



## Azadirachta indica leaf powder as a biosorbent for Ni(II) in aqueous medium

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### ARTICLE INFO

#### Article history:

Received 8 June 2008

Received in revised form 6 September 2008

Accepted 29 September 2008

Available online 7 October 2008

#### Keywords:

Adsorption

Biosorption

*Azadirachta indica* leaf powder

Intra-particle diffusion

Isotherm

Thermodynamics

### ABSTRACT

*Azadirachta indica* leaves are converted to a fine powder for use as a biosorbent for the removal of metal ions in aqueous solution. In this work, the adsorptive interactions between Ni(II) and the powder were studied under a variety of conditions involving variations in pH, Ni(II) concentration, biosorbent amount, interaction time and temperature, all in single batch processes. The experimental data have been interpreted on the basis of existing mathematical models of equilibrium kinetics and thermodynamics. The biosorption of Ni(II) increased in the pH range of 2.0–5.0 with ~92.6% adsorption at pH 5.0 for the highest amount of the biosorbent (4 g/L). The biosorption followed second-order kinetics and intra-particle diffusion was likely to have significant influence in controlling the process. The Langmuir monolayer adsorption capacity varied from 2.4 to 9.1 mg/g and the equilibrium coefficient from 1.09 to 2.78 L/g with strong indication that the Ni(II) ions were held on the biosorbent surface by formation of an adsorption complex. The thermodynamic parameters showed the process to be exothermic in nature supported by appropriate ranges of values of enthalpy change, entropy change and Gibbs energy change.

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### 1. Introduction

Many toxic heavy metals are regularly discharged into the environment as constituents of industrial emissions, effluents and solid wastes, causing serious soil and water pollution. Even at relatively low concentrations, some of the metal ions could be highly toxic towards plant and animal life [1] and it is necessary to remove and if possible, recover the metals from the industrial discharges before being allowed to interact with the natural environment. Nickel is moderately abundant and is the twenty-second most abundant element by weight in the earth's crust [2]. It is mostly found along with sulphides of iron or copper [3].

Nickel is a common pollutant arising from many electroplating and vegetable fat producing industries, metal mining and processing as well as other industrial, urban and agricultural activities. Primary base metal smelters are major sources of Ni. The permissible limit of Ni(II) in drinking water is 0.5 mg/L [4]. Ni(II) can cause dermatitis, dizziness, headache, nausea and carcinogenesis. It is also toxic to the plants.

Daily intake of nickel from food is 100–300 µg/day in most countries. Critical organs for nickel exposure in humans are the respiratory system, especially the nasal cavities, sinuses and the skin. Exposure to nickel has been known to cause occupational asthma in metal-plating workers [4,5]. Many other respiratory effects due to

exposure to nickel are reported, like chronic sinusitis and bronchitis, nasal septal erosions, decreased pulmonary residual capacity, increased respiratory frequency. Nickel and nickel compounds have a strong sensitizing potential on the skin, which is manifested by irritation, eczema and allergic contact dermatitis. Nickel carbonyl is the most acutely toxic nickel compound. Poisoning can lead to headache, vertigo, nausea, vomiting and severe pneumonia. Chronic irritative effects observed in nickel refinery and nickel-plating workers include rhinitis, sinusitis, perforations of the nasal septum and bronchial asthma. High risks have been reported in nickel refinery workers and workers involved in processes with exposure to soluble nickel e.g. nickel sulphate [6], often combined with some exposure to nickel oxide.

Various physicochemical and biological methods are in use for the removal of toxic metal ions from water and the practical application of these methods are dependent on their operational costs as well as difficulties associated with disposal of wastes generated [1,2–4]. These methods are required to address the inadequacy of the conventional treatment methods of chemical precipitation, evaporation, etc., for treating effluents at low metal loadings [1,5–7] and must represent a cost effective remediation technology [8–12]. Liquid-phase adsorption is one of the most efficient methods for the removal of colors, odors, organic, and inorganic pollutants from industrial effluents. While granular or powdered activated carbon is very effective for relatively low-molar-mass organic compounds, the efficiency is much less for metals unless chemically activated [8]. Biosorption, involving use of dead or living biomass, has emerged as a technique with remarkable promise in treating

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### Nomenclature

$b$	Langmuir coefficient for adsorbate–adsorbent equilibrium (L/g)
$C_e$	equilibrium concentration of metal ion in liquid-phase (mg/L)
$C_o$	initial concentration of metal ion solution (mg/L)
$F$	the fractional attainment of equilibrium ( $=q_t/q_e$ )
$\Delta G$	Gibbs free energy (kJ/mol)
$\Delta H$	enthalpy of adsorption (kJ/mol)
$k_{fd}$	film diffusion rate constant ( $\text{min}^{-1}$ )
$k_i$	intra-particle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-0.5}$ )
$k_1$	pseudo first-order adsorption rate constant ( $\text{min}^{-1}$ )
$k_2$	second-order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ )
$K_f$	Freundlich coefficient for adsorption capacity ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ )
$n$	Freundlich coefficient for adsorption intensity
$q_e$	equilibrium concentration of metal ion in solid phase (i.e., amount of metal ion adsorbed per unit mass at equilibrium) (mg/g)
$q_m$	Langmuir monolayer adsorption capacity (mg/g)
$q_t$	amount of metal ion adsorbed per unit mass at any time $t$ (mg/g)
$R$	gas constant ( $\text{kJ K}^{-1} \text{mol}^{-1}$ )
$r$	regression coefficient
$R_L$	dimensionless separation factor
$\Delta S$	entropy of adsorption ( $\text{J K}^{-1} \text{mol}^{-1}$ )
$T$	temperature (K)

metal containing wastewaters [1,13,14]. Biomass is available naturally in large quantities, or obtained as by-products from industrial or agricultural operations, inexpensive [15,16] and easily disposable without requiring expensive regeneration [2].

When choosing the biomass for metal biosorption experiments, its origin is a major factor to be taken into account. For example, abundant natural material, particularly of cellulosic nature can be converted into potential biosorbent for heavy metals and other pollutants. The removal of metals by biosorption may occur by complexation, co-ordination, chelation, ion exchange, adsorption and microprecipitation [2]. The commercial adsorbents used today for the removal of heavy metals from solutions include a variety of natural materials such as clays, activated carbon, gels, alumina, silica, zeolites [14–16] and many biomaterials such as olive cake [10], chitosan beads [17], *Phormidium* sp., algae [18], etc. Aquatic plants like water hyacinth, duckweeds, etc. have received attention for the removal of Ni(II) and other heavy metals [19]. The abilities of native and modified sugar beet pulps to remove Ni(II) from aqueous solutions have also been reported [20]. Ho and McKay [21] tested sorption of Ni(II) on sphagnum moss peat. Biosorption of Ni(II) on deactivated protonated yeast has been successfully investigated by Padmavathy et al. [22]

The Neem (*Azadirachta indica*) is a large evergreen tree of the mahogany family. The beneficial properties of the Neem tree have been part of the Indian folklore for thousands of years and it is dubbed as ‘the village pharmacy’ because of numerous medicinal properties, starting from controlling digestive disorders to diabetes and high cholesterol to cancer. Since ancient times, leaves of Neem tree have been used for antiviral, anti-malarial, antistress and anti-inflammatory treatment [23]. The Neem tree contains more than 100 bioactive ingredients and is rich in proteins. The leaves have a bitter taste due to the presence of “limonoids”. The most important bioactive principle is azadirachtin (repellent) along with gedunin

(anti-malarial), nimbin (anti-inflammatory, anti-pyretic), nimbidin (antibacterial), nimbidol (anti-malarial, anti-pyretic), quercetin (anti-malarial), salannin (repellent), and sodium nimbinatate (spermicide). Young Neem leaves contain 60% water, 23% carbohydrates, 7% proteins, more than 3% minerals, and 1% fat.

The present work centers on designing a biosorbent from mature Neem leaves for use in the removal of nickel(II) ions from water.

## 2. Materials and methods

### 2.1. Biosorbent preparation and adsorbate solutions

The Neem (*A. indica*) tree is widely distributed in the entire northeastern region of India. Mature Neem leaves were collected from a number of tall trees and washed repeatedly with clean water to remove dusts and other insoluble impurities. The leaves were allowed to dry in a shade and then in an air oven at 333 K for several hours till they became crisp. These were crushed in a grinder to obtain *A. indica* leaf powder (AILP). The powder passing through a 200 mesh (74  $\mu\text{m}$ ) sieve was preserved in a clean glass bottle for use as biosorbent.

Ni(II) stock solution of strength 1000 mg/L was made by dissolving 4.953 g of the Nickel nitrate hexa-hydrate [ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] in 1 L double distilled water. The pH of the Ni(II) solution was 5.6. All other solutions of various concentrations were made from this solution.

### 2.2. Adsorption experiments

Batch adsorption experiments were carried out in 100 ml Erlenmeyer flasks by mixing a pre-weighed amount of AILP and 50 ml of aqueous Ni(II) solution of fixed concentration. The flasks were kept in a thermostatic water bath shaker and were agitated for a predetermined time interval at a constant temperature. The parameters such as pH, time of contact, adsorbent amount, metal concentration, and temperature were varied during different sets of batch experiments (Table 1). After adsorption, the mixture was allowed to settle and centrifuged. Ni(II) remaining unadsorbed in the supernatant layer was measured with atomic absorption spectrophotometry (Varian SpectraAA 220). All experiments were repeated several times till reproducible results were obtained at least thrice.

The amount of Ni(II) adsorbed onto AILP at equilibrium,  $q_e$  (mg/g), was calculated using a mass balance relationship as given in Eq. (1):

$$q_e = (C_o - C_e) \frac{V}{W} \quad (1)$$

where  $C_o$  and  $C_e$  are the initial and equilibrium liquid-phase concentrations of Ni(II), respectively (mg/L),  $V$  is the volume of the solution (L), and  $W$  is the weight of the dry AILP (g).

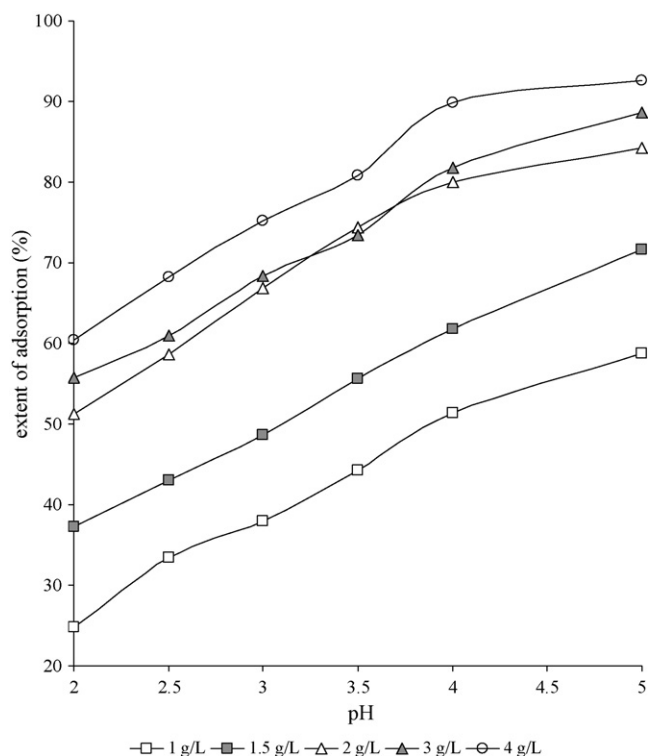
## 3. Results and discussion

### 3.1. Influence of pH

The solution pH is one of the parameters having considerable influence on the adsorption of metal ions [24,25] because the surface charge density of the adsorbent and the charge of the metallic species present depend on the pH. In this work, the extent of Ni(II) biosorption on AILP was investigated for different amounts of AILP at constant Ni(II) concentration (50 mg/L) from pH 2.0 to 5.0. Adsorption experiments were not carried out at pH higher than 5.6 (pH of Ni(II) aqueous solution) as precipitation of Ni(II)-

**Table 1**  
Experimental conditions for the adsorption study.

Type of study	AiLP amount (g/L)	Ni(II) concentration (mg/L)	pH	Temperature (K)	Interaction time (min)
Effect of pH	1.0, 1.5, 2.0, 3.0, 4.0	50	2.0, 2.5, 3.0, 3.5, 4.0, 5.0	303	150
Influence of AiLP amount	1.0, 1.5, 2.0, 3.0, 4.0	10, 20, 30, 40, 50	5.6	303	150
Influence of Ni(II) concentration	1.0, 1.5, 2.0, 3.0, 4.0	10, 20, 30, 40, 50	5.6	303	150
Kinetics	1.0	10, 20, 30, 40, 50	5.6	303	20, 40, 60, 90, 120, 150, 180, 210, 240
Isotherm	0.5, 1.0, 1.5, 2.0, 3.0, 4.0	10, 20, 30, 40, 50	5.6	303	150
Thermodynamics	1.5	10, 20, 30, 40, 50	5.6	303, 308, 313, 323, 328, 333	150



**Fig. 1.** Variation of the extent of adsorption of Ni(II) on different amounts of AiLP at 303 K with pH (Ni(II) 50 mg/L, interaction time 150 min).

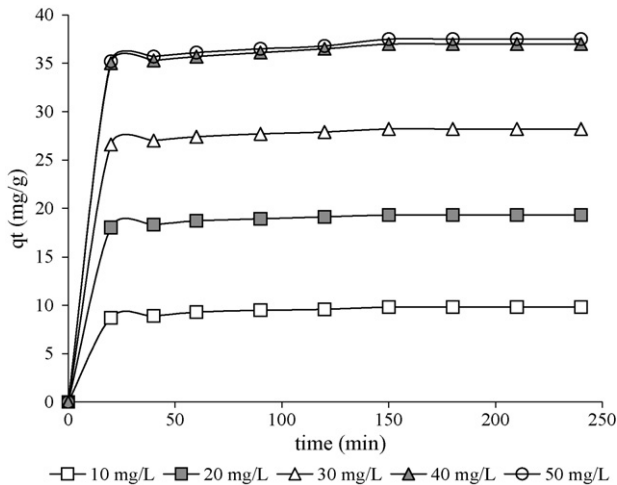
hydroxide starts around pH 7.0, which introduces uncertainty into the interpretation of the results. The extent of adsorption (%) of Ni(II) increased in the pH range, 2.0–5.0 (Fig. 1). At very low pH, the adsorbent surface will be covered with  $H_3O^+$  ions, and Ni(II) ions will have to compete with them for adsorption sites.

That the uptake of nickel(II) is pH-limited has also been observed by other workers. For example, the adsorption capacity of Ni(II) on deactivated protonated yeast was shown to reach a maximum value at pH 6.75 [22]. Metal biosorption has been shown to be the result of ionization of negative functional on the basis of Ni(II) ions competing with the hydronium ions for the sorption sites. At low pH values, the concentration of  $H_3O^+$  far exceeds that of Ni(II) ions and hence, the surface will be covered with  $H_3O^+$  ions, leaving Ni(II) ions unbound. With the pH increasing, the number of hydronium ions come down making some of the sites available for Ni(II) ions and sorption increases till Ni(II) starts binding with  $OH^-$  ions.

The pH dependency of metal ion uptake by a biomass can also be justified by the association–dissociation of certain functional groups, such as the carboxylic groups. At low pH, the carboxylic groups remain in undissociated form and therefore, cannot bind the metal ions in solution, although they may take part in complexation and ion exchange processes [16].

### 3.2. Effects of time and kinetics

Ni(II) biosorption on AiLP at 303 K increased with time till it reached near equilibrium at 150 min (Fig. 2). No change in pH was observed during the experiments. The adsorption was very rapid initially with maximum uptake within 20 min, then slowing down to  $\sim 35$  mg/g (equivalent to  $\sim 90\%$  uptake) in about 150 min. The relatively short equilibrium time of 150 min and a high percentage removal indicates that AiLP possessed a high degree of affinity for Ni(II).

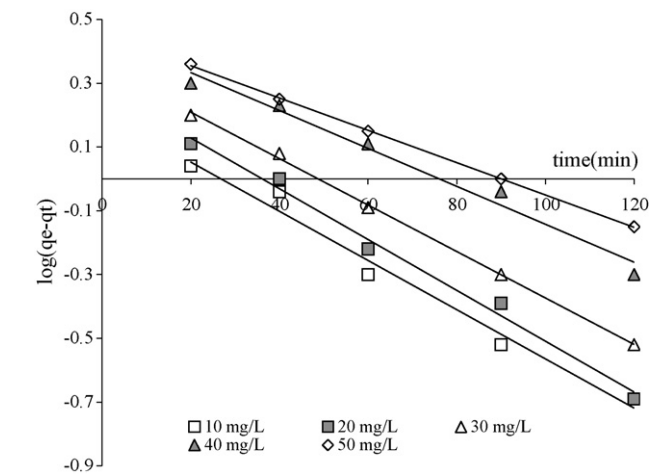


**Fig. 2.** Variation of amount adsorbed per unit mass of AILP with time for different concentrations of Ni(II) (Temperature 303 K, AILP 1 g/L, pH 5.6, Ni(II) concentrations given at the bottom).

**Table 2**

Rate coefficients and regression coefficients for first and second-order kinetics of adsorption of Ni(II) on AILP at 303 K (AILP 1 g/L, pH 5.6).

Ni (mg/L)	$k_1$ (min <sup>-1</sup> )	$r$	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$r$	$k_i$ (min <sup>0.5</sup> )	$r$
10	0.0184	0.98	0.004	0.99	0.10	0.94
20	0.0184	0.99	0.0003	1.00	0.14	0.95
30	0.0161	0.99	0.0001	0.99	0.15	0.96
40	0.0138	0.98	0.000005	0.99	0.20	0.97
50	0.0115	0.99	0.000005	0.99	0.23	0.97
Mean	0.0156	0.99	0.000882	0.99	0.18	0.96



**Fig. 3.** Plots of pseudo first-order kinetics for adsorption of Ni(II) on AILP for different concentrations of Ni(II) at 303 K (AILP 1 g/L, pH 5.6, Ni(II) concentrations at the bottom).

The pseudo first-order kinetic plots obtained by plotting  $\log(q_e - q_t)$  vs.  $t$ , as per the well-known Lagergren equation [26,27]:

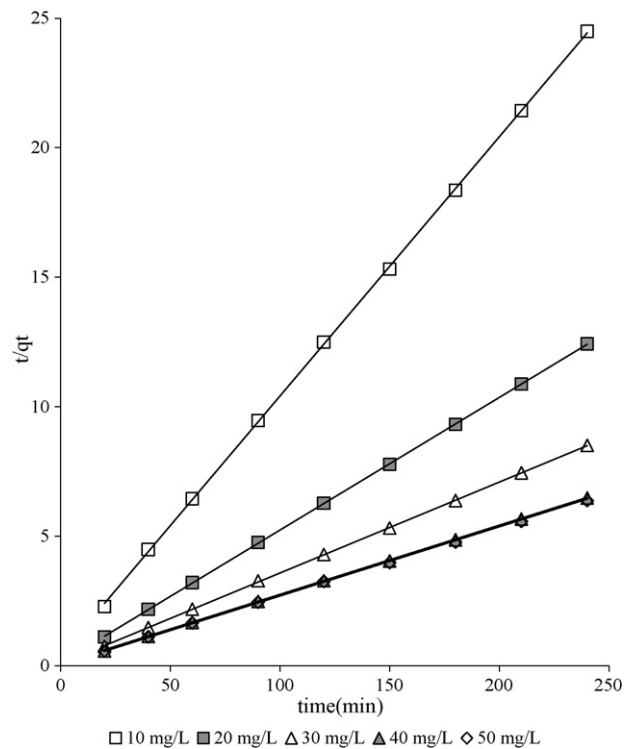
$$\log(q_e - q_t) = -\left(\frac{k_1}{2.303}\right)t + \log q_e \quad (2)$$

for a constant amount of AILP (1.0 g/L) with different Ni(II) concentrations are shown in Fig. 3. In Eq. (2),  $q_t$  and  $q_e$  are the amounts adsorbed per unit mass at time  $t$  and equilibrium time,  $k_1$  is the first-order rate coefficient. All the plots have very good linearity with the regression coefficient of  $\sim 0.99$ . The first-order rate coefficient varies from 0.0115 to 0.0184 min<sup>-1</sup> indicating an appreciably fast reaction (Table 2).

**Table 3**

Deviations between experimental  $q_e$  and those obtained from the plots of first and second-order kinetics at 303 K (AILP 1 g/L, pH 5.6).

Metal (mg/L)	$q_e$ expt (mg/g)	First-order plots		Second-order plots	
		$q_e$ (mg/g)	Deviation (%)	$q_e$ (mg/g)	Deviation (%)
10	9.8	1.62	83.4	10.0	-2.0
20	19.3	1.94	89.9	20.0	-3.6
30	28.2	2.24	92.0	25.0	11.3
40	37.0	2.82	92.4	33.3	10.0
50	37.5	2.88	92.3	33.3	11.2

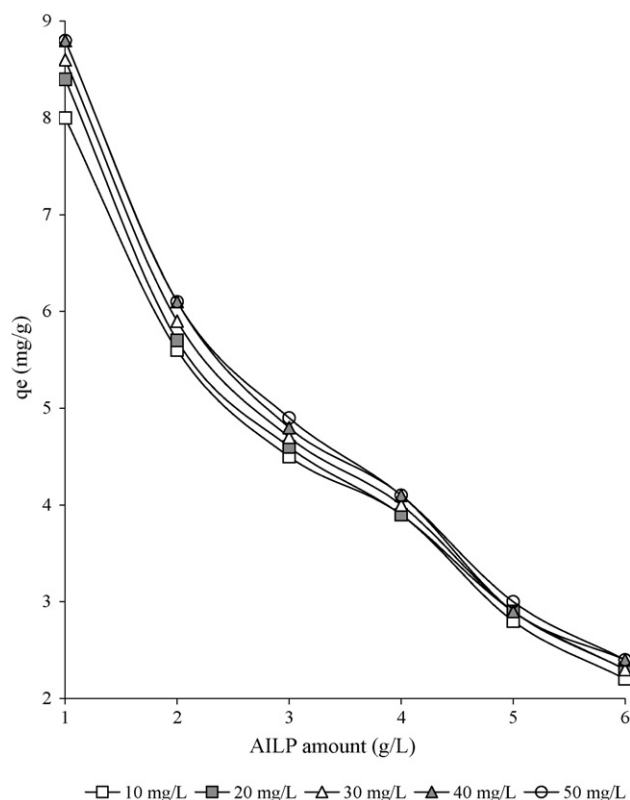


**Fig. 4.** Second-order kinetics plots for adsorption of Ni(II) ions on AILP for different concentrations of metal solutions at 303 K (AILP 1 g/L, pH 5.6).

Linear Lagergren plots do not necessarily confirm a first-order mechanism [28]. This is related mainly to the inherent disadvantage of correctly estimating the values of  $q_e$ . The first-order kinetics is considered to be valid when values of  $q_e$  obtained from the intercept of the Lagergren plots agree with the experimental values. In the present case, the two sets of values do not match (Table 3) and therefore, the validity of the first-order model is uncertain.

The kinetics of the adsorption process was further checked with the second-order kinetic equation [26]:

$$\frac{t}{q_t} = \frac{1}{q_e}t + k_2q_e^2 \quad (3)$$



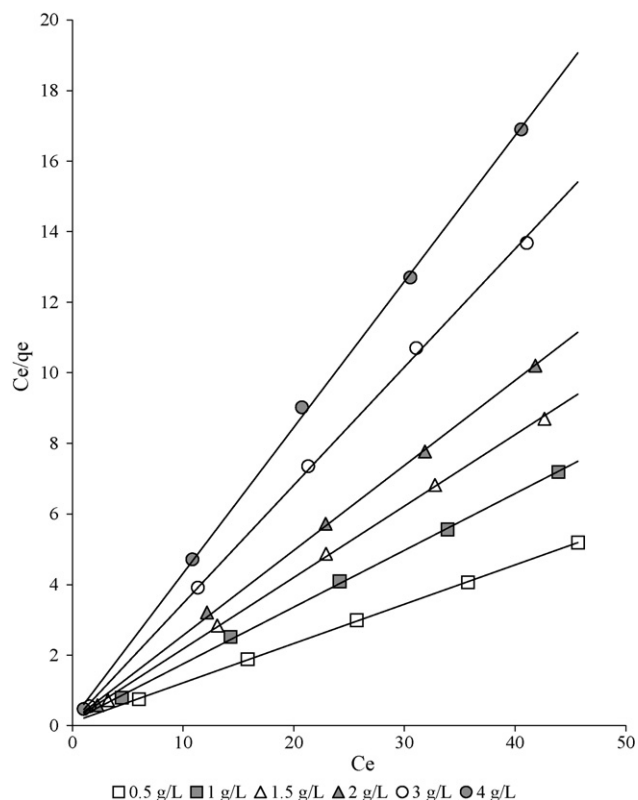
**Fig. 5.** Variation in the amount of Ni(II) adsorbed at equilibrium on unit mass ( $q_e$ ) of AILP at 303 K for different Ni(II) concentrations (given at the bottom) and different AILP amounts (pH 5.6, interaction time 150 min).

by plotting  $t/q_t$  vs.  $t$ . These second-order plots (Fig. 4) are also linear ( $r + 0.99$ ). The second-order rate coefficient varied from  $0.000005$  to  $0.004 \text{ g mg}^{-1} \text{ min}^{-1}$  for Ni(II) concentration range of  $10$ – $50 \text{ mg/L}$  (Table 2), and the  $q_e$  values (experimental and from the second-order plots) show better agreement (Table 3) with less deviation between the two sets. The second-order mechanism is therefore more likely for interactions between Ni(II) and AILP. Such is also the case for biosorption of Ni(II) on moss peat [21] and on Baker's yeast [22]. In the latter case, the second-order rate coefficient was found to be in the range of  $8.27 \times 10^{-3}$  to  $2.14 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$  which are not much different from the values obtained in the present study (Fig. 5).

Adsorption often results from diffusion of the adsorbate into the pores due to existence of a concentration gradient in the liquid–solid interface [29]. In such cases, the intra-particle diffusion model controls the rate of adsorption [27] given by Eq. (4):

$$q_t = k_i \times t^{0.5} \quad (4)$$

where the intra-particle diffusion rate coefficient,  $k_i$ , could be obtained from the plots of  $q_t$  vs.  $t^{0.5}$  provided the linear plots have zero intercept. In the present case, although the plots were lin-



**Fig. 6.** Langmuir isotherms ( $C_e/q_e$  vs.  $C_e$ ) for adsorption of Ni(II) on different AILP amounts and different concentrations of Ni(II) at 303 K under equilibrium conditions.

ear with slopes of  $0.10$ – $0.23 \text{ mg g}^{-1} \text{ min}^{-0.5}$  (equal to  $k_i$ , Table 2), the plots have considerably large intercepts ( $8.4$ – $34.3 \text{ mg/g}$ ). Thus, although intra-particle diffusion of Ni(II) cannot be ruled out, this does not have much say the overall kinetics.

### 3.3. Effect of adsorbent mass and adsorbate concentration

Ni(II) adsorption was influenced by the amount of AILP. With the amount of AILP varied from  $1$  to  $4 \text{ g/L}$  (Ni(II)  $50 \text{ mg/L}$ ), adsorption increased from  $75.2$  to  $88.4\%$  for a constant agitation time of  $150 \text{ min}$  at  $303 \text{ K}$ . On the other hand, for AILP amount of  $1 \text{ g/L}$ , the adsorption decreased from  $98$  to  $75\%$  when Ni(II) concentration was increased from  $10$  to  $50 \text{ mg/L}$  with the same agitation time and adsorption temperature. The amount adsorbed per unit mass ( $q_e$ ) increased gradually with increase in Ni(II) concentration for any AILP amount (Table 4). This may be due to an increase in the number of Ni(II) per unit mass of AILP leading to higher uptake of the metal ions. The  $q_e$  values decreased with the increase in the adsorbent amount for any concentration of Ni(II) due to availability of less number of Ni(II) ions per adsorbent unit mass (Fig. 6).

**Table 4**

Variation in the amount adsorbed per unit mass ( $q_e$ ) at equilibrium (150 min) with AILP amount and Ni(II) concentration at  $303 \text{ K}$  (pH 5.6).

Ni(II) (mg/L)	$q_e$ (mg/g) for AILP amount of					
	0.5 g/L	1.0 g/L	1.5 g/L	2.0 g/L	3.0 g/L	4.0 g/L
10	8.0	5.6	4.5	3.9	2.8	2.2
20	8.4	5.7	4.6	3.9	2.9	2.3
30	8.6	5.9	4.7	4.0	2.9	2.3
40	8.8	6.1	4.8	4.1	2.9	2.4
50	8.8	6.1	4.9	4.1	3.0	2.4



**Table 5**

Freundlich and Langmuir coefficients for adsorption of Ni(II) on AILP and at 303 K. Units of  $q_m$ ,  $K_f$  and  $b$  are respectively mg/g,  $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$  and L/g.

Parameters	AILP amount (g/L)					
	0.5	1	1.5	2	3	4
Freundlich isotherm						
$r$	0.45	0.97	0.94	0.83	0.76	0.93
$n$	0.02	0.03	0.03	0.02	0.01	0.02
$K_f$	7.60	5.40	4.30	3.80	2.80	2.20
Langmuir isotherm						
$r$	0.99	0.99	0.99	0.99	0.99	0.99
$q_m$	9.10	6.30	5.00	4.20	3.00	2.40
$b$	1.09	1.13	1.33	1.59	2.78	2.31
$R_L$	0.03	0.03	0.03	0.03	0.02	0.02

AILP has a larger adsorption capacity than a number of unconventional adsorbents [30] and this may be attributed to easily accessible surface functional groups for metal ion uptake. The chemicals in AILP contain a number of fatty acids like oleic acid, steric acid, palmitic acid, linoleic acid, etc. [31] and FTIR measurements have shown the presence of a large number of functional groups, like OH, COOH, CO, etc., in AILP which might have contributed to the excellent sorption properties of AILP [30].

### 3.4. Adsorption isotherm

The isotherm plots based on the well-known Freundlich equation:

$$q_e = K_f C_e^n \quad (5)$$

or,

$$\log q_e = n \log C_e + \log K_f \quad (6)$$

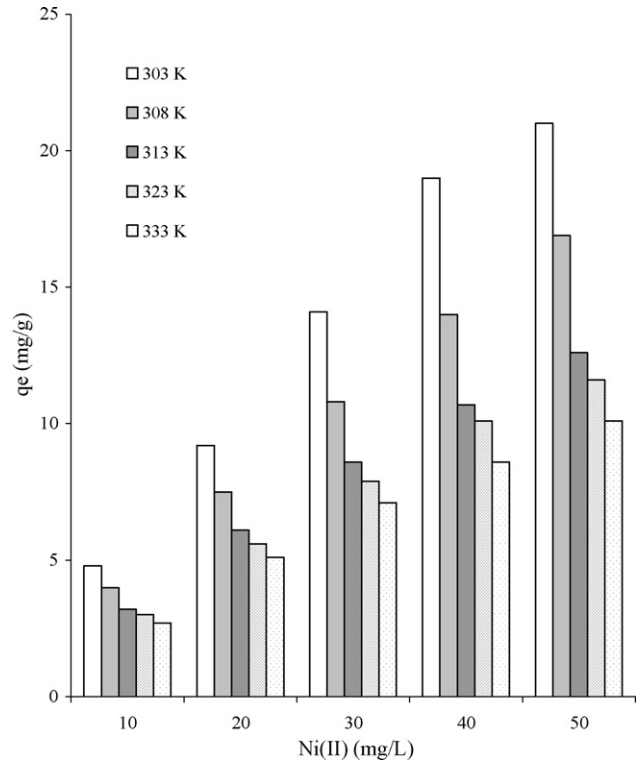
where  $q_e$  and  $C_e$  respectively represent the solid phase and liquid-phase equilibrium concentrations of Ni(II) ions, and  $K_f$  and  $n$  are the Freundlich coefficients, did not show consistently good linearity ( $r+0.45$  to  $+0.96$ ). The values of the adsorption coefficients obtained from the plots (Table 5) have values of 0.01–0.03 for  $n$  and 2.2–7.6  $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$  for  $K_f$ . The Freundlich coefficient  $n$  normally indicates the intensity of adsorption and a low value indicates somewhat lower affinity of the biosorbent for Ni(II) ions. As a whole, the Freundlich model has not much applicability to the biosorption of Ni(II) on AILP since the plots do not have good linearity.

The Langmuir plots (Fig. 6) obtained by plotting  $\log q_e$  vs.  $\log C_e$ , on the basis of the isotherm [28]:

$$\frac{C_e}{q_e} = \frac{q_m}{b} + \frac{C_e}{q_m} \quad (7)$$

are linear with regression coefficient,  $r \sim 0.99$ . The values of the Langmuir monolayer capacity,  $q_m$  and equilibrium constant  $b$  are given in Table 5. The values of  $b$  (1.09–2.78 L/g) were large enough to shift the equilibrium: AILP (solid phase) + Ni(II) (aqueous phase) = AILP...Ni(II) (complex) towards the formation of the adsorbate–adsorbent complex. The Langmuir monolayer capacity  $q_m$  varies from 2.4 to 9.1 mg/g for different amounts of AILP.

The Langmuir monolayer capacity for Ni(II) biosorption on sphagnum moss peat was found to be from 2.42 to 7.54 mg/g with Ni(II) concentration in the range of 10–100 mg/L [21]. Similarly, Baker's yeast has been found to have Langmuir capacity of 7.29–12.27 mg/g for different Ni(II) concentrations [22]. These values are in agreement with the ones obtained for AILP in the present work.



**Fig. 7.** Ni(II) adsorbed,  $q_e$ , per unit mass of AILP for different concentrations of Ni(II) at 303–333 K (AILP amount 1.5 g/L, pH 5.6).

The dimensionless parameter  $R_L$  defined [32,33] as

$$R_L = \frac{1}{1 + b C_e} \quad (8)$$

has values of 0.02–0.03 with respect to adsorption of Ni(II) on AILP at 303 K. The adsorption of the Ni(II) on AILP surface is thus a highly favourable process.

### 3.5. Adsorption thermodynamics

Amount of Ni(II) adsorbed per unit mass of AILP ( $q_e$ ) comes down when temperature is increased from 303 to 333 K suggesting exothermic interactions (Fig. 7). With the rise in temperature, Ni(II) ions escape to the solution phase from the solid phase (AILP adsorbent). The extent of adsorption (%) follows the same trend.

The Gibbs free energy, enthalpy and entropy ( $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ ) of Ni(II) adsorption on AILP are obtained using the equations [34]:

$$\log \left( \frac{q_e}{C_e} \right) = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (9)$$

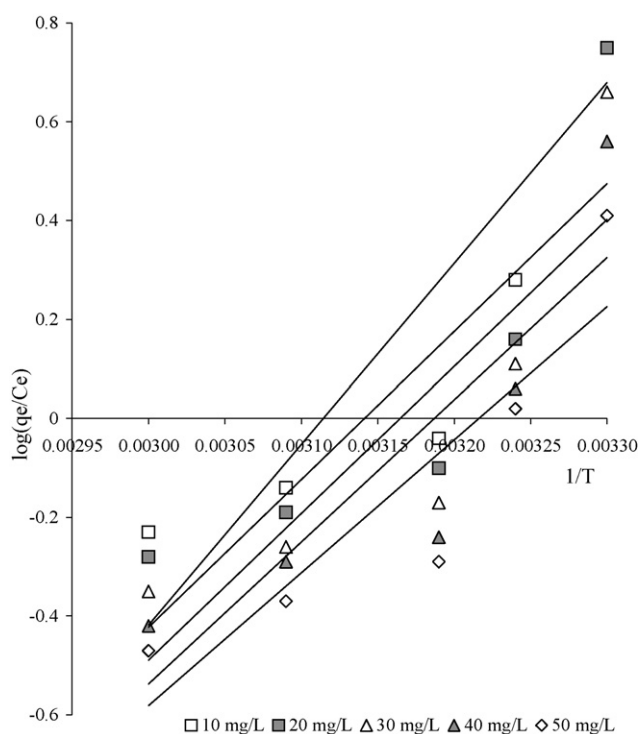
$$\Delta G = \Delta H - T \Delta S \quad (10)$$

from the slope and intercept of the plot of  $\log(q_e/C_e)$  vs.  $1/T$  (van't Hoff plot) and  $\Delta G$  from Eq. (10). The plots are linear ( $r \sim 0.84$ – $0.90$ ) (Fig. 8) and the values of thermodynamic parameters are given in Table 6. The adsorption enthalpy changes from  $-51.5$  to  $-70.1$  kJ/mol. The magnitude of these values indicates moderately strong Ni(II)–AILP bonding.

Ni(II)–adsorption on AILP is accompanied by an entropy decrease and the values vary from  $-165.0$  to  $-218.0 \text{ J K}^{-1} \text{ mol}^{-1}$ . Entropy decrease indicates a positive affinity of the AILP towards Ni(II) ions representing a thermodynamically favourable process [20,32]. Since stability is associated with an ordered arrangement, it is obvious that Ni(II) ions in aqueous solution are in a much more chaotic distribution than Ni(II) ions adsorbed on AILP surface.

**Table 6**  
Thermodynamic parameters for adsorption of Ni(II) ions on AILP for different concentrations of Ni(II) at 303–333 K (AILP 1.5 g/L, pH 5.6).

Metal (mg/L)	$\Delta H$ (kJ/mol)	$\Delta S$ kJ mol <sup>-1</sup>	$\Delta G$ (kJ/mol) at temperature					
			303 K	308 K	313 K	323 K	328 K	333 K
10	-70.1	-0.218	-4.05	-2.96	-1.87	0.31	1.40	1.49
20	-57.3	-0.179	-3.06	-2.17	-1.27	0.52	1.41	2.31
30	-56.9	-0.179	-2.66	-1.77	-0.87	0.92	1.81	2.71
40	-55.1	-0.176	-1.77	-0.89	-0.01	1.75	2.63	3.51
50	-51.5	-0.165	-1.50	-0.68	0.14	1.79	2.62	3.44
Mean	-58.2	-0.183	-2.61	-1.69	-3.88	1.06	1.41	2.69



**Fig. 8.** van't Hoff plots for Ni(II) adsorption on AILP for different concentrations of Ni(II) at 303–333 K (AILP 1.5 g/L, pH 5.6).

Spontaneity of the process of adsorption of Ni(II) on AILP was demonstrated by the decrease in Gibbs energy in the present work. Adsorption Gibbs energy,  $\Delta G$  had negative values in the temperature range of 303–313 K indicating that the AILP particles spontaneously took up the metal ions. The decrease was, however, in a narrow range with the mean values varying from -1.69 to -3.88 kJ/mol in the temperature range of 303–313 K in accordance with the exothermic nature of the adsorption process. Gibbs energy started to increase from 323 K onward thus the spontaneity of the interactions would be lost if the adsorption was carried out at higher temperatures.

#### 4. Conclusion

It is found from this study that the powder made from mature, dried leaves of the tree, *A. indica*, could be a useful biosorbent for the removal of toxic metal ions from aqueous medium. The experiments indicate that:

- (i) Biosorption of Ni(II) increases with the increase in pH of the solution from 2.0 to 5.0. Precipitation of metal hydroxide occurs above pH 5.0. Around 92.6% adsorption is achieved at pH 5.0 for the highest amount of AILP.

- (ii) Second-order kinetics is followed in the biosorption process and it is found that intra-particle diffusion might have some influence in controlling the biosorption process.
- (iii) The process is found to be mass dependent and the amount biosorbed is determined by the AILP amount as well as dye concentration.
- (iv) Langmuir monolayer adsorption capacity of AILP is appreciable, even comparable to that of activated carbon. The isotherm coefficients show that the equilibrium  $\text{AILP} + \text{Ni(II)} = \text{AILP} \cdot \text{Ni(II)}$  complex is in the forward direction ensuring preferential accumulation of Ni(II) on AILP surface.
- (v) The thermodynamics of the biosorption process shows the process to be exothermic in nature supported by appropriate values of enthalpy change, entropy change and Gibbs energy change.

#### Acknowledgement

Financial support for this work by the Council of Scientific and Industrial Research (CSIR), India is gratefully appreciated.

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