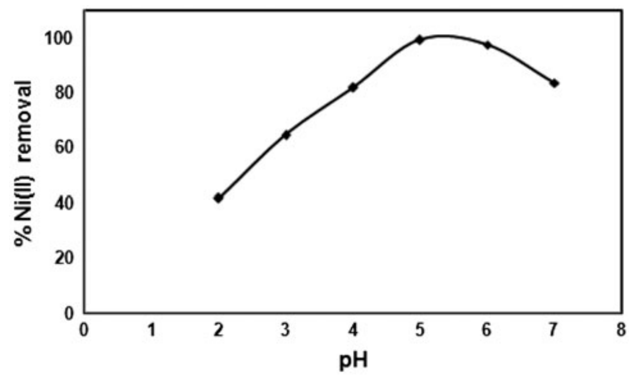

Fig. 2. Effect of pH for the adsorption of Ni(II) ions onto the SMSP [Ni(II) ions concentration = 100 mg/L, adsorbent dose = 0.5 g, volume of sample = 100 mL, equilibrium time = 30 min, and temperature 30˚C].

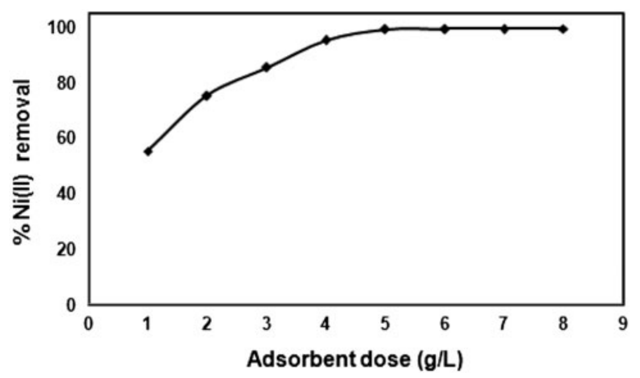

Fig. 3. Effect of adsorbent dose for the adsorption of Ni(II) ions onto the SMSP [Ni(II) ions concentration = 100 mg/L, pH = 5.0, volume of sample = 100 mL, equilibrium time = 30 min, and temperature 30˚C].

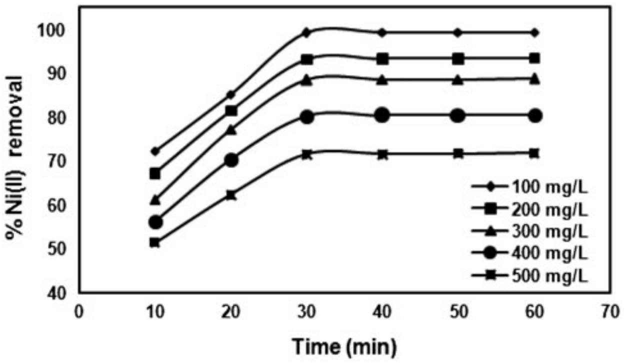

Fig. 4. Effect of contact time for the adsorption of Ni(II) ions onto the SMSP [Ni(II) ions concentration = 100–500 mg/L, adsorbent dose = 0.5 g, pH = 5.0, volume of sample = 100 mL, and temperature 30℃].

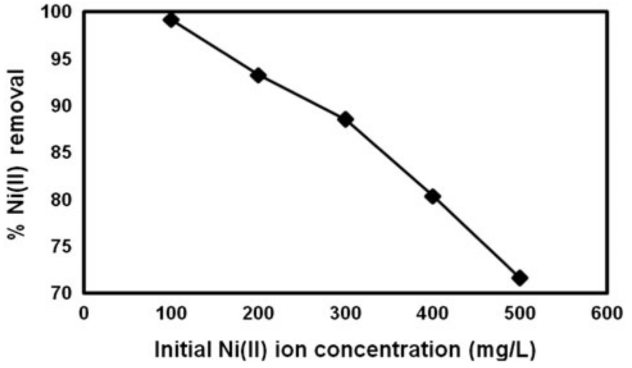

Fig. 5. Effect of initial Ni(II) ions concentration for the adsorption of Ni(II) ions onto the SMSP [Ni(II) ions concentration = 100–500 mg/L, adsorbent dose = 0.5 g, pH = 5.0, volume of sample = 100 mL, equilibrium time = 30 min, and temperature 30℃].

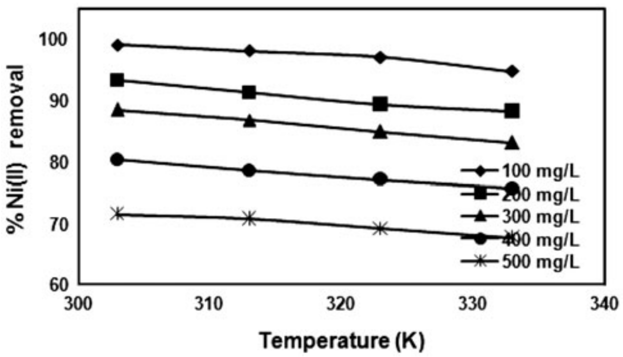

Fig. 6. Effect of temperature for the adsorption of Ni(II) ions onto the SMSP [Ni(II) ions concentration = 100–500 mg/L, adsorbent dose = 0.5 g, pH = 5.0, volume of sample = 100 mL, and equilibrium time = 30 min].

models and the results are depicted in Fig. 7(a) and (b). The adsorption kinetic parameters, experimental q_e, calculated q_e, and coefficient of determination (R^2) values were calculated from the Fig. 7(a) and (b) and these values are listed in Table 1. From Table 1, it was observed that the R^2 values for the pseudo-first-order model were found to be low and also the difference between the calculated q_e and experimental q_e values is high. Therefore, the adsorption of Ni(II) ions onto the SMSP does not follow the pseudo-first-order kinetics. From the Table 1, it was observed that the obtained R^2 values for the pseudo-second-order model are high, which indicates that the applicability of the pseudo-second-order model is a better option to describe the adsorption of Ni(II) ions onto the SMSP. The calculated q_e values were found to be close to the experimental q_e values for all the Ni(II) ions studied, which also confirms the applicability of the pseudo-second-order model. Therefore, it can be concluded that the adsorption of Ni(II) ions onto the SMSP follows the pseudo-second-order kinetic model.

3.4. Adsorption mechanism

The adsorption mechanism i.e. the transport of Ni(II) ions from the bulk solution to the interior part

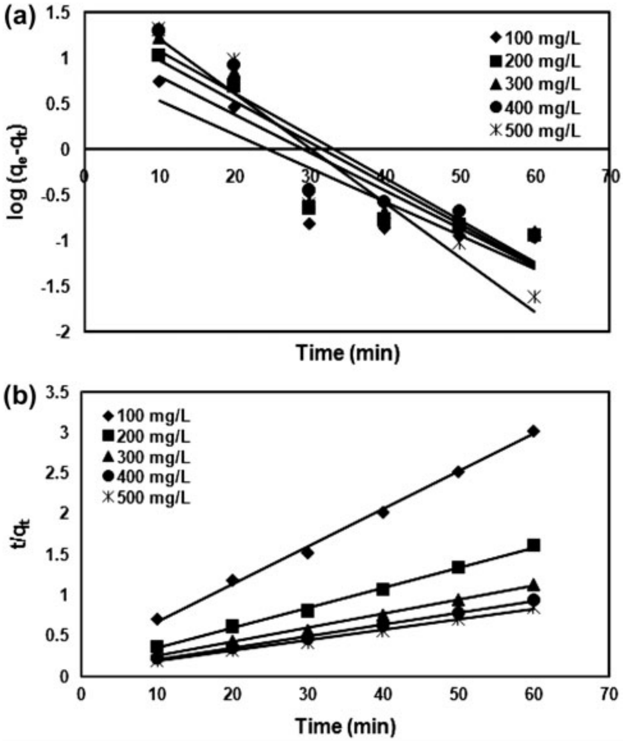

Fig. 7. Adsorption kinetics for the removal of Ni(II) ions by SMSP [Ni(II) ions concentration = 100 mg/L, adsorbent dose = 0.5 g, pH = 5.0, volume of sample = 100 mL, and temperature 30℃].

Table 1
Pseudo-first-order and pseudo-second-order rate constants of Ni(II) ions onto the SMSP

Kinetic model	Parameters	Concentration of Ni(II) ions solution (mg/L)				
		100	200	300	400	500
Pseudo-first-order kinetic equation	k_1 (min^{-1})	0.083	0.094	0.101	0.106	0.136
	q_e, cal (mg/g)	7.745	16.144	25.823	34.674	61.944
	R^2	0.769	0.803	0.807	0.848	0.908
Pseudo-second-order kinetic equation	k_2 (g/mg.min)	0.0103	0.0057	0.0038	0.0033	0.0032
	q_e, cal (mg/g)	21.739	40.667	56.824	67.428	74.074
	h (mg/g.min)	4.878	9.434	12.195	15.152	17.544
	q_e, exp (mg/g)	19.985	37.522	53.352	64.623	71.814
	R^2	0.996	0.997	0.996	0.996	0.997

of the pore through the liquid film followed by the particle diffusion and finally the Ni(II) ions get adsorbed at the end of the pore in the SMSP. The influence of film and particle diffusion on the overall removal of Ni(II) ions by the SMSP was explained by fitting the adsorption kinetic data to the different models such as intraparticle diffusion, Boyd kinetic, and shrinking core models. Fig. 8(a) shows the plot of q_t vs. $t^{1/2}$ is a straight line which does not pass through the origin. This shows that the intraparticle diffusion is not the only rate-limiting step in the adsorption process. The values of k_p, C, and R^2 were calculated from the plots of q_t vs. $t^{1/2}$ (Fig. 8(a)) and these values are listed in Table 2. The dual nature of the curve was observed for the plot of q_t vs. $t^{1/2}$ and which indicates that the first linear portion of the plot is due to the film diffusion and the second linear portion of the plot is due to the particle diffusion. The intercept was observed from the plots which indicate the boundary layer effect on the adsorption process. The larger value of the intercept indicates the greater contribution of the surface adsorption in the rate-limiting step. The actual slowest step in the adsorption process was further checked by applying the adsorption kinetic data to the Boyd kinetic model (Fig. 8(b)). From Fig. 8(b), it was observed that the plots are linear but did not pass through the origin which indicates that the adsorption process is controlled by film diffusion. The effective diffusion coefficient values were estimated and the values are listed in Table 2. The influence of the particle diffusion in the adsorption of Ni(II) ions onto the SMSP was checked by applying the adsorption kinetic data to the shrinking core model (Fig. 8(c)). The results indicates that the particle diffusion may also influence in the adsorption of Ni(II) ions onto the SMSP. The diffusivity values were estimated from the shrinking core model and the values were listed in

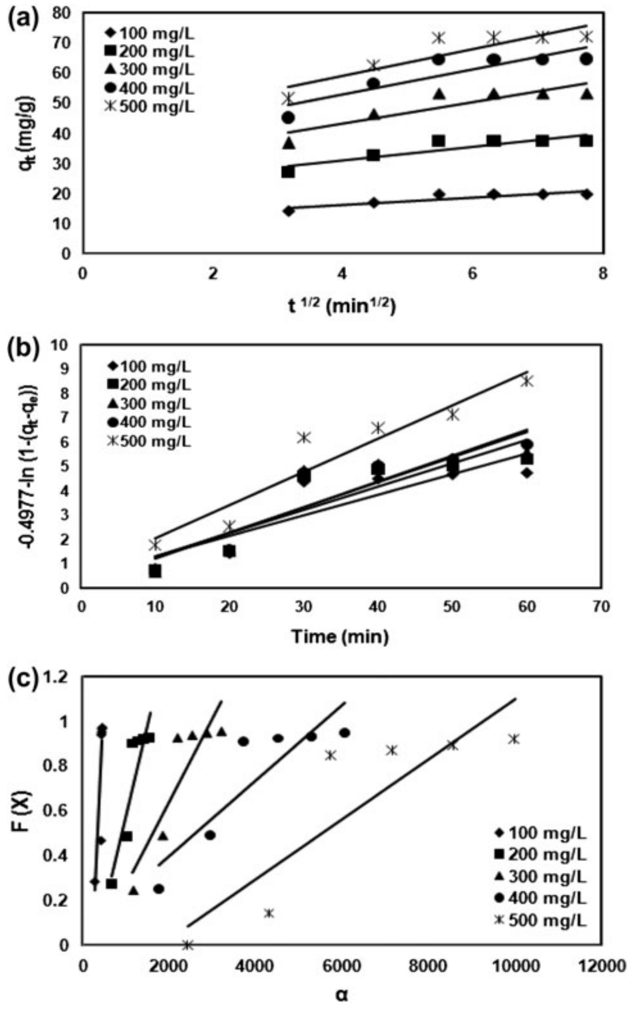

Fig. 8. Adsorption mechanism for the removal of Ni(II) ions by SMSP [Ni(II) ions concentration = 100 mg/L, adsorbent dose = 0.5 g, pH = 5.0, volume of sample = 100 mL, and temperature 30°C].

Table 2
Results of the mechanism for the adsorption of Ni(II) ions onto the SMSP

Conc. of Ni(II) ions solution (mg/L)	Adsorption mechanism							
	Intraparticle diffusion model			Boyd kinetic model			SCM model	
	k_p (mg/g.min$^{1/2}$)	C	R^2	B	D_i ($\times 10^{-12}$ m^2/s)	R^2	D ($\times 10^{-9}$ m^2/s)	R^2
100	1.199	11.63	0.800	0.084	4.444	0.769	4.344	0.796
200	2.255	21.94	0.789	0.095	5.026	0.803	6.365	0.829
300	3.482	29.41	0.777	0.102	5.396	0.807	6.435	0.807
400	4.125	36.25	0.780	0.106	5.607	0.848	6.246	0.789
500	4.404	41.58	0.792	0.137	7.247	0.908	3.484	0.775

Table 2. Based on the above observations, both the film and particle diffusion control the adsorption of Ni(II) ions onto the SMSP.

3.5. Adsorption equilibrium study

The effect of initial Ni(II) ions concentration data was fitted to the two-parameter adsorption isotherm models such as Langmuir [24], Freundlich [25], Temkin [26], and Dubinin–Radushkevich [27] models using MATLAB 7.1, and the graphical representation of these models are given in Fig. 9. The Langmuir constants, q_m (mg/g) and K_L (L/mg) with the R^2 values, SSE and RMSE, were estimated from the plot of q_e vs. C_e at 30˚C and are listed in Table 3. The R_L values were found to be in the range of 0.106–0.0232 for an initial Ni(II) ions concentration in the range of 100–500 mg/L. The R_L values were found to be in between 0 and 1 which indicate the favorable adsorption [31]. The Freundlich constants, K_F ((mg/g)(L/mg)$^{(1/n)}$) and n values with the R^2 values, SSE and RMSE, were estimated from the plot of q_e vs. C_e at 30˚C and are listed in Table 3. The value of n was found to be 3.888 g/L for the present adsorption system. The observed n value lies between 1 and 10 which indicates the adsorption is a physical process [32]. The Temkin isotherm constants, A and B with R^2 values, SSE and RMSE, were calculated from the plot of q_e vs. C_e at 30˚C, and these values were listed in Table 3. The heat of adsorption (b) values for the present adsorption system was found to be less than 8 kJ/mol, which indicates a weak interaction between the Ni(II) ions and the SMSP. The adsorption process, as given by the heat of adsorption, can be expressed as physical adsorption [33]. The Dubinin–Radushkevich constants, $q_{m,\,D}$ and β_D with R^2 values, SSE and RMSE, were estimated from the plot of q_e vs. C_e at 30˚C and these values were listed in Table 3. The magnitude of E was used to evaluate the type of adsorption mechanism. The estimated value of E in the present adsorption system was found to be below 8 kJ/mol, which indicates the adsorption process follows the physical adsorption type [34].

Based on the R^2 values, the order of best fit of adsorption isotherm models studied for Ni(II) ions removal by SMSP was given as follows: Freundlich > Temkin > Langmuir > Dubinin–Radushkevich isotherm models. From the results, it was observed that the adsorption isotherm data were best fitted to the Freundlich adsorption isotherm model based on the high R^2 values with low error values than other adsorption isotherm models. The applicability of the Freundlich adsorption isotherm model indicates the multilayer adsorption of Ni(II) ions onto the SMSP. The comparison of the maximum monolayer adsorption capacity of the different adsorbents for Ni(II) ions removal is given in Table 4. It shows that the SMSP studied in this work has higher adsorption capacity.

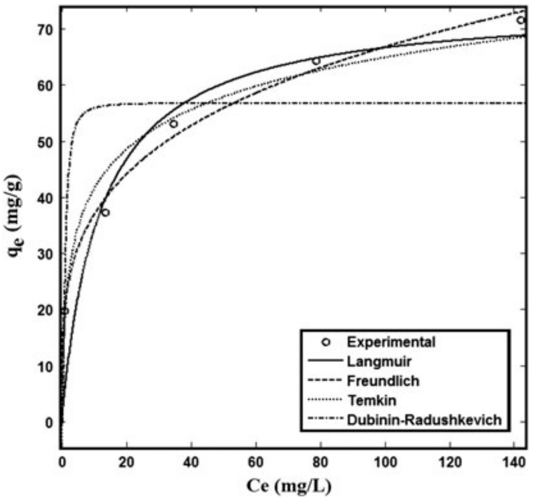

Fig. 9. Adsorption isotherms for the removal of Ni(II) ions by SMSP [Ni(II) ions concentration = 100–500 mg/L, adsorbent dose = 0.5 g, pH = 5.0, volume of sample = 100 mL, equilibrium time = 30 min, and temperature 30˚C].

Table 3
Adsorption isotherm constants for the removal of Ni(II) ions by the SMSP

Adsorption isotherm model	Parameters	Values	R^2
Langmuir	q_m (mg/g)	74.55	0.8625
	K_L (L/mg)	0.0843	
	SSE	240.2	
	RMSE	8.949	
Freundlich	K_F ((mg/g) (L/mg)$^{(1/n)}$))	20.43	0.9905
	n (g/L)	3.888	
	SSE	16.68	
	RMSE	2.358	
Temkin	A	5.926	0.9552
	B	4.415	
	b (kJ/mol)	0.571	
	SSE	78.34	
	RMSE	5.11	
Dubinin–Radushkevich	$q_{m, D}$ (mg/g)	56.80	0.6288
	β ((mol.K/kJ)^2)	5.284×10^{-8}	
	E (kJ/mol)	3.076	
	SSE	648.5	
	RMSE	12.73	

3.6. Adsorption thermodynamic study

The results of the adsorption thermodynamic studies were shown in Fig. 10. The thermodynamic parameters such as change in free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) were estimated from the Eq. (18) and the slope and intercept of the plot of log K_c vs. $1/T$ (Fig. 10). The values of the thermodynamic parameters are listed in Table 5. The calculated K_c values for the adsorption of Ni(II) ions onto the SMSP are listed in Table 5. It was observed from the results that the K_c values decreased with the increase in temperature which results in the shift of equilibrium to the left i.e. the desorption of the adsorbed Ni(II) ions from the spent SMSP is favored at high temperatures. The negative value of ΔG° confirms the spontaneous nature and feasibility of the adsorption process. The ΔG° values were decreased as the temperature was increased from 303 to 333 K, which is an indication of the physical adsorption process. The negative value of ΔH° confirms the exothermic nature of the adsorption process, while the negative value of ΔS° suggested that the decrease in Ni(II) ions concentration in solid-liquid interface indicating thereby the increase in Ni(II) ions concentration onto the SMSP surface. It also confirms the decreased randomness at the solid-liquid interface during the adsorption process.

Table 4
Comparison of the maximum monolayer adsorption capacity of the SMSP for Ni(II) ions removal with the other adsorbents

Adsorbents	q_m (mg/g)	References
Sulfuric acid-treated cashew nut shell	456.3	[3]
Orange peel	158	[5]
H_3PO_4-treated rice bran	102	[6]
Surface modified *Strychnos potatorum* seeds	74.55	This study
Mango peel	39.75	[7]
Modified coir pith	38.9	[8]
Meranti sawdust	35.971	[9]
Barely straw untreated	35.8	[10]
Cashew nut shell	18.868	[11]
Tea factory waste	18.42	[12]
Parthenium hysterophorus L. activated carbon	17.24	[13]
Irish peat moss	14.50	[14]
Corncobs	13.50	[15]
Dye-loaded sawdust	9.87	[16]
Coir pith	9.5	[8]
Dye groundnut shells	7.49	[16]

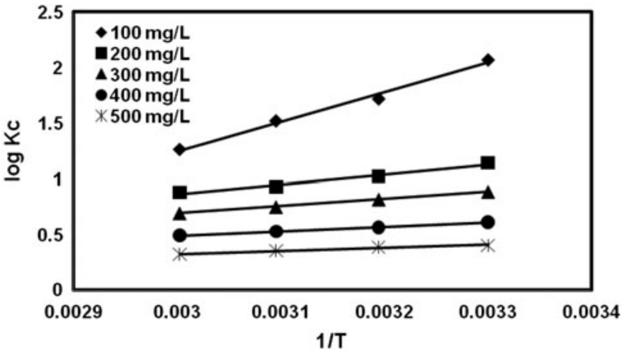

Fig. 10. Adsorption thermodynamics for the removal of Ni(II) ions by SMSP [Ni(II) ions concentration = 100–500 mg/L, adsorbent dose = 0.5 g, pH = 5.0, volume of sample = 100 mL, and equilibrium time = 30 min].

3.7. Desorption study

Desorption studies give an idea about the adsorption mechanism based on the recovery of the metal ions from spent adsorbent. Batch desorption studies were carried out by chemical regeneration of the spent SMSP. The results are listed in Table 6. It was observed from Table 6 that the percentage recovery of Ni(II) ions increased with the increase in concentration of hydrochloric acid (HCl) and it reaches a constant value

Table 5
Thermodynamic parameters for the adsorption of Ni(II) ions onto the SMSP

Conc. of Ni(II) ions solution (mg/L)	ΔH° (kJ/mol)	ΔS° (J/mol/K)	ΔG° (kJ/mol)			
			30°C	40°C	50°C	60°C
100	−50.797	−128.573	−11.995	−10.283	−9.381	−8.026
200	−17.142	−35.001	−6.611	−6.111	−5.718	−5.590
300	−12.448	−24.125	−5.136	−4.897	−4.635	−4.419
400	−7.536	−13.212	−3.546	−3.378	−3.268	−3.144
500	−5.152	−9.209	−2.326	−2.315	−2.179	−2.059
Conc. of Ni(II) ions solution (mg/L)			K_c values			
			30°C	40°C	50°C	60°C
100			116.925	52.0223	32.898	18.157
200			13.793	10.468	8.407	7.532
300			7.681	6.564	5.618	4.935
400			4.086	3.662	3.376	3.113
500			2.517	2.434	2.251	2.104

Table 6
Desorption of Ni(II) ions from spent SMSP using HCl

Conc. of Ni(II) ions solution (mg/L)	Removal efficiency	Percentage recovery of Ni(II) ions			
		0.2 M	0.25 M	0.30 M	0.35 M
100	99.152	70.52	83.75	92.28	93.11
200	93.24	66.29	78.24	85.66	85.87
300	88.48	62.78	73.36	80.14	80.29
400	80.34	54.58	65.32	73.43	73.58
500	71.57	40.35	52.84	60.57	62.41

(approx.) at 0.30 M HCl. The desorption results suggested that the interaction between the adsorbent and adsorbate may be an ion exchange or chemical adsorption or physical adsorption process or all together. But a majority of the adsorption process here is an ion exchange and physical adsorption process, and a little amount of chemical adsorption is also possible.

4. Conclusion

The SMSP seeds were found to be a potential adsorbent for the removal of Ni(II) ions from the aqueous solution. The adsorption process was found to decrease with the increase in initial ions concentration and temperature but it was found increased with the increase in solution pH, adsorbent dose, and contact time. The optimum conditions for the maximum removal of Ni(II) ions by the SMSP were found to be: pH of 5.0, adsorbent dose of 5 g/L, contact time of 30 min, and temperature of 30°C. The pseudo-second-order kinetic model was found to be the best correlated to the adsorption kinetic data for Ni(II) ions adsorption. The rate of adsorption of Ni(II) ions by the SMSP process was controlled by both internal and external diffusion process. The effective diffusivity values were calculated for the adsorption system at 30°C: 4.444×10^{-12}, 5.026×10^{-12}, 5.396×10^{-12}, 5.607×10^{-12}, and $7.247 \times 10^{-12}\ \mathrm{m^2/s}$ for an initial Ni(II) ions concentration of 100–500 mg/L, respectively. The adsorption isotherm data showed good fit to the Freundlich model than the Langmuir, Temkin, and Dubinin–Radushkevich models. Thus, the adsorption process was multilayer on the heterogeneous surface of the adsorbent. The maximum Ni(II) ions adsorption capacity of the SMSP was found to be 74.55 mg/g at 30°C. The thermodynamic studies indicated that the adsorption process was found to be feasible, spontaneous, and exothermic in nature.

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