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Removal of Ni(II) from aqueous solution by *Lycopersicum esculentum* (Tomato) leaf powder as a low-cost biosorbent

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ABSTRACT

The present study investigates the biosorption potentiality of *Lycopersicum esculentum* leaves powder as a low-cost agricultural waste biomass for the removal of Ni(II) ion from aqueous solution in batch method. The experimental kinetic data were modeled using pseudo-first-order, pseudo-second-order, and intraparticle diffusion model. It was found that the biosorption was better described by pseudo-second-order kinetic model. Langmuir and Freundlich isotherm models were applied to analyze the experimental data and to predict the relevant isotherm parameters. The best interpretation for the experimental data was given by the Langmuir isotherm, and the maximum biosorption capacity for Ni(II) is 58.82 mg/g at 323 K. Thermodynamic parameters such as ΔG°, ΔH°, and ΔS° were calculated, and it was observed that the adsorption process was feasible, spontaneous, and endothermic.

Keywords: Lycopersicum esculentum leaves powder; Biosorption; Nickel; Isotherms; Kinetics

1. Introduction

Removal of heavy metals from wastewater and industrial effluents is an area of research receiving increasing attention because they are non-biodegradable and have the ability to accumulate in living organisms. Among the different heavy metals, nickel is one of the common and most toxic pollutants released into the natural waters from various industrial activities such as electroplating, battery manufacturing, mineral rocessing, steam-electric power plants, paint formulation, porcelain enameling, and so on [1]. Ni(II) belongs to the so-called "essential" metals and is identified as a component in a number of enzymes, participating in important metabolic reactions such as ureolysis, hydrogen metabolism, methane biogenesis, and acidogenesis [2]. Excessive level intakes of nickel can cause acute and chronic nickel poisoning causes headache, vomiting, chest pain, tightness, cyanosis, skin dermatitis, rapid respiration, pulmonary fibrosis, renal edema, and severe damage to the lungs, kidney, nervous system, and mucous membranes [3]. The World Health Organization (WHO) recommends a maximum acceptable concentration of nickel and US Environmental Protection Agency requires nickel not to exceed 0.5 mg/L in drinking water [4]. Hence, it is necessary to

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remove Ni(II) from water at least below the regulatory level.

Many methods have been developed to treat wastewater polluted by heavy metals, including chemical precipitation, ion exchange, electrolysis, coagulation, and membrane separation, but these methods [5–9] have disadvantages such as secondary pollution, high cost, high energy input, and large quantities of chemical reagents or poor treatment efficiency at low metal concentration. A promising alternative is biosorption since it has high efficiency and low cost, wide adaptability and selectivity in removing different kinds of heavy metals, and stable performance in purifying wastewater of low metal concentrations [10].

An immense interest has been recently directed to the removal of heavy metals from solutions using different biomaterials as sorbents. The use of natural biomaterials is a promising alternative due to their relative abundance and low commercial value [11]. Of late, agricultural by-products and plant wastes such as tobacco stem [12], *Moringa oleifera* bark [13], cashew nut shell [14], barley straw [15], loquat bark [4], and formaldehyde-treated waste tea leaves [16] are widely used as biosorbents. Tomato (*Lycopersicum esculentum*) is an herbaceous, usually sprawling plant in the night shade family that is typically cultivated for the purpose of harvesting its fruits for human consumption. Tomato plants typically reach 1–3 m (1–10 feet) in height and have a weak and woody stem that often vines over other plants. The leaves are 10–25 cm long, odd pinnate with 5–9 leaflets on petioles, and each leaflet measures up to 8 cm long with a serrated margin. Agricultural materials contain polysaccharides and lignin which are associated with functional groups responsible for metal ion sorption [17]. The abundant natural occurrence and presence of a large amount of surface functional groups make various agricultural wastes good alternatives to expensive synthetic adsorbents [18]. The use of tomato leaves is a promising alternative due to their relative abundance, simple preparation, and no commercial value. To the best of our knowledge, there are no reports on the application of this biosorption for the removal of toxic divalent cations from aqueous solutions.

The main objectives of the present study include: (1) characterizing the biosorbent through BET, FTIR, and SEM; (2) ability in the removal of Ni(II) ions from aqueous solution; (3) the effects of experimental parameters such as initial pH, biosorbent dosage, initial Ni(II) ion concentration, and temperature on the biosorption process for a specific period of contact time were investigated; and (4) to understand the kinetic, equilibrium, and thermodynamics mechanism.

2. Materials and methods

2.1. Materials and chemicals

All the chemicals and reagents used in the present study are of analytical grade and used without further purification. $NiCl_2 \cdot 6H_2O$ was obtained from Qualigens Fine Chemicals, Mumbai, India. HCl, NaOH, and H_2SO_4 were obtained from S.D. Fine Chemicals, Mumbai, India. The pH of the solutions was adjusted by the addition of either 0.1 M HCl or 0.1 M NaOH solutions. Double distilled water was used throughout the study and the stock solutions were subsequently diluted with distilled water.

2.2. Preparation of biosorbent

L. esculentum leaves were collected from the fields of tomatoes, Kammapalli village nearby Somala, Chittoor District, Andhra Pradesh, during July–August 2012. The leaves were separated from tree and the foreign matters were removed from the leaves and washed with tap water and distilled water to remove dirt. The leaves were sundried for 2 days. Then, they were grinded to fine powder with mechanical grinder. A weighed amount of uniform sized waste tomato leaves powder (10 g) was transferred into a round bottom flask (250 mL) and 100 mL of distilled water was added. The resulting mixture was stirred for 7 h with 250 rpm using magnetic stirrer at room temperature. Finally, the biomass was separated from the solution by filtration and washed with distilled water several times until no color was detected in the filtrate. Finally, it was dried in an oven at 333 K for 6 h and kept in a desiccator for further use. The resulting biomass was designated as the *L. esculentum* leaves powder (LELP) for further representation.

2.3. Preparation of stock solution

Stock solution of Ni(II) was prepared by dissolving the required amount of $NiCl_2$ $6H_2O$ in double distilled water. A stock solution was slightly acidified with 2–3 drops of concentrated H_2SO_4 to avoid precipitation. Fresh dilutions were prepared and used for each experiment. All the working solutions were obtained by diluting the stock solution with distilled water.

2.4. Instrumentation

Metal ion concentrations were determined by atomic absorption spectrometry (AAS), Shimadzu, model AA6300. The FTIR spectra of samples were recorded on a Thermonicolet-200 series spectrophotometer over the range 4,000–500 cm^{-1} using KBr pellets. The surface morphology of LELP before and after Ni(II) biosorption was studied with a scanning electron microscope (Carl Zeiss, EVO MA 15, England). A digital pH meter (Digisum D1-7007, India) was used for the measurements of pH.

2.5. Batch biosorption studies

Batch experiments were performed at 303 K in 125-mL flasks containing 50 mL of metal solution those were stirred with a magnetic stirrer at 180 rpm. To study the effect of pH on metal uptake by LELP, it was varied from 2.0 to 8.0 by gradually adding 0.1 M HCl/NaOH. Required quantity of biomass was added to each flask, and the mixtures were stirred for 3 h, which was the enough duration to achieve equilibrium. For kinetic studies, the metal ion concentrations were varied between 30 and 90 mg/L. The thermodynamic parameters were studied at 303, 313, and 323 K in a temperature-controlled shaking incubator. After each experiment, the filtrate was filtered by using filter paper (Whatman filter paper no. 41) and the filtrate was analyzed by using AAS. The amount of metal bound by the biosorbent was calculated from the difference between the initial and final concentrations of the metal ions in solution. The amount of Ni (II) adsorbed by the sorbent at equilibrium was obtained using the Eq. (1):

$$q_e = \frac{(C_i - C_e)V}{M} \tag{1}$$

where q_e (mg/g) was the adsorption capacity at equilibrium, C_i and C_e were initial and equilibrium concentration (mg/L) of Ni(II), respectively, M (g) was the adsorbent dosage, and V (L) was the volume of the solution.

3. Results and discussion

3.1. Characterization of the biosorbent

BET, FTIR, and SEM analysis were carried out for characterization of LELP. Physico-chemical characterization of LELP was performed to obtain a better interpretation of the mechanism involved during the biosorption process. The values of moisture content, bulk density, ash content, and pH$_{\mathrm{PZC}}$ have been determined and presented in Table 1. Moisture content, ash content, bulk density, and PZC determinations procedures were discussed in our earlier publication [19]. The surface properties of LELP (like surface arc, pore volume, and pore radius) results have been determined and presented in Table 1.

3.1.1. FTIR analysis

The FTIR spectra of pure and Ni(II)-loaded LELP in the range of 4,000–500 cm^{-1} were recorded to confirm the type of functional groups that are usually responsible for the biosorption process and presented in Fig. 1(a). The broad and strong bands at 3,100–3,600 cm^{-1} were due to the overlapping of –OH and –NH$_2$ stretching vibrations. The peak located at 1,735 cm^{-1} is due to stretching of carbonyl group of –COOH. The peak at 1,624 cm^{-1} is attributed to the stretching vibration of the carboxyl group (–C=O). Symmetric stretching vibration of ionic carboxylic groups (–COO^{-}) results a peak at 1,455 cm^{-1}. The strong bands within 1,100–1,000 cm^{-1} are due to the C–O group, which are characteristic peaks of polysaccharides.

Fig. 1(b) shows the FTIR spectrum of Ni(II)-loaded LELP. Due to the interaction of the functional groups on the biosorbent with Ni(II), the IR peaks might shift to lower or higher wave numbers and new infrared peaks belonging to the adsorbate or splitting of original bands may appear. Shifting of bands to lower frequencies indicates bond weakening, while a shift to higher frequencies indicates an increase in bond

Table 1
Physico-chemical and BET characteristics of the LELP

Parameters of SMLP	Moisture content (%)	2.25	
	Bulk density (g mL^{-1})	0.52	
	Ash content (%)	2.32	
	PZC	3.5	
	Methods	Surface properties	Values
Pore size	BJH desorption method	Pore volume	0.003 cc/g
		Pore radius DV (r)	15.5996 Å
Surface area	Single point surface area	Surface area	5.0518 m^2/g
	Multiple point BET	Surface area	8.80 m^2/g
	BJH desorption method	Surface area	2.600 m^2/g

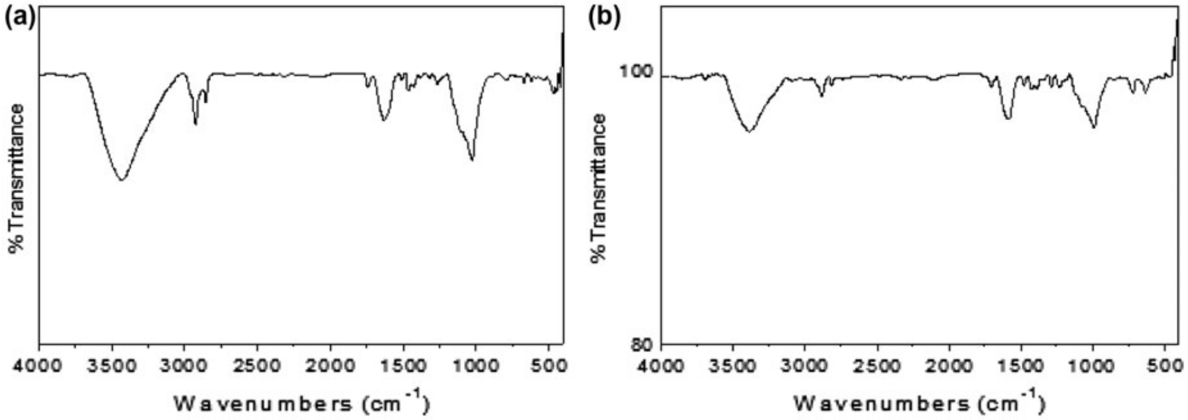

Fig. 1. FTIR spectra of (a) pure LELP and (b) Ni(II)-loaded LELP.

strength [20]. After biosorption of Ni(II) ions from aqueous medium, there are significant changes in the IR signals of some functional groups on the LELP. Moreover, the wave numbers shifted from 3,433, 2,921, 1,735, 1,624, 1,455, and 1,026 cm^{-1} to 3,438, 2,924, 1,743, 1,626, 1,464, and 1,030 cm^{-1}, respectively, after Ni(II) biosorption onto LELP. The results of FT-IR analysis demonstrated that the biosorption of Ni(II) onto LELP occurred through chemical interaction, involving the N and O atoms of the functional groups of LELP in complex formation with Ni(II) ions in aqueous solutions (Fig. 2) [21].

3.1.2. SEM analysis

Scanning electron microscopy is an extremely useful tool to identify the active biosorptive surface sites on surface of the biosorbent. The scanning electron micrographs of pure and Ni(II)-loaded LELP are shown in Fig. 3(a and b). Pure LELP shows the smooth surface with small pores. After metal loading, there is a distinct change in the surface morphology of the biosorbent.

3.2. Influence of solution pH

One of the most important factors affecting biosorption of metal ions is the acidity of solution. Hence, the effects of solution pH were studied in the range of 2–6. The initial pH of the Ni(II) solution was changed by adding 0.1 N HCl or 0.1 N NaOH solutions as required. The removal % of Ni(II) ion increased as pH increased from 2 to 5.5. At lower pH values, hydrogen ion concentration in solution increased, which competes with Ni(II) ions for the binding sites of the biosorbent and reduced the adsorbed amounts of Ni (II) ion. At higher pH values, the presence of hydrogen ions in the solution decreased and the biosorbent (LELP) surface also deprotonated, resulting in

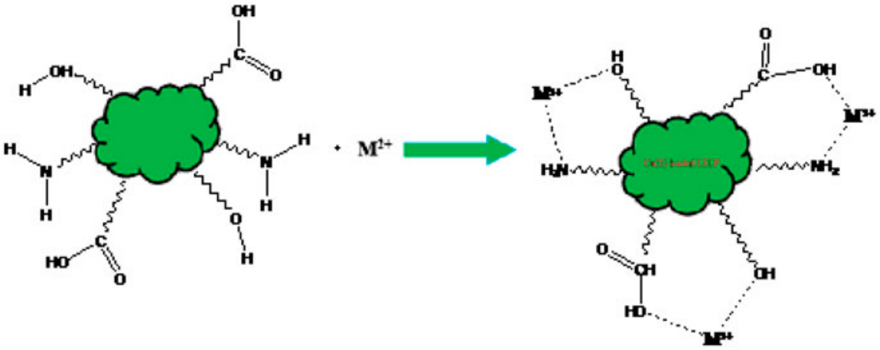

Fig. 2. Schematic diagram of biosorption of Ni(II) on LELP.

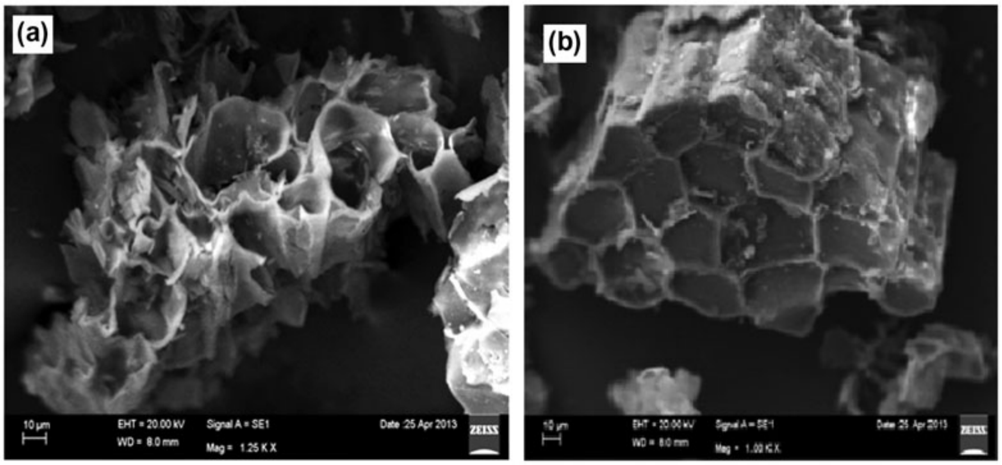

Fig. 3. SEM images of (a) pure LELP and (b) Ni(II)-loaded LELP.

increased biosorption of Ni(II). Decrease in Ni(II) biosorption above pH 5.5 might be attributed to the speciation of the metal, such as the formation of $Ni(OH)_2$ ions that do not adsorb well. Hence, the optimal pH of 5.5 was selected for further batch experiments.

3.3. Effect of biosorbent dose

The effect of the biosorbent dosage on the removal of Ni(II) ions was studied by varying the biosorbent dosage in the range of 0.1–0.6 g/L with 200 rpm stirring speed and at pH 5.5 in 100 mL Ni(II) solutions with a concentration of 25 mg/L. A rapid removal percentage of Ni(II) increases with increasing biosorbent dosage. It can be explained as on increasing the adsorbent dose, the "active sites" available for sorption of Ni(II) ions also increase and consequently more biosorption takes place. The maximum biosorption of Ni(II) onto LELP was observed at 0.4 g. After reaching the maximum removal, there was no appreciable increase in Ni(II) removal percentage. Hence, the biosorbent dose of 0.4 g/L was selected as optimum dose for further Ni(II) biosorption experiments.

3.4. Effect of initial metal ion concentration and contact time

Contact time is one of the important parameters for successful biosorption application. The efficiency of metal ions removal is also largely affected by the initial concentration of metal ions in aqueous solutions. The initial Ni(II) ion concentration was varied (30–90 mg/L) with varying contact times (15–120 min). Removal of Ni(II) was extremely rapid in the first few minutes. The sorption equilibrium was achieved in 105 min. After this equilibrium period, the amount of metal ions adsorbed did not show time-dependent change. Hence, the equilibrium time is maintained as 105 min for all batch biosorption studies.

3.5. Biosorption kinetic models

Kinetic models were used to thoroughly examine the rate of the biosorption process and to propose potential rate-controlling step. In order to understand the mechanisms involved in the biosorption process, three kinetic models, i.e. pseudo-first-order, pseudo-second-order, and intraparticle diffusion models, were applied to the experimental data at different initial Ni (II) ion concentrations to describe the mechanism of the biosorption process.

The pseudo-first-order rate equation [22] is generally expressed as follows (Eq. (2)):

$$\log\,(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \tag{2}$$

where q_e (mg/g) and q_t (mg/g) are the amounts of Ni (II) sorbed at equilibrium and at time t. K_1 (min^{-1}) is the rate constant of first-order biosorption process. The pseudo-first-order kinetic constants were determined from slope of the plot of log ($q_{e-}q_t$) vs. t (figure not shown) and the values are shown in Table 2. The R^2 values are very less suggesting that the biosorption of Ni(II) ions does not follow pseudo-first-order kinetic model.

The kinetic data were further analyzed using Ho's et al. [23] pseudo-second-order kinetic model. The linearized form of the equation is expressed as (Eq. (3)):

Table 2
Kinetic parameters for the biosorption of Ni(II) onto LELP at different metal ion concentrations

	Lagergren-first-order			Pseudo-second-order			Weber and Morris		
Ni(II) conc. (mg/L)	K_1 (1/min)	R^2	SSE	K_2 (g/mg min)	R^2	SSE	K_{id} (mg/g min$^{-0.5}$)	R^2	SSE
30	0.027	0.995	0.987	0.0180	0.999	0.0100	0.217	0.937	0.9072
50	0.018	0.951	0.994	0.0227	0.999	0.0026	0.188	0.968	0.9454
70	0.020	0.993	0.995	0.0273	0.999	0.0007	0.160	0.982	0.9638
90	0.025	0.958	0.995	0.0179	0.999	0.0016	0.261	0.962	0.9570

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

where q_e and q_t are the amount of the Ni(II) removal per unit mass of biosorbent (mg/g) at equilibrium and at time t (min), and K_2 (g/mg min) is the pseudo-second-order rate constant. The biosorption rate constant (K_2) is obtained from linear plot of t/q_t vs. t (figure not shown) and the values are included in Table 2. As shown in Table 3, the R^2 values are close to unity (0.999) for all Ni(II) concentrations indicating the applicability of the pseudo-second-order kinetic model and the biosorption of Ni(II) onto LELP.

The intraparticle diffusion model is based on the theory proposed by Weber and Morris (Eq. (4)) [24].

$$q_t = K_{id} t^{0.5} + c \tag{4}$$

where q_t (mg/g) is the amount adsorbed at time t (min), K_{id} is the intraparticle diffusion rate constant (mg/g min$^{-0.5}$), and C is the intercept that gives an idea about the thickness of the boundary layer. The intraparticle diffusion model coefficient values are calculated from the plot of q_t vs. $t^{0.5}$ (figure not shown) and are given in Table 2. The first stage can be attributed to the diffusion of adsorbate through the solution to the external surface of the biosorbent. The second stage describes the gradual sorption, where intraparticle diffusion is rate-limiting step. The third stage is attributed to the final equilibrium due to extremely low metal ion concentration left in solution and the reduction of interior active sites present on the biosorbent.

In addition, the sum of square error (SSE) test was carried out to predict the best fit (Eq. (5)).

$$\text{SSE} = \sum \frac{(q_{t,e} - q_{t,m})^2}{q_{t,e}^2} \tag{5}$$

where $q_{t,e}$ and $q_{t,m}$ are the experimental biosorption capacities of metal ions (mg/g) at time t and the corresponding values that are obtained from the kinetic models. SSE values for all kinetic models are calculated and are summarized in Table 2. Pseudo-second-order model has the lowest SSE values when compared with the pseudo-first-order and intraparticle diffusion models. Based on the low SSE values, it can be concluded that biosorption of Ni(II) onto LELP follows pseudo-second-order model.

3.6. Equilibrium isotherms

To examine the relationship between sorbent and sorbate at equilibrium and the maximum sorption capacity of biosorbent Langmuir, Freundlich isotherm models are widely used.

The linearized form of the Langmuir isotherm is (Eq. (6)):

$$\frac{1}{q_e} = \frac{1}{q_m b}\left[\frac{1}{C_e}\right] + \frac{1}{q_m} \tag{6}$$

Table 3
Langmuir and Freundlich isotherm constants and correlation coefficients for Ni(II) biosorption onto LELP at different temperatures

	Langmuir				Freundlich			
Temp. (K)	q_m (mg/g)	b (L/mg)	χ^2	R^2	K_f (mg/g)	$1/n$	χ^2	R^2
303	47.61	0.500	5.42	0.999	16.48	0.466	13.76	0.993
313	52.63	0.345	8.49	0.999	14.58	0.515	19.58	0.994
323	58.82	0.229	12.77	0.999	12.44	0.579	28.92	0.993

where q_e is the equilibrium metal ion concentration on the sorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer biosorption capacity of the sorbent (mg/g), and b is the Langmuir constant related to the free energy of sorption. The maximum monolayer biosorption capacity was found to be 58.82 mg/g of Ni(II) ions onto LELP.

Another parameter in the Langmuir isotherm, a dimension less separation factor (R_L), is defined as follows (Eq. (7)):

$$R_L = \frac{1}{(1 + bC_0)} \tag{7}$$

where C_0 (mg/g) is the initial metal concentration and b is the Langmuir constant. For favorable biosorption, R_L must lie within the range 0–1. The R_L value indicates the shape of the isotherm as follows:

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$R_L = 0$	Favorable
$0 < R_L < 1$	Irreversible

In this study, the R_L values lies between 0 and 1 indicate favorable biosorption.

The Freundlich isotherm is used for modeling the biosorption of metal ions on heterogeneous surfaces, and the linearized form of the isotherm is as follows (Eq. (8)):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{8}$$

where K_f (mg/g) is a constant relating the biosorption capacity and $1/n$ is an empirical parameter relating the biosorption intensity. The values of Freundlich constants K_f and $1/n$ are included in Table 3. For all cases, the Langmuir equation fits the experimental data better than the Freundlich equation. It is clear that the Freundlich model could not fit all the experimental data well, as R^2 values are generally lower and the χ^2 values are higher than Langmuir model.

3.7. χ^2 analysis

χ^2 test was adopted in order to find the suitability of an isotherm that fits best the experimental data. The χ^2 statistics is basically the sum of the squares of the difference between the experimental and calculated data from models, with each squared difference is divided by corresponding data obtained by calculation. The equation for evaluating the best fit model is as follows (Eq. (9)):

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{9}$$

where $q_{e,m}$ is the equilibrium capacity obtained from the model (mg/g) and q_e is the experimental equilibrium capacity (mg/g). From Table 3, lower χ^2 values of Langmuir isotherm model show that the experimental data correlate well with the Langmuir isotherm than the Freundlich isotherm.

3.8. Effect of temperature

To study the effect of temperature, biosorption experiments were carried out at three different temperatures (303, 313, and 323 K). The experimental result showed that the biosorption capacity of LELP increases with the increase in temperature. This indicates that the biosorption of Ni(II) ions onto LELP is endothermic in nature. The increase in biosorption with increase in temperature may be attributed to either increase in the number of active sites present on the surface of the biosorbent or the increase in the attractive forces between the metal ions and the biosorbent.

The biosorption process depends on temperature and is associated with several thermodynamic parameters. Thermodynamic parameters such as of Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were used to evaluate the thermodynamic feasibility of the process and to confirm the nature of the biosorption process.

The parameters were determined by using the following the Eqs. (10) and (11):

$$\Delta G^o = -RT \ln K_L \tag{10}$$

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{11}$$

where R is the universal gas constant (8.314 J/mol K), T is the temperature (K), and K is obtained by multiplying Langmuir constant b and q_m. The changes in enthalpy (ΔH°) and entropy (ΔS°) were estimated from the slope and intercept of the plot of ln K_L vs. $1/T$ (figure not shown). The negative values of ΔG°, −7.985, −7.544, and −6.983 kJ/mol, suggest that the sorption of Ni(II) onto LELP is a spontaneous process and thermodynamically favorable under the experimental conditions. The Gibbs free energy (ΔG°) is small and negative but increases with the increasing temperature. The positive value of ΔH° (10.29 kJ/mol) suggests that biosorption of Ni(II) onto LELP is endothermic. The positive value of ΔS° (0.0518 J/mol K) indicates increased randomness at the biosorbent/solution interface during the biosorption of Ni(II) onto LELP.

4. Conclusions

This study focused on the biosorption of Ni(II) onto LELP from aqueous solution. Kinetic data were fitted well to a pseudo-second-order kinetic model compared to pseudo-first-order and intraparticle diffusion kinetic models. The equilibrium data were well fitted by the Langmuir isotherm model with maximum monolayer sorption capacity of 58.82 mg/g for Ni(II) ions. Thermodynamic parameters such as ΔG°, ΔH°, and ΔS° were calculated, and it was observed that the biosorption of Ni(II) onto LELP was spontaneous and endothermic. Hence, LELP could be utilized as an alternative, low-cost biosorbent for the removal of Ni(II) from aqueous solution.

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References

[1] V.K. Gupta, A. Rastogi, A. Nayak, Biosorption of nickel onto treated alga (*Oedogonium hatei*): Application of isotherm and kinetic models, J. Colloid Interface Sci. 342 (2010) 533–539.

[2] N. Akhtar, J. Iqbal, M. Iqbal, Removal and recovery of nickel(II) from aqueous solution by loofa sponge-immobilized biomass of *Chlorella sorokiniana*: Characterization studies, J. Hazard. Mater. 108 (2004) 85–94.

[3] M.V. Subbaiah, Y. Vijaya, N.S. Kumar, A.S. Reddy, A. Krishnaiah, Biosorption of nickel from aqueous solutions by *Acacia leucocephala* bark: Kinetics and equilibrium studies, Colloids Surf. B 74 (2009) 260–265.

[4] World Health Organization (WHO), Guidelines for Drinking-water Quality, Incorporating First Addendum to 3rd ed., Vol. 1, Recommendations, World Health Organization, Geneva, 2006, p.595.

[5] M. Naushad, Surfactant assisted nano-composite cation exchanger: Development, characterization and applications for the removal of toxic Pb^{2+} from aqueous medium, Chem. Eng. J. 235 (2014) 100–108.

[6] Mu. Naushad, Z.A. AlOthman, M. Islam, Adsorption of Cd^{2+} ion using a new composite cation-exchanger polyaniline Sn(IV) silicate: Adsorption kinetics and thermodynamic studies, Inter. J. Environ. Sci. Technol. 10 (2013) 567–578.

[7] K.G. Bhattacharyya, S.S. Gupta, Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review, Adv. Colloid Interface Sci. 140 (2008) 114–131.

[8] M. Puanngam, F. Unob, Preparation and use of chemically modified MCM-41 and silica gel as selective adsorbents for Hg(II) ions, J. Hazard. Mater. 154 (2008) 578–587.

[9] M.Q. Jiang, X.Y. Jin, X.Q. Lu, Z.L. Chen, Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay, Desalination 252 (2010) 33–39.

[10] D. Yang, J. Debing, G. Huili, Z. Lianbi, Y. Xiaosong, Biosorption of aquatic cadmium(II) by unmodified rice straw, Bioresour. Technol. 114 (2012) 20–25.

[11] B. Noureddine, A. Mohammed, B. Abdelghani, E.L.M. Mohammed, Biosorption characteristics of cadmium (II) onto *Scolymus hispanicus* L. as low-cost natural biosorbent, Desalination 258 (2010) 66–71.

[12] W. Li, L. Zhang, J. Peng, N. Li, S. Zhang, S. Guo, Tobacco stems as a low cost adsorbent for the removal of Pb(II) from wastewater: Equilibrium and kinetic studies, Ind. Crops Prod. 28 (2008) 294–302.

[13] D.H.K. Reddy, D.K.V. Ramana, K. Seshaiah, A.V.R. Reddy, Biosorption of Ni(II) from aqueous phase by *Moringa oleifera* bark, a low cost biosorbent, Desalination 268 (2011) 150–157.

[14] P.S. Kumar, S. Ramalingam, S.D. Kirupha, A. Murugesan, T. Vidhyadevi, S. Sivanesan, Adsorption behavior of nickel(II) onto cashew nut shell: Equilibrium, thermodynamics, kinetics, mechanism and process design, Chem. Eng. J. 167 (2011) 122–131.

[15] A. Thevannan, R. Mungroo, C.H. Niu, Biosorption of nickel with barley straw, Bioresour. Technol. 101 (2010) 1180–1776.

[16] S. Jasmin, M.R. Jan, A. Haq, M. Zeeshan, Equilibrium, kinetic and thermodynamic studies for sorption of Ni (II) from aqueous solution using formaldehyde treated waste tea leaves, J. Saudi Chem. Soc. Available from: http://dx.doi.org/10.1016/j.jscs.2012.04.004.

[17] H. Hasar, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk, J. Hazard. Mater. 97 (2003) 49–57.

[18] E. Pehlivan, B.H. Yanik, G. Ahmetli, M. Pehlivan, Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp, Bioresour. Technol. 99 (2008) 3520–3527.

[19] G. Yuvaraja, M.V. Subbaiah, A. Krishnaiah, *Caesalpinia bonducella* leaf powder as biosorbent for Cu(II) removal from aqueous environment: Kinetics and isotherms, Ind. Eng. Chem. Res. 51 (2012) 11218–11225.

[20] D.D. Amarendra, P.D. Shashi, G. Krishna, S. Mika, Strengthening adsorptive amelioration: Isotherm modeling in liquid phase surface complexation of Pb (II) and Cd(II) ions, Desalination 267 (2010) 25–33.

[21] W. Zengdi, Y. Ping, Q. Rongjun, C. Hou, W. Chunhua, R. Shuhua, Adsorption kinetics, thermodynamics and isotherm of Hg(II) from aqueous solutions using buckwheat hulls from Jiaodong of China, Food Chem. 136 (2013) 1508–1514.

[22] S. Lagergren, Zur Theorie Der Sogenannten Adsorption Geloster Stoffe. K. Sven. Vetenskapsakad [About the theory of so called adsorption of soluble substances, Kungliga Svenska Vetenskapsakademiens, Handlingar], Band 24 (1898) 1–39.

[23] Y.S. Ho, G. McKay, D.A.J. Wase, C.F. Forster, Study of the sorption of divalent metal ions on to peat, Adsorpt. Sci. Technol. 18 (2000) 639–650.

[24] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civil Eng. 89 (1963) 31–60.