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Removal of Ni(II) ions from aqueous solution by using low cost biosorbent prepared from jackfruit (*Artocarpus heterophyllus*) leaf powder

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Batch adsorption technique is utilized for the removal of Ni(II) ions in aqueous solution by jackfruit leaf powder (JLP) under different experimental conditions. Jackfruit (*Artocarpus heterophyllus* L., family Moraceae) leaf powder (JLP) has been prepared from clean, mature leaves of the tree, which are dried in the sun and in an air oven at 373-383 K for 3-4 h and ground to a powder. 50-100 mesh fractions are taken, washed with water and dried for 4 h at 373-383 K and preserved in a desiccator. Sorption of Ni(II) is found to be dependent on *p*H of the medium. The process is characterized with Freundlich, Langmuir and Temkin isotherms and the adsorption coefficients are computed in each case. Langmuir monolayer capacity for Ni(II) sorption on JLP is 11.5 mg/g that could be considered as substantial. The kinetics of adsorption have been worked out by applying first-order, second-order and intra particle diffusion models. The biosorption process is endothermic showing increase in uptake with temperature in the range of 303 to 323 K. Ni(II) is held to the surface by various functional groups present on JLP surface as seen from FTIR measurements.

Keywords: Jackfruit leaf powder, Biosorption, Ni(II), Isotherm, Kinetics

Heavy metal ions cause serious environmental concerns because of the toxicity[1] associated with them. The removal of these metal ions from wastewater has been an important area of research since the conventional treatment technology cannot get rid of them. Nickel occurs in two oxidation states in nature namely Ni(0) and Ni(II). Divalent nickel is considered as toxic to most organisms at concentrations higher than 5.0 mg/L. It is generally encountered in wastewater streams from industries such as non-ferrous metals, mineral processing, electroplating, porcelain enameling, copper sulfate manufacturing, and battery and accumulator manufacturing. Therefore, it is essential to regulate the concentration of Ni(II) before discharging to any water stream. Acute poisoning with Ni(II) causes headache, dizziness, vomiting, chest pain, rapid respiration and extreme weakness[2]. Higher concentrations of nickel are known to be carcinogenic.

The most conventional techniques for removal of Ni(II) from industrial wastewater are filtration, chemical precipitation, adsorption, electro-deposition, ion exchange, etc[3]. These separation techniques are less effective and are very expensive. Biosorption of heavy metals is an effective separation process for the removal and recovery of heavy metal ions from aqueous solutions. It utilizes the ability of biological materials to accumulate heavy metals from waste streams by either metabolically mediated or purely physicochemical pathways of uptake[4]. Biosorption of metals by biomass has been much explored in recent years. This novel approach is competitive, effective and cheap[5]. Different forms of inexpensive plant material such as peat and pith[6], plant wood, root, leaves and bark[7-9], sawdust[9], papaya wood[10], cork biomass[11], dehydrated wheat bran[12], tea-industry waste[13], grape stalks waste[14] have been widely used as biosorbents. In the present study, the Jackfruit (*Artocarpus heterophyllus*) Leaf Powder (JLP) has been tried as a cheap biosorbent to adsorb Ni(II) from aqueous solution.

Experimental Section

Preparation of the biosorbent

The biosorbent from Jackfruit Leaf Powder or JLP (*Artocarpus heterophyllus* L., family Moraceae) was prepared from the mature leaves of the tree. Mature leaves were collected from various trees of Jackfruit. The leaves were washed repeatedly with lots of water to remove dust and soluble impurities. They were further dried in the sun at 308-310 K and were carried to the laboratory in plastic bags. The leaves were then kept in an air oven at 373-383 K for 3-4 h till they could be crushed to a powder in a grinder. The powder was sieved and 50-100 mesh fractions were chosen as the biosorbent. This fraction was again thoroughly washed with distilled water to remove all the soluble materials, dyes and pigments. The washed JLP was dried for 4 h in an air oven at 373-383 K and preserved as the biosorbent in glass bottles in a desiccator.

Preparation of nickel stock solution

Ni(II) stock solution of strength 1000 mg/L was prepared by dissolving the required quantity of the Nickel nitrate hexahydrate [$Ni(NO_3)_2.6H_2O$; E Merck, Mumbai] in 1 L double distilled water. All other solutions of various concentrations were made by diluting this stock solution with double distilled water.

Batch adsorption studies

All the adsorption experiments were carried out in batch equilibrium method in 100 mL Erlenmeyer flasks by mixing a pre-weighed amount of JLP and 50 mL of Ni(II) solution of fixed concentration. The flasks were kept in a temperature controlled water bath shaker (NSW, New Delhi) and were agitated for a predetermined time interval at a constant temperature. The solutions were filtered to separate JLP and Ni(II) remaining unadsorbed in solution was determined with atomic absorption spectrophotometer (Perkin-Elmer Analyst 200: wave length 232.00 nm; slit 1.8/1.35 mm). The experiments were done at 303, 313 and 323 K to determine the effect of temperature. The percentage of biosorption was calculated by using the relation $[(C_0–C_t)/C_0] \times 100$, where C_0 is the initial concentration of Ni(II) and C_t is the concentration at time t min. The amount of Ni (II) adsorbed on JLP surface i.e., q_t (mg/g) in t min was calculated from the relation $q_t = (C_0–C_t)/m$. Different sets of experiments were carried out to determine the effects of *p*H, contact time, JLP amount, Ni(II) concentration and temperature.

Results and Discussion

Biosorbent characterization

The presence of various functional groups was determined from FT-IR measurements on JLP (Fig. 1). The band at 3430.4 cm^{-1} could be assigned to bonded OH groups, that at 2924.1 cm^{-1} to asymmetric $–CH_2$ group, that at 1604.4 cm^{-1} to CO and CN stretching bonds and the one at 1068.3 cm^{-1} to C=S bonding. The cation exchange capacity (CEC) of JLP was measured to have a value of 2.21 meq/g (Copper bisethylenediamine complex method)[15]. The SEM micrographs revealed the JLP particles to be fibrous in nature with the topography of a nonporous adsorbent with irregular, stepped appearance (Fig. 2). The specific surface area of JLP was found to be 246.9 m^2/g by using methylene blue dye adsorption method[16]. The high surface area of the JLP might be due to the presence of large number of steps and other deformities in the external surface of the particles.

Effect of biosorbent amount

The effects of JLP amount (1-5 g/L) on adsorption of Ni(II) were analyzed with different initial

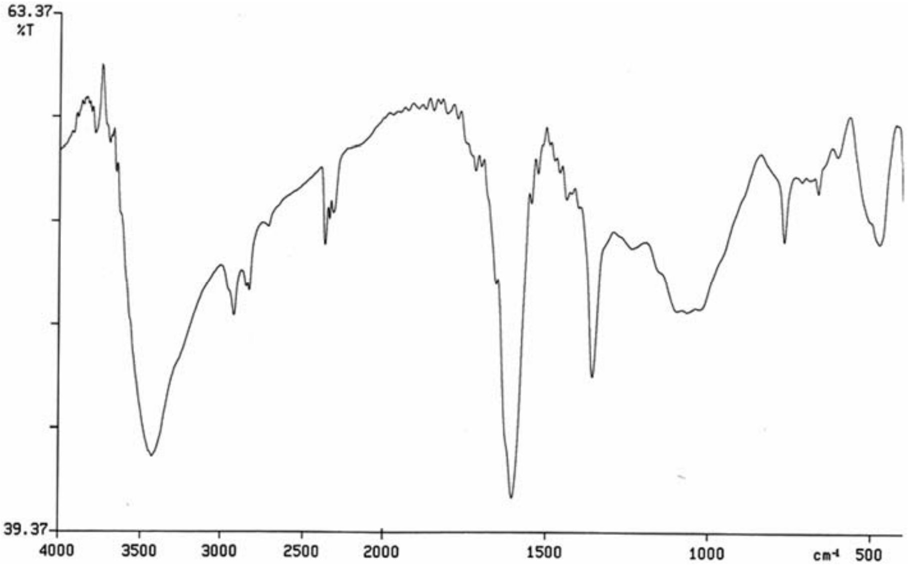

Fig. 1 — FT-IR spectra of JLP

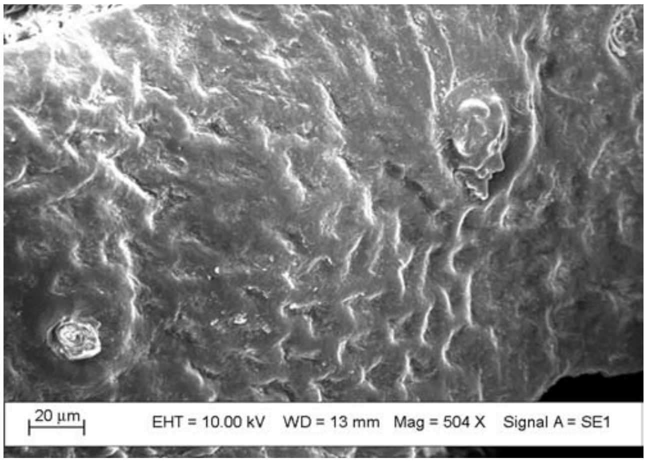

Fig. 2 — SEM micrograph of JLP

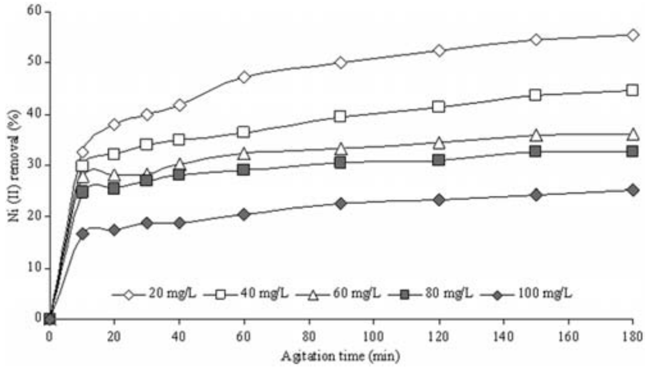

Fig. 3 — Effects of contact time on Ni(II) adsorption by JLP (JLP 2 g/L, pH 5.6 ± 0.2, 303 K)

concentrations (20, 40, 60, 80 and 100 mg/L). The adsorption capacity per unit mass, q_e, decreased from 9.7 to 3.2 mg/g for 20 mg/L and from 12.3 to 8.8 mg/g for 100 mg/L Ni(II) concentrations respectively. In general, the increase in biomass concentration reduces metal sorption per gram of biomass[17]. At a given Ni(II) concentration, the lower the biomass concentration in suspension, the higher is the Ni(II)/JLP ratio and consequently, Ni(II) retained by the sorbent per unit mass is also higher unless the biomass reaches saturation. High biomass concentrations can exert a shell effect, protecting the active sites from being occupied by Ni(II). For example, Basha *et al.* (2009)[18] measured the adsorption capacity of a biosorbent obtained from *Cystoseira indica*, a brown seaweed for sorption of Ni(II) and found that when the initial Ni(II) concentration was 91.45 mg/L and the sorbent dose was 0.5, 1.0, 1.5, 2.0, and 2.5 g/L, the biomass had the maximum sorption capacity at the lowest biomass amount.

Effects of *p*H

Influence of pH (range: 2.0 to 7.0) on sorption of Ni(II) (concentration 40 mg/L) on JLP (2 g/L) was very significant. The sorption was very low at pH 2.0, increased up to 52% at pH 6.0 and thereafter, decreased to 48% at pH 7.0. The decreasing sorption of Ni(II) at pH 7 and above was due to the beginning of Ni(II) hydroxide precipitation that decreased Ni(II)-JLP interactions[19]. The pH dependency of Ni(II) sorption on JLP could be explained on the basis of association-dissociation of certain functional groups, such as the carboxylic groups[20]. At low pH, most of the carboxylic groups are not dissociated and could not bind the metal ions in solution. With increasing pH, these groups dissociate forming negative fragments on the sorbent surface and these interact with Ni(II) ions[19]. Sorption of Ni(II) from aqueous solution on sphagnum moss peat[21] followed a similar pattern in the pH range of 4.0 to 7.0.

Effects of contact time

The removal of Ni(II) ions per gram of JLP as a function of interaction time at 303 K is shown in Fig. 3. Maximum sorption was achieved in the first 40 min and then, the interactions slowed down and gradually approached equilibrium in 180 min. For Ni(II) concentration of 20 mg/L, q_e varied from 4.185 mg/g at 40 min to 5.545 mg/g at 180 min. Similar trend was followed at other Ni(II) concentrations. The rapid uptake was probably due to the abundant availability of active sites on the bare biomass, and with the gradual occupancy of these sites, the sorption became less efficient and slow[22]. Ni(II) sorption on chitosan coated perlite also attained equilibrium in 180 min[23].

Kinetics of adsorption

In order to examine the controlling mechanism of the biosorption process such as mass transfer and chemical reaction, the pseudo-first-order, the pseudo-second-order and the intra-particle diffusion kinetic models were used to test the experimental data of Ni(II) biosorption on JLP. The first-order rate equation of Lagergren[24] is represented as

$$\log (q_e – q_t) = \log (q_e) – (k_1 / 2.303) t \quad \text{... (1)}$$

where q_e and q_t (mg/g) are the sorption capacities at equilibrium and at time t, respectively and k_1 is the rate coefficient of pseudo-first order sorption (L/min). The values of k_1 can be obtained from the slope of the linear plot of log (q_e□q_t) *vs* t. The results obtained

Table 1 — Kinetic parameters for sorption of Ni(II) on JLP at 303 K

C_0 mg/L	First-order model				Second-order model			Intra particle diffusion model		
	q_e(exp) mg/g	q_e(cal) mg/g	$k_1 \times 10^2$ min^{-1}	r	q_e(cal) mg/g	$k_2 \times 10^2$ g/mg/min	r	k_{id} mg/g/min$^{0.5}$	Intercept.	r
20	5.5	3.0	2.16	0.99	5.7	1.83	0.99	0.434	6.9	0.99
40	8.9	3.9	1.77	0.96	9.1	1.32	0.99	0.315	9.0	0.99
60	10.9	3.9	1.98	0.96	11.0	1.52	0.99	0.277	7.3	0.99
80	13.0	3.5	1.50	0.99	13.2	1.46	0.99	0.288	5.1	0.99
100	12.6	5.5	1.59	0.99	12.9	0.86	0.99	0.220	2.8	0.99
mean	10.2	4.0	1.80	0.98	10.4	1.39	0.99	0.307	6.2	0.99

from the application of pseudo first order kinetics are given in Table 1.

The second order kinetics[25] assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites and may be expressed in the form

$$t / q_t = 1/(k_2 q_e^2) + (1/q_e)\, t \qquad \text{... (2)}$$

The plot of t/q_t *vs.* t should give a linear relationship with a slope of $1/q_e$ and an intercept of $1/(k_2 q_e^2)$. This allows the computation of k_2, the second order rate coefficient (g/mg/min). These plots for Ni(II) on JLP are shown in Fig. 4 and the rate coefficients are listed in Table 1.

The mean value of k_1 is 1.80×10^{-2} min^{-1} indicating a fast sorption process of Ni(II) on JLP at 303 K in accordance with the experimental observations. However, there is large deviation between the experimentally measured q_e values and those obtained from the Lagergren plots. This indicates that pseudo first order kinetics is not sufficient to describe the mechanism. The second order plots have high linearity (r = 0.99) and q_e values obtained from these plots are very close to the experimental q_e values for different initial Ni(II) concentrations (Table 1). Thus, the second order kinetic model provides a better explanation of the kinetics of biosorption of Ni(II) on JLP. The mean k_2 value of 1.39×10^{-2} g/mg/min suggests fast interactions between JLP particles and Ni(II) ions – again, in conformity with the experimental observations. Biosorption of Ni(II) from aqueous solutions onto Baker's yeast (*Saccharomyces cerevisiae*)[26] and the cone biomass of *Thuja orientalis* have also been shown to follow second order kinetics[27].

The equation used to describe intra particle diffusion was given by Weber and Morris[28] and has the following simplified form:

$$q_t = k_i\, t^{0.5} \qquad \text{... (3)}$$

where k_i is the intra particle diffusion rate coefficient (mg/g/min$^{0.5}$). To satisfy this equation all the plots should pass through origin. But in actual practice the plots do not have zero intercepts. This means that sorption of Ni(II) by JLP particles are complex and both surface adsorption as well as intra particle diffusion contributes to rate determining step.

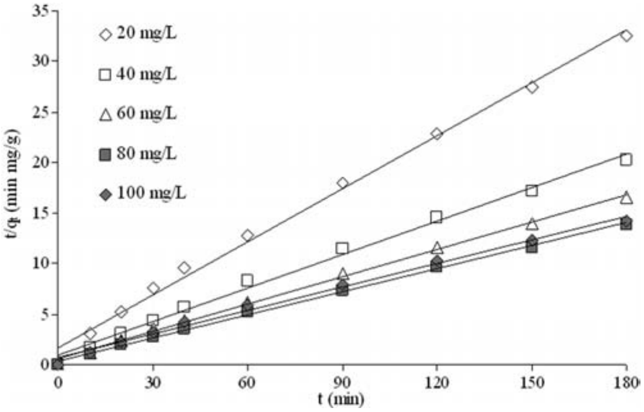

Fig. 4 — Pseudo second-order kinetic plots for adsorption of Ni(II) on JLP ((JLP 2 g/L, pH 5.6 ± 0.2, 303 K)

Adsorption isotherms

The analysis of adsorption data is important for developing an equation which accurately represents the results and which could be used for design purposes. Out of several isotherm equations, the Langmuir isotherm model was used to fit the experimental data. The Langmuir isotherm assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface[29]. The mathematical expression of Langmuir isotherm model is

$$C_e/q_e = 1/(b.q_m) + (1/q_m)\times C_e \qquad \text{... (4)}$$

where C_e is the concentration of the adsorbate in liquid phase in equilibrium, q_e is the amount adsorbed per unit mass in equilibrium, q_m is the amount adsorbed per unit mass to form a monolayer and b is the Langmuir coefficient related to affinity. A plot of

C_e/q_e vs. C_e gives a straight line, slope of which gives the value of q_m and intercept gives the value of b. The Langmuir parameter, b, can be used to predict the affinity between the sorbate and the sorbent using the dimensionless separation factor, R_L, defined as[30]

$$R_L = 1/1+bC_o \qquad \text{... (5)}$$

where b is the Langmuir constant (L/mg) and C_o is the initial Ni(II) concentration (mg/L). If the R_L values are equal to zero or one, the adsorption is either linear or irreversible; if the values are in between zero and one, adsorption is highly favorable; and R_L values greater than 1 indicate unfavorable sorption.

Figure 5 shows the Langmuir plots for Ni(II) sorption on JLP and Table 2 provides the Langmuir coefficients. The Langmuir monolayer capacity, q_m decreased from 12.7 to 10.1 mg/g as JLP amount varied from 1 to 5 g/L with a mean q_m value of 11.5 mg/g. The Langmuir monolayer capacity for Ni(II) biosorption obtained in the present work can be compared with that obtained on sphagnum moss peat of 2.42 to 7.54 mg/g with Ni(II) concentration in the range of 10 to 100 mg/L[31]. Similarly, Baker's yeast had been found to have q_m values of 7.29-12.27 mg/g (mean: 11.40 mg/g) for different Ni(II) concentrations[26]. In another work, q_m value for Ni(II) sorption by *Thuja orientalis* cone biomass was found to be 12.42 mg/g[27]. The average b value of 0.14 L/mg obtained in the present work is similar to that of Neem leaf powder[32] and bagasse fly ash, a sugar industry waste[33]. The R_L value between 0 and 1 signifies strong, favourable sorption of Ni(II) on JLP.

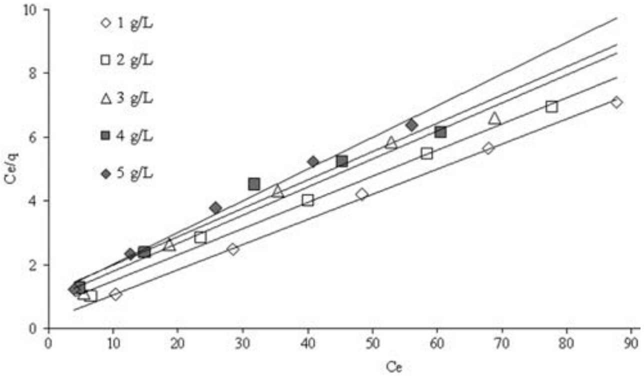

Fig. 5 — Langmuir isotherm plots for adsorption of Ni(II) on JLP (pH 5.6 ± 0.2, contact time 180 min, initial Ni(II) concentrations- 20, 40, 60, 80 and 100 mg/L, 303 K)

Table 2 — Langmuir isotherm coefficients for sorption of Ni(II) on JLP at 303 K

JLP amount (g/L)	1	2	3	4	5	Mean
q_m (mg/g)	12.7	12.2	11.4	11.3	10.1	11.5
b (L/mg)	0.29	0.12	0.10	0.08	0.10	0.14
R_L	0.03	0.08	0.09	0.11	0.09	0.08
r	0.99	0.99	0.99	0.98	0.99	0.99

Thermodynamic parameters

The Gibbs energy, enthalpy and entropy (ΔG, ΔH, ΔS), for the adsorption process are obtained from the experiments carried out at three different temperatures (303, 313 and 323 K) using the standard equations[34]. All the thermodynamic parameters are listed in Table 3. The positive values of adsorption enthalpies indicated that sorption of Ni(II) ions on JLP surface was an endothermic process and would be favoured by an increase in temperature. The process was accompanied by a decrease in entropy from 193 to 54 J/K/mol (mean: 92 J/K/mol) which was quite natural since the randomly distributed Ni(II) ions in solution were likely to have some kind of ordered structure on being adsorbed on JLP surface. However, the ordered structure is likely to be distorted as the temperature rises from 303 to 323 K resulting in an entropy decrease. As a measure of spontaneity, the biosorption of Ni(II) on JLP was accompanied by a decrease in Gibbs energy from 2.954 to 2.032 to 1.110 kJ/mol when the temperature was increased from 303 to 323 K. When the concentration of Ni(II) was low (20 mg/L), the decrease in Gibbs energy was much more. For other Ni(II) concentrations (40, 60, 80 and 100 mg/L), Gibbs energy decreased with rise in temperature. The general trend is thus favourable to Ni(II) sorption on JLP. The increase in enthalpy, ΔH (11.10 kJ/mol) and entropy (39 J/K/mol) had been reported for Ni(II) sorption on *Chlorella vulgaris* biomass[35] along with Gibbs energy decrease of – 0.649 kJ/mol at 298 K.

Table 3 — Thermodynamic parameters for sorption of Ni(II) on JLP

C_0 (mg/L)	ΔH (kJ/mol)	ΔS (J/K/mol)	ΔG(kJ/mol)		
			303K	313K	323K
20	59.5	193	1.182	-0.744	–2.671
40	30.0	92	2.195	1.278	0.361
60	29.5	87	3.203	2.334	1.465
80	14.6	36	3.675	3.316	2.957
100	20.9	54	4.514	3.974	3.435
Mean	30.9	92	2.954	2.032	1.110

Conclusion

The sorption of Ni(II) on JLP is strongly *p*H dependent and maximum sorption is recorded at *p*H 6.0. The sorption capacity increases with increasing biosorbent amount and maximum removal is found around 40 min. The average Langmuir sorption capacity, q_m is 11.5 mg/g for Ni(II) on JLP. The sorption mechanism follows pseudo second order kinetics with close agreement between experimental and calculated q_e values. The Gibbs free energy decreases with rise in temperature from 303 to 323 K and hence the sorption of Ni(II) on JLP is thermodynamically favorable. Thus, jackfruit leaf powder could be a potential biosorbent for the treatment of Ni(II) in aqueous wastewater system.

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