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The use of Neem biomass for the biosorption of zinc from aqueous solutions

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Abstract

An adsorbent was developed from mature leaves and stem bark of the Neem (*Azadirachta indica*) tree for removing zinc from water. Adsorption was carried out in a batch process with several different concentrations of zinc by varying pH. The uptake of metal was very fast initially, but gradually slowed down indicating penetration into the interior of the adsorbent particles. The data showed that optimum pH for efficient biosorption of zinc by Neem leaves and stem bark was 4 and 5, respectively. The maximum adsorption capacity showed that the Neem biomass had a mass capacity for zinc (147.08 mg Zn/g for Neem leaves and 137.67 mg Zn/g Neem bark). The experimental results were analyzed in terms of Langmuir and Freundlich isotherms. The adsorption followed pseudo-second-order kinetic model. The thermodynamic assessment of the metal ion-Neem tree biomass system indicated the feasibility and spontaneous nature of the process and ΔG° values were evaluated as ranging from −26.84 to −32.75 (Neem leaves) kJ/mol and −26.04 to −29.50 (Neem bark) kJ/mol for zinc biosorption. Due to its outstanding zinc uptake capacity, the Neem tree was proved to be an excellent biomaterial for accumulating zinc from aqueous solutions.

Keywords: Biosorption; Neem; Zinc; Waste water; Kinetics; Gibbs free energy

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1. Introduction

Heavy metal ions contribute to a variety of adverse health effects. Zinc is one of the toxic heavy metal. In the Dangerous Substances Directive (76/464/EEC) of the European Union, zinc has been registered as List 2 Dangerous Substance with Environmental Quality Standards being set at 40 μg/L for estuaries and marine waters and at 45–500 μg/L for freshwater depending on water hardness [1]. Zinc is widely used in coating iron and other metals, in wood preservatives, catalysts, photographic paper, accelerators for rubber vulcanisation, ceramics, textiles, fertilizers, pigments and batteries [2], and as a consequence it is often found in the wastewaters arising from these processes. The most significant industrial sources arise from electroplating, mining industry effluents and acid mine drainage. For instance, zinc concentrations of over 620 mg/L have been recorded in drainage from abandoned copper mines in Montana, USA [3].

The main techniques currently used for metal removal include chemical precipitation, electrochemical deposition, evaporation, cementation, membrane process, ion-exchange and activated carbon adsorption [4,5]. However, the application of these methods is often limited due to their inefficiency, high capital investment or operational costs. In this context the biosorption process has been recently being evaluated. The major advantages of biosorption include low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, possible of regeneration of biosorbent and metal recovery [6,7]. The efficiency of biomass depends on factors such as number of sites on the biosorbent material, their accessibility and chemical state (i.e. availability), and the affinity between sites and metal (i.e. binding strength) [6–12].

The present work aims to develop a non-conventional adsorbent from the leaves and stem bark of the *Azadirachta indica* (Neem) tree to be used for toxic pollutants, such as zinc in aqueous medium. The Neem tree, *A. indica* (Meliaceae) is native

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to Southeast Asia and grows in many countries throughout the world [13,14]. The potentiality of Neem has been widely explored for solving various problems related to agriculture, public health, population control and environmental pollution. Awareness about the Neem-based technology, whether for pest management, public health, family welfare programmes, reforestation, etc. [15], has grown several fold and production and commercialization of various Neem products for domestic use and exports have been taken up aggressively by various agencies. The present work reports the study of the biosorption kinetics and the biosorption equilibrium of zinc by Neem leaves and stem bark powder. In this study, efficiency of Neem leaves and stem bark powder in removal of heavy metal zinc was investigated in detail. The influence of initial concentration of heavy metal, pH, adsorbent dose and contact time on biosorption of metal ions was studied.

2. Materials and methods

2.1. Chemicals

All the chemicals used were of analytical grade and they were used without further purification. Zn $(NO_3)_2$ (Qualigens Fine Chemicals, Mumbai; minimum assay 99%) was used as the source of zinc and all the solutions were made in double-distilled water. For experiments at different pH, the pH of zinc solutions was adjusted by addition of 0.1 M HNO_3 and 0.1 M NaOH solutions.

2.2. Instruments

Metal concentrations were measured with a PerkinElmer (AAnalyst 300) atomic absorption spectrophotometer. A TOA.V. pH meter (HM 30P) was used to check the pH of the metal solutions. Other instruments such as shaker (PA 250/25. H), Octagon siever (OCT-DIGITAL 4527-01) and Shimadzu (AW 220) electric balance were used.

2.3. Experimental procedure and conditions

Mature Neem leaves and bark collected from a number of tall Neem trees were washed repeatedly with water to remove dust and soluble impurities and were allowed to dry at room temperature in a shade. The leaves and bark were then kept in an air oven at 333–343 K for 24 h. The dried leaves and bark were then converted into fine powder by grinding in a mechanical grinder. The powder was sieved. After drying for several hours at room temperature, the leaves powder and bark powder were preserved in glass bottles for use as adsorbents.

The zinc solutions were prepared by diluting standard zinc solution to the desired concentrations. The freshly diluted solutions were used for each biosorption study. The biosorption experiments were conducted in 250 mL flasks containing 100 mL of zinc solutions with initial concentrations ranging from 25 to 800 mg/L. During the adsorption process, the flasks were agitated on a shaker for 12 h under ambient temperature (25 °C). At the designed period of 5, 15, 20, 30, 60, 100, 120 and 150 min, 5 and 12 h, 10 mL of the solution were collected for analysis. To determine the concentration of the remaining metal ions, the biomass in the sample solutions was removed by filtration and the filtrate was analyzed to measure the zinc concentration. The amount bound on the biomass was assumed to be the difference between the initial metal concentration and that found in the supernatant. The effects of following parameters such as pH, biomass size, biomass dose, initial metal ion concentration and contact time were studied. Biosorption experiments were carried out in duplicate.

2.4. Analytical methods

The instrument was calibrated within the linear range of analysis and a correlation coefficient of 0.99 or greater was obtained for the calibration curve. 10 mL clear supernatants after filtration were analyzed for zinc ion concentrations using an Atomic Absorption Spectrometer (AAnalyst 300) at a wavelength of 213.9 nm. The instrument was periodically checked throughout the analysis with known standards. Three readings were obtained for each sample, and a mean value was computed along with standard deviations for each sample. The amount bound on the biomass was assumed to be the difference between the initial metal concentration and that found in the supernatant.

3. Results and discussion

3.1. Influence of initial pH

The solution pH is one of the parameters having considerable influence on the biosorption of metal ions [16], because the surfaces charge density of the adsorbent and the charge of the metallic species present on the pH. In the present work, the extent of zinc biosorption was investigated in the pH range 1.0–6.0 with a constant amount of Neem leaves powder 0.15 g/100 mL and Neem stem bark 0.15 g/100 mL for a zinc solution of concentration 100 mg/L. The results are shown in Fig. 1. The biosorption of zinc was maximum at pH 4.0 for Neem leaves powder and

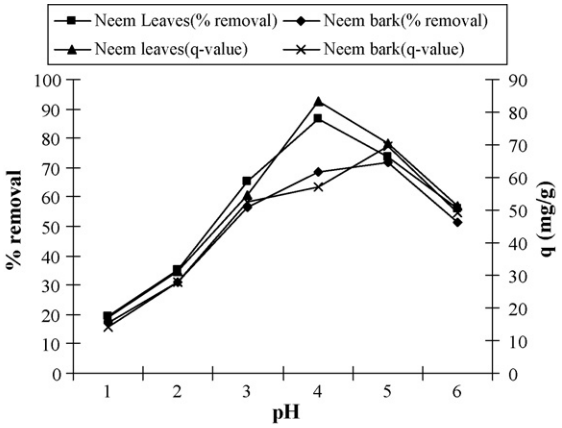

Fig. 1. Effect of pH on biosorption of zinc (for Neem leaves, adsorbent dose = 0.15 g/100 mL, Zn conc. 100 mg/L: for Neem bark, adsorbent dose = 0.15 g/100 mL, Zn conc. 100 mg/L).

5.0 for Neem stem bark powder. The maximum zinc biosorption for Neem leaves powder was 86.48% (pH 4) and for Neem bark powder 71.86% (pH 5). Biosorption could not be carried out beyond pH 6.0 due to the precipitation of $Zn(OH)_2$ and therefore experiments were done in pH range 4–5.

At pH value above optimum pH, there is a net negative charge on the biomass cells and the ionic state of ligands is such to promote the uptake of metal ions. As the pH lowered, however the over all surface charge on the biomass cells become positive, which will inhibit the approach of positively charge metal cations. It is likely that protons will then compete with metal ions for ligands and thereby decreases the interaction of metal ions with the cells [17]. Whereas at higher pH (above 5), the ligands (–COOH, $–NH_2$) attract positively charged metal ions and binding occurs, indicating that the major process is an ion-exchange mechanism that involve an electrostatic interaction between the positively charged groups in cell walls and metallic cations [17–19]. Similar trend was reported for biosorption of Zn(II) on silica gel [20] when the extent of biosorption increased from 0 to 90% in pH range of 2.0–6.0. The authors interpreted the process as due to ion-exchange and the large discrepancies at higher pH were attributed to metal removal by other possible mechanisms such as precipitation.

According to the results of this initial experiment, the further biosorption investigations were performed at pH 4 for Neem leaves powder and pH 5 for Neem bark powder as an optimal value, respectively.

3.2. Effect of adsorbent particle size and adsorbent dose

The effect of altering the adsorbents particle size on the *q* (mg/g) showed that there was a more dominant removal of zinc by the smaller particles. This was most probably due to the increase in the total surface area, which provided more biosorption sites for the metal ions. At smaller particles the removal efficiency for Neem leaves particle was more than stem bark. This was not the case with the biosorption of zinc for the larger particle size. The enhanced removal of sorbate by smaller particles has been noted previously during a study for the color removal by silica [21]. The maximum biosorption was occurred with 0.250 mm adsorbent particle size for Neem leaves powder and 0.2 mm for Neem bark powder, respectively.

Adsorbent dose in aqueous solution seemed to influence the adsorption capacity *q*, for lower values of biomass doses there was an increase in the adsorption capacity *q* [22]. It was suggested that an increase in adsorbent dose interferes between the binding sites and caused electrostatic interaction between cells. Adsorbent dose added into the solution determines the number of binding site available. An increase in adsorbent quantities strongly affects the quantities of zinc removed from aqueous solutions to a certain limit and than decreases. This effect was also reported in literature for biosorption phenomenon of heavy metals [23,24]. The effect was most marked with the biosorption of zinc by Neem stem bark powder. The dose values at which maximum biosorption were 0.15 g/100 mL for Neem leaves powder and 0.20 g/100 mL for Neem bark powder, respectively.

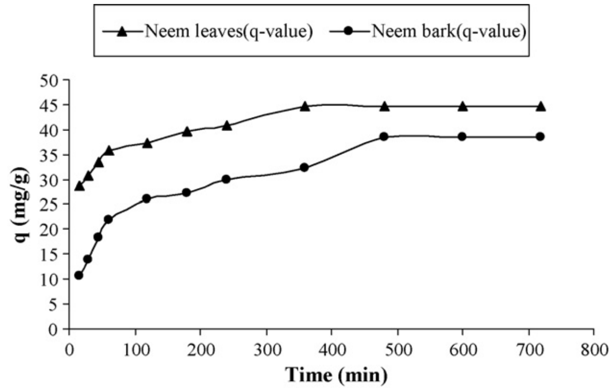

Fig. 2. Adsorption profile (for Neem leaves, pH 4, adsorbent dose = 0.15 g/100 mL: for Neem bark, pH 5, adsorbent dose = 0.20 g/100 mL).

3.3. Biosorption profile

Previous experimental studies showed that biosorption is dependent on different time intervals. Batch biosorption experiments were carried out at optimum conditions. Kinetic studies revealed that maximum adsorption capacities and metal removal efficiencies for zinc were achieved generally in first 15 min biosorption takes place very rapidly and then it continues at slower rate upto maximum biosorption. Equilibrium was reached in a contact time of 6 h. Fig. 2 showed the time course of biosorption, when the initial metal concentrations (C_o) were 100 mg/L.

In first 15 min biosorption is sharp due to decrease in pH of solution because protons were released by biosorbent. Kinetic study revealed that biosorption take place in two phases, rapid surface biosorption within 15 min and slow intracellular biosorption upto end time agrees with pervious experimental studies [25,26,9].

3.4. Effect of initial metal concentration

The experimental data shown in Fig. 3 indicates that the adsorption capacity increased with increase in initial metal ion

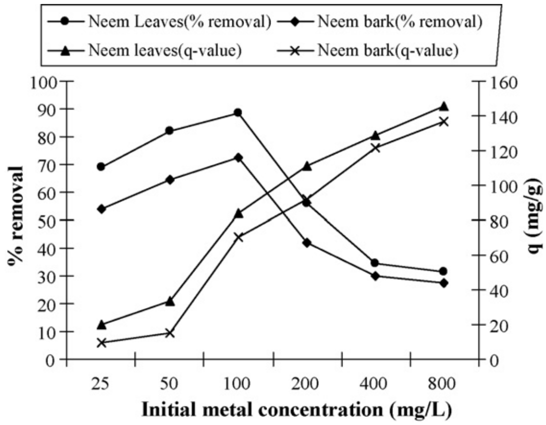

Fig. 3. Effect of initial metal concentration on biosorption of zinc (for Neem leaves, pH 4, adsorbent dose = 0.15 g/100 mL: for Neem bark, pH 5, adsorbent dose = 0.20 g/100 mL).

concentration for metal on the biomass upto 100 ppm but furthermore adsorption capacity becomes saturated. The increase in metal zinc concentration increased the uptake affinity (q) and decreased the percentage removal of zinc, except 100 mg/L at which there was percentage removal, i.e. 88.66% for Neem leaves powder and 72.73% for Neem bark powder, respectively. This biosorption characteristic represented that surface saturation was dependent on the initial metal ion concentrations. At low concentrations, biosorption sites took up the available metal more quickly. However, at higher concentrations, metal ions need to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate [18].

3.5. Kinetics modelling

The order of adsorbate–adsorbent interactions has been described by using various kinetic models. Traditionally, the pseudo-first-order model derived by Lagergren and Sven [27] has found wide application. On the other hand, several authors [28–31] have shown that second-order kinetics can also very well describe these interactions in certain specific cases. The pseudo-first-order rate equation of Lagergren:

$$\log(q_\mathrm{e} - q_t) = \log q_\mathrm{e} - \frac{k_{1,\mathrm{ad}}\, t}{2.303} \quad (1)$$

where q_t and q_e (mg/g) are the amount adsorbed at time t and at equilibrium, and $k_{1,\mathrm{ad}}$ (min^{-1}) is the Lagergren rate constant of the pseudo-first-order adsorption process.

Plot of $\log(q_\mathrm{e} - q_t)$ versus t gives a straight line for first-order kinetics (Fig. 4), which allows computation of the adsorption rate constant, $k_{1,\mathrm{ad}}$. The Lagergren first-order rate constant $k_{1,\mathrm{ad}}$, q_e and R^2 determined from the model indicate that this model had failed to estimate q_e since the experimental value of q_e differs from estimated one.

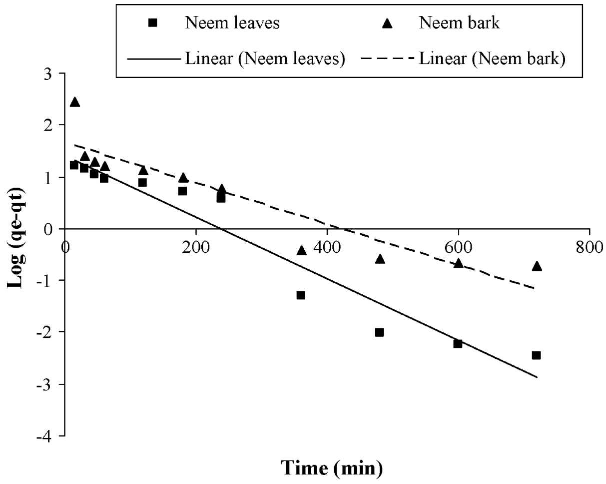

Fig. 4. The pseudo-first-order (Lagergren) plot (for Neem leaves, pH 4, adsorbent dose = 0.15 g/100 mL: for Neem bark, pH 5, adsorbent dose = 0.20 g/100 mL).

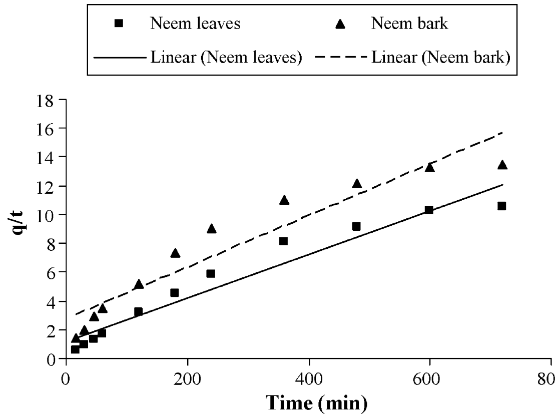

Fig. 5. The pseudo-second-order plot (for Neem leaves, pH 4, adsorbent dose = 0.15 g/100 mL: for Neem bark, pH 5, adsorbent dose = 0.20 g/100 mL).

The best fit for the experimental data of this study was achieved by the application of pseudo-second-order kinetic equation. The pseudo-second-order model is based on the assumption that biosorption follows a second-order mechanism. So, the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites [28]:

$$\frac{t}{q_t} = \frac{1}{k_{2,\mathrm{ad}}\, q_\mathrm{e}^2} + \frac{t}{q_\mathrm{e}} \quad (2)$$

where $k_{2,\mathrm{ad}}$ (g/mg min) is the second-order rate constant.

The plot of t/q_t versus t gives a linear relationship (Fig. 5), which allows computation of q_e, $k_{2,\mathrm{ad}}$ and h without having to know any parameter beforehand. The coefficient of correlation for second-order kinetic model was equal to 0.9447 (Neem leaves) and 0.9093 (Neem bark) and the estimated value of q_e also agreed with the experimental one. Both factors suggest that the biosorption of zinc ions followed the second-order kinetic model, indicating that the rate-limiting step was a chemical biosorption process between zinc and Neem biosorbents.

The above two equations cannot identify the diffusion mechanism. To identify the diffusion mechanism, Weber and Morris model is thus applied [32]. According to this theory:

$$q_t = k_i t^{0.5} + C \quad (3)$$

where k_i is the intraparticle diffusion rate constant ($\mathrm{mg/g\,h^{1/2}}$) and C (mg/g) is a constant that gives an idea about the thickness of the boundary layer. If the Weber–Morris [33] plot of q_t versus $t^{0.5}$ gives a straight line, then the biosorption process is controlled by intraparticle diffusion only.

The k_i and C can be calculated from slope and intercept of the plots q_t versus $t^{0.5}$. It can be seen from Fig. 6 that the regression was linear, but the plot did not pass through the origin, suggesting that biosorption involved intraparticle diffusion, but that was not the only rate-controlling step. Other kinetic models may control the biosorption rate.

The pseudo-first-order Lagergren model, pseudo-second-order model and Weber–Morris model parameters are given in Table 1.

3.6. Equilibrium modelling

To examine the relationship between sorbed (q_e) and aqueous concentrations (C_e) at equilibrium, biosorption isotherm models

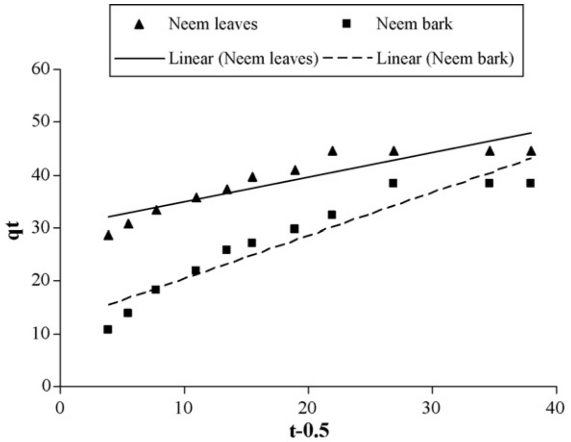

Fig. 6. The Weber Morris plot.

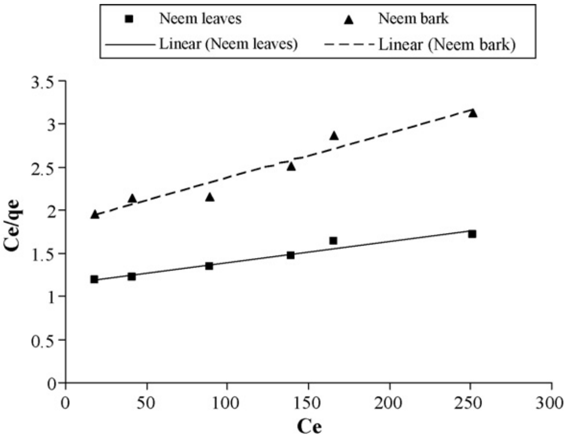

Fig. 7. The Langmuir plot (for Neem leaves, pH 4, adsorbent dose = 0.15 g/100 mL: for Neem bark, pH 5, adsorbent dose = 0.20 g/100 mL).

are widely employed for fitting the data, of which the Langmuir and Freundlich equations are the most widely used. To get the equilibrium data, initial zinc concentrations were varied while the biomass weight in each sample was kept constant. Six hours of equilibrium periods for biosorption experiments were used to ensure equilibrium conditions. This time was chosen considering the results of kinetics of zinc removal by Neem biosorbents, which will be further presented.

If the metal ions are taken up independently on a single type of binding site in such a way that the uptake of the first metal ion does not affect the biosorption of the next ion, then the biosorption process would follow the Langmuir adsorption isotherm equation [34], which was linearised to the form:

$$\frac{C_e}{q_e} = \frac{1}{(q_o\ K_L)} + \frac{C_e}{q_o} \tag{4}$$

where q_o and K_L are the Langmuir constants.

The capacity of Neem biomass in binding with zinc was determined by plotting C_e/q_e against C_e using the above equation. Fig. 7 showed the data linearised to fit the Langmuir equation. The plots of specific biosorption (C_e/q_e) against equilibrium concentration (C_e) gave the linear isotherm parameters of q_o, K_L and the coefficient of determination and these are presented in Table 2. The R^2 values suggested that the Langmuir isotherm provided a good model of the biosorption system. The adsorption capacity, q_o which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage, showed that the Neem biomass had a mass capacity for zinc (147.08 mg Zn/g for Neem leaves and 137.67 mg Zn/g Neem bark).

The Freundlich equation is another model which has been commonly used to describe adsorption isotherms. Its linearised form is represented by the equation [35]:

$$\log q_e = \log K_F + \frac{\log C_e}{n} \tag{5}$$

where q_e is the amount adsorbed per unit mass of adsorbent and C_e is the equilibrium concentration (mg/L).

The plot of $\log q_e$ versus $\log C_e$ was linear (Fig. 8) and constants K_F and n can be evaluated from the slopes and intercepts. The Freundlich constants are shown in Table 2. It was found that the adsorption equilibrium data was better fitted by the Langmuir isotherm, although it can also be modelled by the Freundlich isotherm, in the concentration range studied, since it presented the greater coefficient of correlation.

The apparent Gibbs free energy of the biosorption processes ($\Delta G°$ads) corresponding to zinc ion on the biomass was evaluated using the Bockris-Swinkel's adsorption isotherm equation as reported by Rudresh and Mayanna [36]. The equation is

Table 1
The pseudo-first-order (Lagergren), pseudo-second-order and Weber Morris parameters (for Neem leaves, pH 4, adsorbent dose = 0.15 g/100 mL: for Neem bark, pH 5, adsorbent dose = 0.20 g/100 mL)

	q exp (mg/g)	Pseudo-first-order parameters			Pseudo-second-order parameters		
		q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg min)	R^2
Neem leaves	44.65	69.25	1.248	0.9397	46.01	0.009	0.9913
Neem bark	38.45	47.24	1.982	0.8558	40.17	0.002	0.9879

Weber Morris parameters

Neem leaves				Neem bark			
q_e (mg/g)	K_i (mg/g h$^{1/2}$)	C	R^2	q_e (mg/g)	K_i (mg/g h$^{1/2}$)	C	R^2
47.23	38.75	21.24	0.9866	41.84	28.88	19.95	0.9793

Table 2
The Langmuir isotherm and Freundlich isotherm parameters (for Neem leaves, pH 4, adsorbent dose = 0.15 g/100 mL: for Neem bark, pH 5, adsorbent dose = 0.20 g/100 mL)

	q exp (mg/g)	Langmuir parameters			Freundlich parameters			
		q_o (mg/g)	K_L (dm^3/g)	R^2	q_e (mg/g)	K_F (L/mg)	*n*	R^2
Neem leaves	145.92	147.08	0.025	0.9919	203.42	11.05	1.8007	0.891
Neem bark	136.79	137.67	0.053	0.9901	122.81	9.80	1.0062	0.8649

Table 3
Apparent Gibbs free energy ΔG°ads (kJ/mol) of the metal ions between the biomass and aqueous phase

Neem leaves	C_i (mg/L)	24.91	50.25	101.65	199.25	400.27	798.61
	ΔG°	−32.75	−32.23	−30.10	−29.66	−28.68	−26.84
Neem bark	C_i (mg/L)	25.06	51.01	101.30	198.93	3.98.99	801.73
	ΔG°	−29.50	−29.29	−28.89	−28.26	−27.10	−26.04

expressed as:

$$G^{o}_{ads} = -2.30RT\ \log\left[\frac{55.4\theta}{C_o(1/\theta)} x \frac{\theta + n(1-\theta)^{n-1}}{n^n}\right] \quad (6)$$

where C_o is the initial concentration of zinc ion in the solution.

The values of ΔG°ads were then evaluated at various initial metal ion concentrations. The data is presented in Table 3. The negative values of ΔG° indicated the spontaneous biosorption nature of zinc ion by the Neem adsorbents and suggested strong biosorption of zinc ions on the biomass surface. In general, it is of note that up to −20 kJ/mol are consistent with electrostatic interaction between charged molecules and surface indicative of physical adsorption while more negative than −40 kJ/mol involve chemisorption. The order of magnitude of the values indicates a physicochemical mechanism for the biosorption of metal ions on to the Neem biosorbents.

Zinc uptake by Neem biomass, as quantified in this study from batch experiments, was compared with literature values of other biosorbents (Table 4). Although the data collated in Table 4 may not represent equivalent or optimised conditions or with various zinc removal mechanisms in each case, it still provides a useful comparison for engineers in their decision of suitable biosorbent selection in engineering practice. The uptake of zinc by Neem biomass in this study is comparable with these data. Indeed zinc uptake by Neem biomass in this study was significantly higher than most of the selected biosorbents.

Table 4
Comparison of zinc uptake capacity

Biosorbent	Zinc uptake (mg/g)	Reference
Bentonite	52.91	[37]
Red mud	12.59	[38]
Blast furnace slag	17.65–98.08	
Scarp rubber	100	
Peat	9.28–12.1	[39]
Bacillus subtilis	137	[3]
Sargassa sp.	70	
Fungal biomass	98	
Lignin	95	[40]
Chitosan	58.83	[41]
Amberlite IRC-718	156.89	
Lewatit TP-207	89.56	
Biosolids	36.87	[42]
Activated carbon C	4.01–18.53	[43]
Powered waste sludge	168	[44]
Neem bark	137.67	This study
Neem leaves	147.08	This study

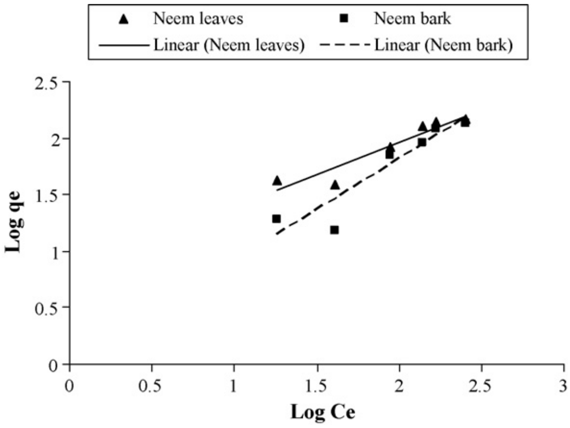

Fig. 8. The Freundlich plot (for Neem leaves, pH 4, adsorbent dose = 0.15 g/100 mL: for Neem bark, pH 5, adsorbent dose = 0.20 g/100 mL).

4. Conclusion

1. Neem can be obtained without excessive cost.
2. Non-living biomass of Neem presents sufficient adsorption capacity for zinc ions, in comparison with other types (sources) of biosorbent materials found in literature.
3. The obtained results show that pH, adsorbent particle size, adsorbent dose, initial metal concentration and contact time highly affect the overall metal uptake capacity of biosorbent.
4. The present results demonstrate that the Langmuir model fits better than the Freundlich model for the adsorption equilibrium data in the examined concentration range.
5. The suitability of a pseudo-second-order chemical reaction for the biosorption of zinc ions onto this biomass is apparent, as this kinetic model describes adequately the largest part of the process.

6. Neem biomasses had a mass capacity for zinc (147.08 mg Zn/g for Neem leaves and 137.67 mg Zn/g Neem bark).

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