

Azadirachta indica (Neem) leaf powder as a biosorbent for removal of Cd(II) from aqueous medium

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Abstract

A biosorbent, Neem leaf powder (NLP), was prepared from the mature leaves of the *Azadirachta indica* (Neem) tree by initial cleaning, drying, grinding, washing to remove pigments and redrying. The powder was characterized with respect to specific surface area ($21.45 \text{ m}^2 \text{ g}^{-1}$), surface topography and surface functional groups and the material was used as an adsorbent in a batch process to remove Cd(II) from aqueous medium under conditions of different concentrations, NLP loadings, pH, agitation time and temperature. Adsorption increased from 8.8% at pH 4.0 to 70.0% at pH 7.0 and 93.6% at pH 9.5, the higher values in alkaline medium being due to removal by precipitation. The adsorption was very fast initially and maximum adsorption was observed within 300 min of agitation. The kinetics of the interactions was tested with pseudo first order Lagergren equation (mean $k_1 = 1.2 \times 10^{-2} \text{ min}^{-1}$), simple second order kinetics (mean $k_2 = 1.34 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$), Elovich equation, liquid film diffusion model (mean $k = 1.39 \times 10^{-2} \text{ min}^{-1}$) and intra-particle diffusion mechanism. The adsorption data gave good fits with Langmuir and Freundlich isotherms and yielded Langmuir monolayer capacity of 158 mg g^{-1} for the NLP and Freundlich adsorption capacity of 18.7 L g^{-1} . A 2.0 g of NLP could remove 86% of Cd(II) at 293 K from a solution containing 158.8 mg Cd(II) per litre. The mean values of the thermodynamic parameters, ΔH , ΔS and ΔG , at 293 K were $-73.7 \text{ kJ mol}^{-1}$, $-0.24 \text{ J mol}^{-1} \text{ K}^{-1}$ and $-3.63 \text{ kJ mol}^{-1}$, respectively, showing the adsorption process to be thermodynamically favourable. The results have established good potentiality for the Neem leaf powder to be used as a biosorbent for Cd(II).

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1. Introduction

Heavy metals are natural constituents of the Earth's crust and are present in varying concentrations in all ecosystems. Human activity has drastically changed the biogeochemical cycles and natural balances of some heavy metals. These metals are stable and persistent environmental contaminants, and they have a tendency to accumulate in the soil, seawater, freshwater and sediments. Being toxic, they have adverse effects on the environment and human health. One of the well known toxic metal, Cd enters the atmosphere from mining industry and burning of coal and household wastes. Cadmium

particles in air can travel long distances before falling to the ground or water. Humans are exposed to this toxic metal [1] through breathing in contaminated workplace (battery manufacturing, metal soldering or welding industries), eating foods contaminated with it (low levels of Cd(II) are found in all foods, highest in shellfish, liver and kidney meats), breathing cadmium in cigarette smoke (doubles the average daily intake), drinking contaminated water, breathing contaminated air near the burning of fossil fuels or municipal waste, etc.

The ubiquitous nature of heavy metals, their toxicity even in trace quantities, and their tendency for bioaccumulation in food chain and the stricter environmental regulations to heavy metal discharges make it necessary to develop processes for the removal of heavy metals from wastewater. Adsorption onto solid adsorbents can effectively remove

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pollutants from both aqueous and gaseous streams, and therefore, has considerable environmental significance. Activated carbon is usually used for removal of trace pollutants, odor, taste and colors from contaminated water. However, adsorbent-grade activated carbon is comparatively expensive with difficulties in regeneration and this has led to a large volume of work trying to develop low cost adsorbents [2]. Many novel materials have been developed as adsorbents in recent years particularly from various plant materials with the objective of replacing activated carbon with cheaper, more effective and recyclable alternatives. Such low cost adsorbents [3,4] have found use for treatment of various pollutants in water and wastewater. The present work uses a non-conventional adsorbent developed from a well known bioresource—the leaves of the *Azadirachta indica* (Neem) tree, to remove Cd(II) from aqueous medium.

Medicinal and germicidal activities of the leaves, bark and seeds of the Neem tree (*A. indica*) have been well documented. A large range of useful products such as antimalarials, spermicidal, antituberculosis agents, antipyretics, anti viral drugs, antiseborrhoeics, antiallergic medicines, antienzymic, antifungal agents, etc., have been extracted from the Neem [5–9]. Fresh Neem leaves have been shown to contain as much as 59.4% moisture, 22.9% carbohydrates, 7.1% proteins, 6.2% fiber, 3.4% minerals, 1% fats and a host of other chemicals [10]. The insecticidal properties of the various segments of the Neem tree are due to a number of active ingredients like azadirachtin, salannin, meliantriol, nimbin, nimbidin, etc. The presence of a number of fatty acids like oleic acid, steric acid, palmitic acid, linoleic acid, etc., has also been reported [11,12].

2. Materials and methods

2.1. Preparing biosorbent

Mature Neem leaves, collected from a number of tall Neem trees (District Morigaon, Assam, India) were washed repeatedly with water to remove dust and soluble impurities, dried at room temperature in a shade and then in an air oven at 333–343 K for 30 h when the leaves became crisp. These were crushed into a fine powder in a mechanical grinder to obtain the Neem leaf powder (NLP). The NLP was sieved and the 53–74 μ fraction was separated, washed further with double distilled water till the washings were free of colour and turbidity. Water from the wet powder was removed by soaking with filter papers and the powders required about 120 h to completely dry up. It was preserved in glass bottles for use as a biosorbent.

Cd(II) was used in the form of Cd(NO₃)₂·4H₂O (Glaxo India, Mumbai, 99% purity) without further purification. A stock solution containing 1000 mg Cd(II)/L was prepared in

double distilled water and solutions for adsorption experiments were prepared by appropriate dilution.

2.2. Characterization of the adsorbent

The specific surface area of the NLP powder was determined by adsorbing the dye, methylene blue on it and finding the monolayer capacity by Langmuir method [13]. Scanning electron microscopy (JEOL JSM 35CF at RSIC, Shillong, India) was used to study surface topography of the Neem leaf powder. FTIR spectra of the adsorbent samples were recorded by the nuzol method (Perkin-Elmer Spectrum RX I).

2.3. Adsorption experiments

The batch adsorption was carried out in 100 mL borosil conical flasks by agitating a pre-weighed amount of the NLP powder with 50 mL of the aqueous Cd(II) solution at a constant temperature, water bath shaker (NSW, Mumbai) for a pre-determined time interval at a constant speed. The standard experimental conditions for the adsorption experiments were as follows:

(a) Initial Cd(II) concentration (mg L ⁻¹)	36.5, 72.9, 109.4, 158.8, 182.3, 218.8
(b) Amount of adsorbent (g L ⁻¹)	0.4, 0.6, 1.0, 1.6, 2.0
(c) pH	2.0–9.0
(d) Agitation time (min)	20, 40, 60, 120, 180, 240, 300
(e) Adsorption temperature, <i>T</i> (K)	293, 303, 313
(f) Particle size (μ m) of NLP	53–74

The pH of the aqueous solutions of Cd(II) was ~6.5 which did not change much with dilution. For measuring effects of pH on adsorption, the pH of the adsorptive solution was adjusted by adding aqueous 0.1N HCl or NaOH drop by drop. The pH was measured at the beginning and at the end of the experiment. The majority of the experiments were done without adjusting the pH, i.e., at the natural pH of the Cd(II) solution. After adsorption was over, the mixtures were allowed to settle for 10 min, the supernatant liquid was centrifuged for 20 min and the metal ion remaining unadsorbed was determined with Atomic Absorption Spectrometer (Varian SpectrAA 220, Lamp current 4 mA, air–acetylene oxidizing flame, 228.8 nm wavelength, slit width 0.5 nm, optimum working range 0.02–3.0 μ g mL⁻¹).

2.4. Kinetics of adsorption

The kinetics of the interactions were studied by determining the amount adsorbed at different agitation times for various amounts of the adsorbent at constant Cd(II) concentration. The kinetics was tested with respect to the pseudo first order model of Lagergren given by the equation:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t \quad (1)$$

and the second order kinetic model given by the equation:

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \quad (2)$$

where q_t and q_e are the amount adsorbed at time t and at equilibrium, k_1 is the pseudo first order rate constant; $h = k_2 q_e^2$, where k_2 is the second order rate constant.

The adsorption data were further analyzed using the following.

(a) Elovich equation [14]:

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \quad (3)$$

(b) Intra-particle diffusion equation [15]:

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

(c) Liquid film diffusion equation [16]:

$$\ln(1 - F) = -kt \quad (5)$$

where α is the initial sorption rate constant, β the desorption rate constant, k_p the intra-particle diffusion rate constant and F is the fractional attainment of equilibrium (q_t/q_e).

2.5. Adsorption isotherm

The adsorption data were fitted to the most widely used two parameter Langmuir equation valid for monolayer chemisorption:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (6)$$

where q_m is the amount of Cd(II) adsorbed per unit mass of the adsorbent in a single monolayer, b is k_a/k_d (k_a and k_d are the adsorption and the desorption rate constants for the adsorption equilibrium, $\text{Cd(II)} + \text{NLP} = \text{Cd(II)} \cdot \text{NLP}$), C_e and q_e are the equilibrium liquid phase and solid phase concentrations of Cd(II) [2]. A plot of (C_e/q_e) versus C_e yields a straight line for chemisorptive behaviour. The slope and the intercept of the plot give the values of q_m and b .

An extension of the Langmuir equation was made by introducing a dimensionless equilibrium parameter, R_L [17], called the separation factor, given by:

$$R_L = \frac{1}{1 + bC_o} \quad (7)$$

where C_o is the initial liquid phase concentration of Cd(II) in equilibrium with the adsorbent. For favourable adsorption, $0 < R_L < 1$.

The empirical Freundlich isotherm in the logarithmic form given by:

$$\log q_e = \log K_f + n \log C_e \quad (8)$$

where K_f and n are Freundlich coefficients was also tested. This equation is valid for $n < 1$ and the coefficients are

obtained from the slope and the intercept of the plots of $\log q_e$ versus $\log C_e$.

2.6. Thermodynamic parameters

The thermodynamic parameters for the adsorption process were evaluated from the well known relation:

$$\log K = -\frac{\Delta G}{2.303RT} = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (9)$$

where $K = (q_e/C_e)$ and ΔG , ΔH and ΔS are, respectively, Gibbs energy change, enthalpy change and entropy change for the process at constant temperature (T). Plot of $\log K$ versus $(1/T)$ should yield a straight line with slope, $-\Delta H/2.303R$, and intercept, $\Delta S/2.303R$. Values of ΔH and ΔS could be used to find ΔG .

2.7. Desorption study

Desorption experiments were carried out by saturating NLP with Cd(II) by passing an aqueous solution (100 mg L^{-1}) through a pyrex column (length 30 cm, i.d. 1.5 cm) packed with NLP (actual length of NLP column 1.5 cm) from the top till the inlet and the outlet concentrations became equal. The column was washed once with about 70.0 mL double distilled water to remove metal ions loosely attached to the column walls and the adsorbent. The desorption was then carried out by passing:

- double distilled water (pH 7.0);
- dilute nitric acid (pH 4.0);
- dilute alkali (NaOH, pH 10.0).

respectively, with a flow rate of 1.6 mL min^{-1} at 300 K.

2.8. Column study

An identical glass column (length 30 cm, i.d. 1.5 cm) was used as a fixed-bed reactor for column study. NLP was packed into it by a dry packing technique [18,19]. The bed was supported and closed by glass wool plugs to ensure good liquid distribution. The effective length of the NLP column was 1.5 cm (a long column practically does not allow any liquid flow) which was rinsed with distilled water and left overnight to ensure a closely packed arrangement of particles without voids, channels, or cracks. The metal ion solution was fed from the top at a fixed flow rate of 1.6 mL min^{-1} keeping a constant head of 2 cm. Samples of the eluate were collected periodically and analyzed for the Cd(II) concentration (C_v) using AAS (Varian SpectraAA 220). The flow through the column was continued till the outlet and inlet concentrations were equal. The breakthrough curve was obtained by plotting C_v/C_o (C_o is 100 mg L^{-1} , the concentration of Cd(II) at the inlet) against the cumulative volume of Cd(II) solution passing through the column. A value of ~ 1.0 for the ratio C_v/C_o indicates the exhaustion point of the column.

3. Results and discussion

3.1. Characterization of the biosorbent

3.1.1. Surface area of the biosorbent

The average monolayer capacity for methylene blue adsorption on Neem leaf powder was measured as 8.76 mg g^{-1} and the cross-sectional area of the dye molecule being $1.30 \times 10^{-18} \text{ m}^2$, the specific surface area is $21.45 \text{ m}^2 \text{ g}^{-1}$. This is three to four times higher than that of a number of other biosorbents reported in the literature, e.g., coffee residue ($2.57 \text{ m}^2 \text{ g}^{-1}$), pyrolyzed coffee residue ($3.91 \text{ m}^2 \text{ g}^{-1}$), coffee residue bound on clay ($6.48 \text{ m}^2 \text{ g}^{-1}$) [20], but much less when compared to that of commercial activated carbon ($\sim 1100 \text{ m}^2 \text{ g}^{-1}$).

3.1.2. Surface topography

The electron micrographs (Fig. 1) show the powder as an assemblage of fine particles of irregular shape and size. The particles have a large number of steps, kinks and broken edges in them and these are likely to play important role as possible active sites for adsorption.

3.1.3. Surface functional groups

FTIR measurements showed the presence of the following functional groups on the Neem leaf powder:

- OH ($3597\text{--}3600 \text{ cm}^{-1}$),
- NH₂ (3399 cm^{-1}),
- ≡CH (3297 cm^{-1}),

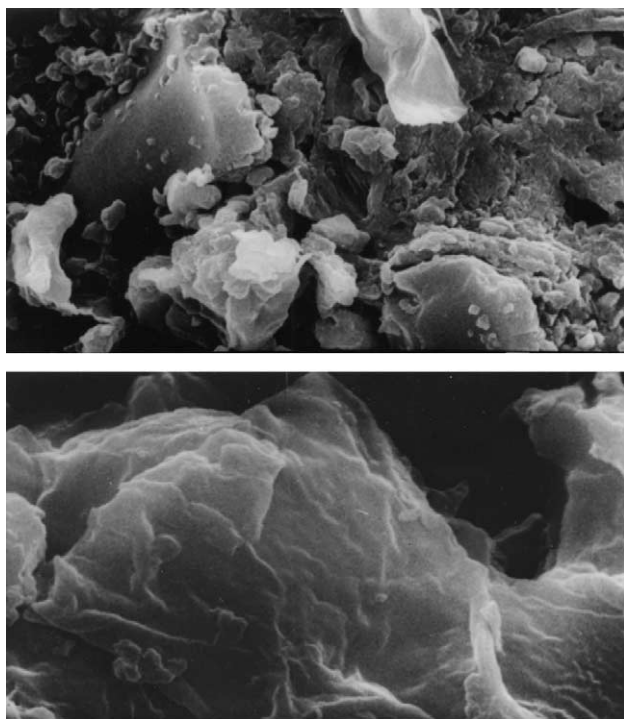


Fig. 1. SEM photographs of Neem Leaf powder at $\times 4000$ (top) and $\times 6600$ (bottom) magnification.

- $>C=N-$ (1656 cm^{-1}),
- $\equiv C-C\equiv$, $\equiv C-N<$ and $\equiv C-O-$ (1160 cm^{-1}),
- $>C=O$ ($1633, 1656, 1672, 1688, 1714 \text{ cm}^{-1}$),
- $>C=C<$ (1656 cm^{-1}) and
- $>C=S$ (1105 cm^{-1}).

The polar groups on the surface of the Neem leaf powder are likely to determine the adsorption characteristics of NLP as these groups give rise to considerable cation exchange capacity [21–23].

3.2. Effect of pH

pH is an important controlling parameter in all the adsorption processes. For a typical experiment with Cd(II) solution of concentration 36.5 mg L^{-1} , adsorbent amount of 0.8 g L , interaction time of 3 h, temperature 300 K , it was seen that there was no adsorption between pH 2.0 and 3.5, and the adsorption was only 8.8% at pH 4.0, but the adsorption increased to 70.0% at pH 7.0 and 93.6% at pH 9.5 (Fig. 2). The adsorption was insignificant at highly acidic pH, but increased continuously from moderately acidic pH to alkaline pH. The increased removal of Cd(II) in alkaline pH might be due to the onset of precipitation. At low pH, adsorption of Cd(II) could not compete with H⁺ ions for appropriate sites on the adsorbent surface. However, with increasing pH, this competition weakens and Cd(II) ions replace H⁺ ions bound to the adsorbent or forming part of the surface functional groups such as OH, COOH, etc. It is also possible that the adsorption of the metal ions may take place through binding of both Cd²⁺ and Cd(OH)⁺ ions to the adsorbent surface.

A similar trend with Cd(II) was observed with adsorption increasing from 40.9 to 46.6% on *Pinus radiata* bark and from 26.1 to 36.9% on chemically modified tannins in the pH range 1.0–5.0 [24]. Abia et al. [25] also found a similar trend for the adsorption of Cd(II) on the biomass cassava

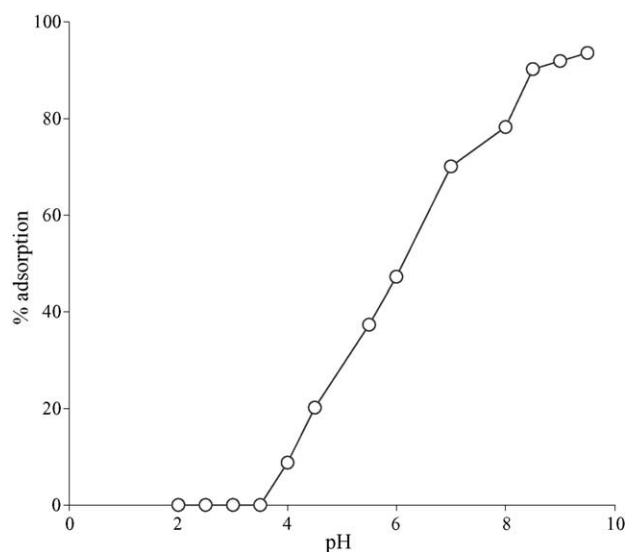


Fig. 2. Influence of pH on adsorption of Cd(II) on NLP at 298 K (NLP 0.8 g L^{-1} , Cd(II) 36.5 mg L^{-1} , interaction time 3 h).

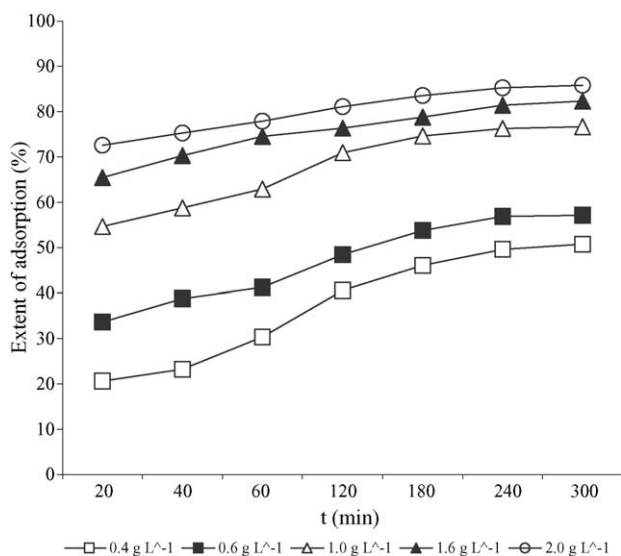


Fig. 3. Variation of the extent of adsorption of Cd(II) (concentration 158.8 mg L⁻¹) on NLP with increase in interaction time at 293 K.

tubers. Feng and Aldrich [26] investigated the effect of pH on adsorption of Cu²⁺, Cd²⁺ and Pb²⁺ on biomass derived from the marine alga *Ecklonia maxima* and showed that the increase in biosorption levels with increases in pH could be explained by the influence of the number of negative surface charges arising from the dissociation of functional groups. In addition, this could partly explain the low concentration of metal ions retained by the biosorbent at pH values below 4.0, since most of the functional groups are likely to dissociate at neutral pH only.

Taty-Costodes et al. [27] have found similar influence of pH on adsorption of Cd(II) and Pb(II) on sawdust of *Pinus sylvestris*. The maximum uptake of the ions was obtained at pH 5.5 in the range of 2.0–9.0. The metal ions face stiff competition from H₃O⁺ ions at low pH for the exchange sites of the sorbent. The metal uptake depends on these sites as well as on the nature of the metal ions in solution. The carbonyl and hydroxyl groups of polyphenols could be responsible for the adsorptive property of the sawdust. The oxygen atoms of each carbonyl and hydroxyl group are considered as strong Lewis base centers because of the presence of vacant doublet electrons, which allow coordination with the electron deficient metal ions. Othman [28] suggested that the large discrepancies at high pH could be due to metal removal by other mechanisms such as precipitation.

3.3. Kinetics of adsorption

The effect of agitation time on the extent of adsorption of Cd(II) on NLP is shown in Fig. 3. The adsorption advanced towards equilibrium within 300 min for NLP amount of 0.4–2.0 g L⁻¹ of Cd(II) solution of concentration 159.0 mg L⁻¹. Adsorption increased from 82.0 to 201.4 mg g⁻¹ (extent of adsorption 20.7–50.7%) for NLP amount of 0.4 g L⁻¹ in the time interval 20–300 min. Such

behaviour is common in a batch reactor with either constant adsorbent amount and varying initial adsorbate concentration or vice versa [29]. An increase in the adsorbent amount results in a decrease in the interaction time to reach apparent equilibrium. However, the fraction of the metal removed from the aqueous phase increases with an increase in the adsorbent amount. The nature of the adsorbent and its compactness affect the time needed to reach equilibrium. In the present case, the adsorbate–adsorbent interactions approached pseudo equilibrium at around 300 min.

The kinetics of Cd(II) adsorption on Neem leaf powder (NLP) was studied at a constant Cd(II) concentration of 158.8 mg L⁻¹ at 293 K with five different NLP amounts of 0.4, 0.6, 1.0, 1.6 and 2.0 g L⁻¹ and interaction time from 20 to 300 min in each case. The Lagergren plots (Fig. 4) of log(*q_e - q_t*) versus time were linear in nature. The pseudo first order rate constant obtained from the slopes of the best-fit lines (correlation coefficient, *R* = 0.97–0.99), was in the range of 9.90 × 10⁻³ to 14.51 × 10⁻³ min⁻¹ with a mean value of 12.0 × 10⁻³ min⁻¹. Cd(II) adsorption follows first order kinetics in a wide variety of materials [25,27,30–33] and the values of the rate constant reported conform to the values obtained in this work. The mechanism of adsorption of other heavy metals has also been tested with the first order kinetics. For example, Ho and McKay [3] have suggested first order adsorption kinetics for Pb(II) on peat with *k*₁ in the range of 3.66–4.40 × 10⁻² min⁻¹. Dakiky et al. [34] have reported similar rate constant values for adsorption of Cr(VI) on a variety of novel adsorbents (wool 3.96 × 10⁻³ min⁻¹, cactus leaves 6.80 × 10⁻³ min⁻¹, sawdust 9.00 × 10⁻³ min⁻¹, almond 8.80 × 10⁻³ min⁻¹, olive cake 8.99 × 10⁻³ min⁻¹).

Although effective in many cases, the pseudo first order equation has been found to be unsatisfactory in providing a concrete mechanism of the adsorption process in an equally good number of cases [14,23]. In such cases, the experimen-

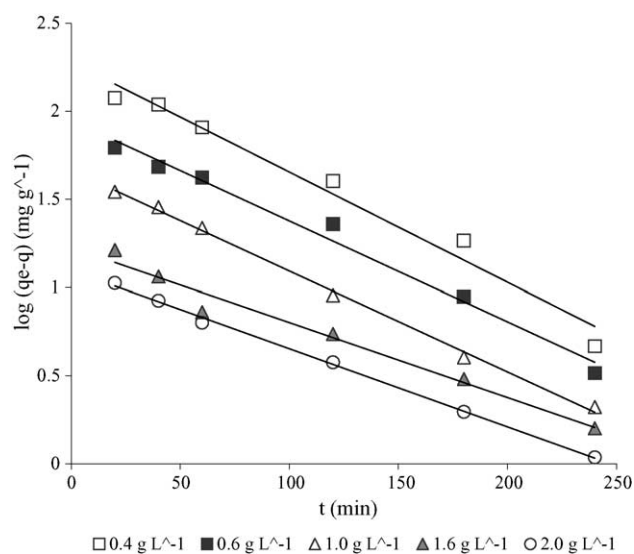


Fig. 4. Lagergren plots for pseudo first order kinetics of the interactions between Cd(II) and NLP at 293 K (Cd (II) concentration 158.8 mg L⁻¹).

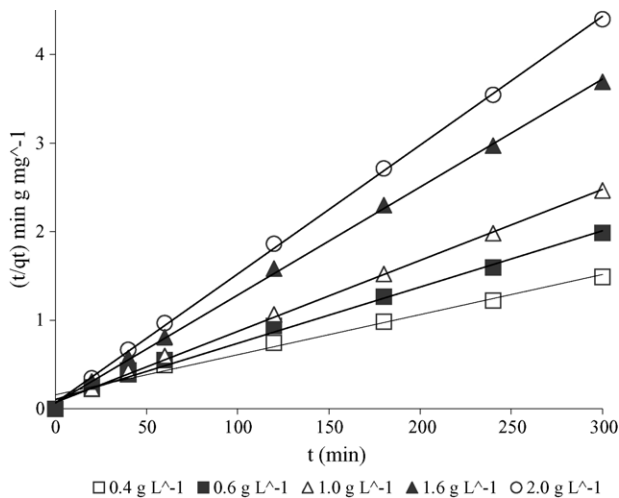


Fig. 5. Plots of pseudo second order kinetics for adsorption of Cd(II) (concentration 158.8 mg L^{-1}) on NLP at 293 K.

tal results differ in two important aspects: (i) $k_1(q_e - q_t)$ does not represent the number of available sites and (ii) $\log(q_e)$ is not equal to the intercept of the plot of $\log(q - q_t)$ against t . In the present work, $\log q_e$ values based on the experimental q_e values did not match the values obtained from the Lagergren plots. The pseudo second order model, based on Eq. (2) considering the rate-limiting step as the formation of chemisorptive bond between the adsorbate and the adsorbent, was therefore, applied.

The plot of t/q_t versus t (Fig. 5) yielded linear plots ($R \approx 0.99$) indicating the interactions to be akin to second order kinetics and suggesting chemisorption as the rate-controlling step [23]. The second order rate constant, k_2 , was in the range of 1.29×10^{-4} to $3.15 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$. Second order kinetics was also postulated for adsorption of Pb(II), Cu(II) and Ni(II) on peat [21] with k_2 values in the ranges of 8.69×10^{-3} to 4.59×10^{-1} , 8.97×10^{-3} to 9.64×10^{-2} and 1.59×10^{-2} to $1.75 \times 10^{-1} \text{ g mg}^{-1} \text{ min}^{-1}$, respectively. On the other hand, Taty-Costodes et al. [27] found the value of $10.89 \text{ g mg}^{-1} \text{ min}^{-1}$ for Cd(II) adsorption on *Pinus sylvestris* saw dust.

Plots of q_t versus $\ln t$ as per Elovich Eq. (3) also yielded straight lines (Fig. 6) with high linearity ($R \sim 0.99$). This equation does not predict any definite mechanism, but is useful in describing adsorption on highly heterogeneous adsorbents [14] such as the NLP when the interactions are predominantly chemical in nature [14,35]. The Elovich constants, α and β , had values in the ranges of $0.01\text{--}17.92 \times 10^3 \text{ mg g}^{-1} \text{ min}^{-1}$ and $41.21\text{--}4.04 \text{ g mg}^{-1}$, respectively, for NLP amounts of 0.4, 0.6, 1.0, 1.6 and 2.0 g L^{-1} at a constant Cd(II) concentration of 158.8 mg L^{-1} . The constants depended significantly on the amount of adsorbent with the adsorption rate constant, α , being much more sensitive. Since α represents the initial rate of adsorption, the results indicate that the rate could be enhanced many times by increasing the adsorbent amount, i.e., by providing a large surface area for interaction. Similar results are also obtained

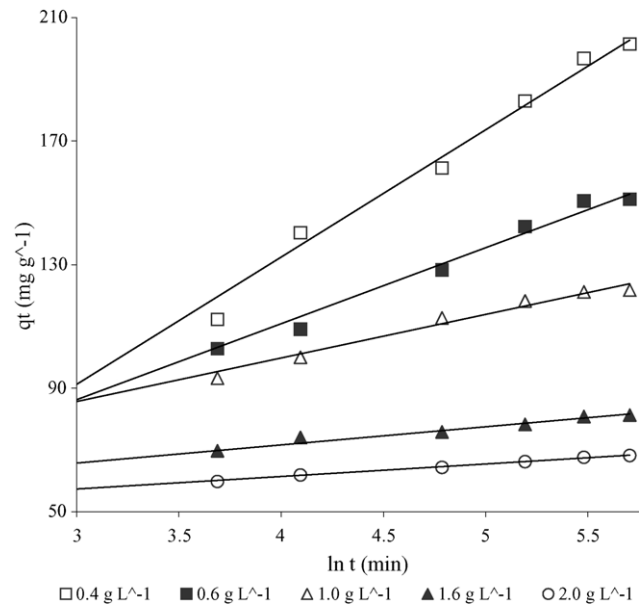


Fig. 6. Elovich plots for adsorption of Cd(II) (concentration 158.8 mg L^{-1}) on NLP at 293 K.

by Ho and McKay [35] for adsorption of Cu(II) on peat. The successful application of Elovich equation points to a possible chemisorption type interaction between Cd(II) and NLP.

Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates followed by diffusion of the solute molecules into the interior of the pores, which may be the slowest and rate-determining step. The plots of q_t versus $t^{0.5}$ (Fig. 7) exhibit more than one slope. The first, sharp portion is likely to represent fast adsorption on the external surface, and the second nearly flat portion a slow diffusion into the interior surfaces of the particles [35]. These results are in conformity

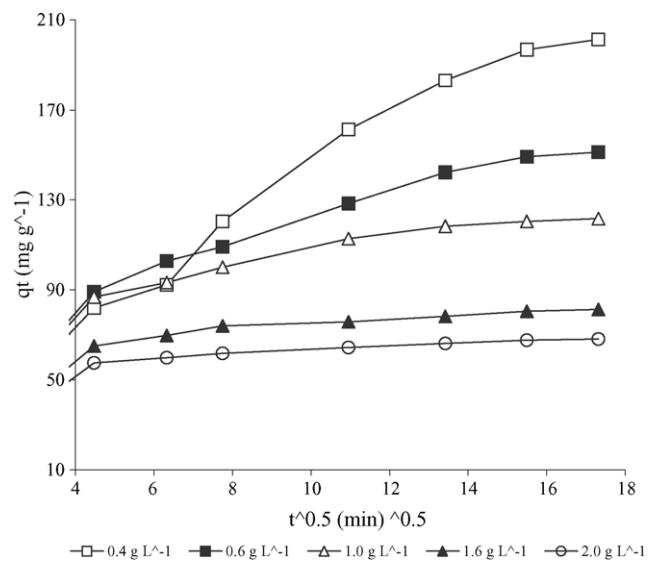


Fig. 7. Plots of q_t vs. $t^{0.5}$ for adsorption of Cd(II) (concentration 158.8 mg L^{-1}) on NLP at 293 K.

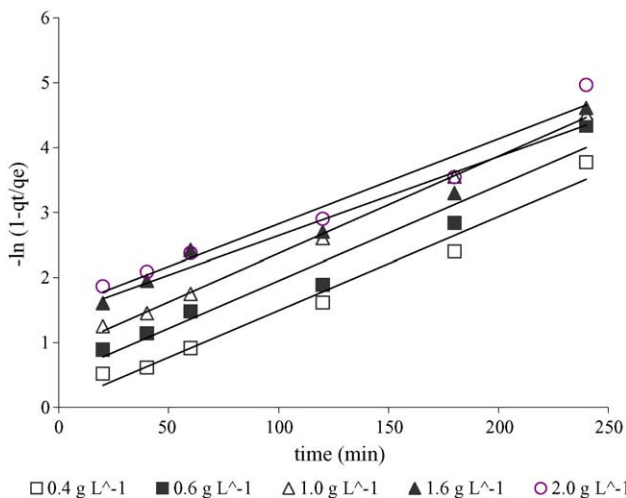


Fig. 8. Plots of liquid diffusion model for adsorption of Cd(II) (concentration 158.8 mg L⁻¹) on NLP at 293 K.

with the values of the Elovich coefficients, which showed very fast initial rate of adsorption. The second portion of the plots (Fig. 7) might also be due to adsorption on the steps and fissures of the surface as seen from the SEM measurement.

The plots of $-\ln(1 - F)$ versus t as per the liquid film diffusion model (Fig. 8) were also linear ($R = 0.98-0.99$) with intercepts of 0.05 to 1.52 for various NLP amounts (0.4, 0.6, 1.0, 1.6 and 2.0 g L⁻¹) at constant Cd(II) concentration (158.8 mg L⁻¹). The plots however do not pass through the origin except for the lowest amount of NLP. Thus the liquid film diffusion (Eq. (5)) is not the predominant mechanism for Cd(II) adsorption on NLP.

3.4. Adsorption isotherms

At a constant temperature, the extent of adsorption was dependent on the amount of the biosorbent as well as on Cd(II) concentration. The results for a constant agitation time of 5 h are presented in Table 1. Adsorption increased rapidly as more and more of the adsorbent was added, but it showed a decreasing trend when Cd(II) concentration was increased.

The two parameter Langmuir isotherm gives a good account of the constant temperature adsorption data (Fig. 9), but the application of the empirical Freundlich isotherm yields less satisfactory results (Fig. 10). The values of the

Table 1
Extent of adsorption (%) of Cd(II) on Neem leaf powder at 300 K for a constant interaction time of 5 h

Cd(II) (mg L ⁻¹)	Extent of adsorption (%) for NLP amount (g L ⁻¹)				
	0.4	0.6	1.0	1.6	2.0
36.5	69.3	76.0	88.6	95.4	97.0
72.9	62.5	68.2	85.1	90.7	93.4
109.5	59.6	62.6	81.5	87.9	90.5
158.8	50.5	57.1	76.7	82.3	85.9
182.3	43.6	46.4	67.1	78.7	81.2
218.8	36.1	35.9	55.5	67.1	71.1

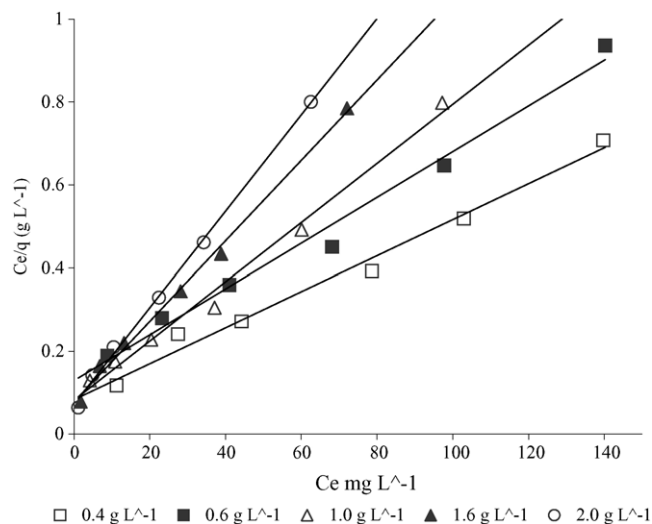


Fig. 9. Langmuir isotherms for adsorption of Cd(II) (concentration 36.5, 72.9, 109.5, 158.8, 182.3, 218.8 mg L⁻¹ for each NLP amount shown at the bottom, interaction time 5 h) on Neem Leaf powder at 293 K.

adsorption and the correlation coefficients are given in Table 2. The linearity of Langmuir plots ($R > 0.99$) suggests strong bonding involving chemical forces between Cd(II) ions and NLP particles. Langmuir monolayer capacity (q_m) of the Neem Leaf powder decreased from 250.0 to 86.2 mg g⁻¹ as NLP amount was varied from 0.4 to 2.0 g L⁻¹. The equilibrium parameter, b , showed an increase from 0.048 to 0.161 L mg⁻¹ in the same range of adsorbent amount. The dimensionless parameter, R_L , remained between 0.05 and 0.15 ($0 < R_L < 1$) for the whole range of adsorbent amounts in accordance with the requirement of a favourable adsorption process.

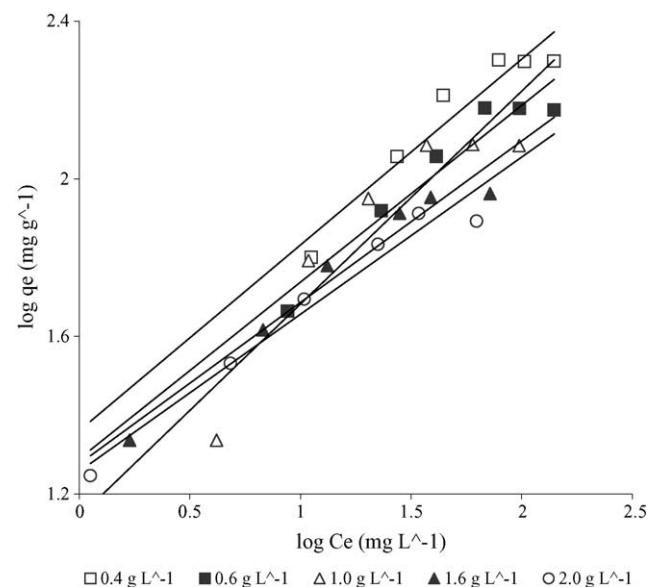


Fig. 10. Freundlich isotherms for adsorption of Cd(II) (concentration 36.5, 72.9, 109.5, 158.8, 182.3, 218.8 mg L⁻¹ for each NLP amount shown at the bottom, interaction time 5 h) on Neem Leaf powder at 293 K.

Table 2

Adsorption coefficients for Cd(II)–NLP interactions at 293 K (agitation time 5 h, Cd(II) 36.5, 72.9, 109.5, 158.84, 182.3 and 218.8 mg L⁻¹ for each NLP amount)

NLP (g L ⁻¹)	Langmuir isotherm			Freundlich isotherm			
	<i>R</i>	<i>q_m</i> (mg g ⁻¹)	<i>b</i> (L mg ⁻¹)	<i>R_L</i>	<i>R</i>	<i>K_f</i> (L g ⁻¹)	<i>n</i>
0.4	0.99	250.0	0.048	0.138	0.96	23.0	0.47
0.6	0.99	181.8	0.043	0.153	0.96	19.5	0.45
1.0	0.99	140.9	0.087	0.081	0.92	13.9	0.54
1.6	0.99	130.1	0.099	0.072	0.98	18.9	0.41
2.0	0.99	86.2	0.161	0.046	0.98	18.1	0.40
Mean	0.99	157.8	0.088	0.098	0.96	18.7	0.45

The monolayer capacity of NLP is quite large (mean value 157.8 mg g⁻¹) compared to many other adsorbents reported in the literature including commercial activated carbon. A few recently reported values of Langmuir coefficients for adsorption of Cd(II) are given below:

Adsorbent	<i>q_m</i> (mg g ⁻¹)	<i>b</i> (L mg ⁻¹)	Reference
Crab Shell	0.0122	–	[36]
Chitin	14.71	0.038	[37]
Cassava waste	0.87	0.061	[25]
PEI-silica gel	38.46	0.026	[38]
Modified biomass	0.94	0.021	[25]
Sawdust of <i>Pinus sylvestris</i>	19.08	0.057	[27]
Coffee residues on clay	39.52	0.024	[20]
Activated carbon	95.24	0.003	[20]
Low grade Phosphate	7.54	0.201	[39]
Bone char	0.0042	0.014	[40]
Neem leaf powder	157.80	0.088	This work

The Freundlich plots (Fig. 10) were of slightly less linearity compared to the Langmuir plots, but the values of the coefficients conform to those required for favourable adsorption. The adsorption affinity, *n*, had values from 0.40 to 0.54 (0 < *n* < 1) and the adsorption capacity, *K_f*, was in the range of 13.9–23.0 Lg⁻¹. Both Langmuir monolayer capacity and Freundlich adsorption capacity were dependent on adsorbent amount and both showed higher values when the amount was less. It is likely that increasing the amount of the adsorbent per unit volume of the solute solution makes less surface available per unit mass of the adsorbent for interaction with Cd(II) ions. A comparison of the Freundlich coefficients obtained in this work with a few values obtained by other workers is given below:

Adsorbent	<i>n</i>	<i>K_f</i> (L g ⁻¹)	Reference
Chitin	0.45	1.42	[37]
Cassava waste	0.77	18.05	[25]
Coconut coir pith	0.48	27.51	[33]
Low grade phosphate	0.57	2.06	[39]
Neem leaf powder	0.45	18.70	This work

3.5. Thermodynamic studies

When the adsorption was carried out at higher temperatures, the amount adsorbed came down (Fig. 11) indicating the interactions to be exothermic. For Cd(II) concentration of

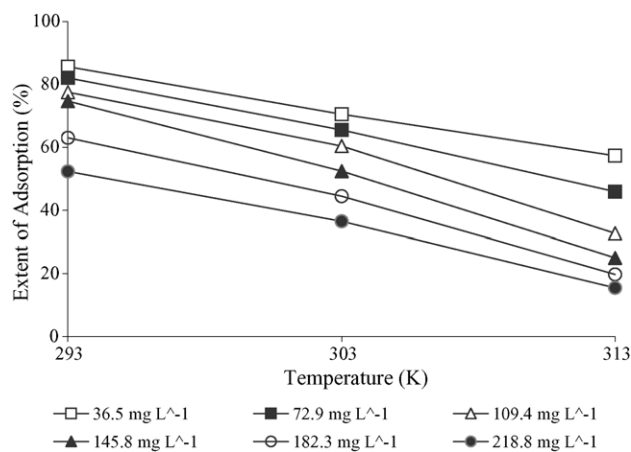


Fig. 11. Variation of the extent of adsorption of Cd(II) (concentrations given at the bottom) on NLP (1.0 g L⁻¹) with increase in temperature for an interaction time of 180 min.

36.5 mg L⁻¹, adsorption on NLP (1.0 g L⁻¹) decreased from 85.7% at 293 K to 70.5% at 303 K and 57.3% at 313 K. The thermodynamic parameters were calculated from the plots of log *q_e*/*C_e* versus 1/*T* (Fig. 12). The values of the three parameters, Δ*H*, Δ*S* and Δ*G* are given in Table 3 and they are in

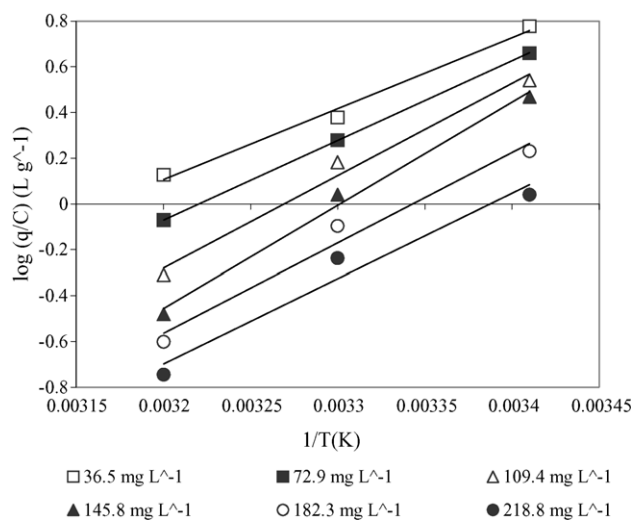


Fig. 12. Plots of log(*q*/*C*) vs. (1/*T*) for adsorption of Cd(II) (concentrations given at the bottom) on NLP (1.0 g L⁻¹) for an interaction time of 180 min.

Table 3

Thermodynamic parameters for adsorption of Cd(II) on Neem Leaf Powder (NLP amount 1.0 g L⁻¹, agitation time 180 min)

Cd(II) (mg L ⁻¹)	-ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	-ΔG (kJ mol ⁻¹) at temperature		
			293 K	303 K	313 K
36.5	65.2	-0.19	10.10	8.22	6.34
72.9	66.7	-0.22	3.66	1.51	-0.64
109.5	77.3	-0.25	3.12	0.59	-1.94
158.8	86.3	-0.29	2.82	0.03	-3.00
182.3	75.6	-0.25	1.42	-1.11	-3.64
218.8	71.3	-0.24	0.67	-1.74	-4.15
Mean	73.7	-0.24	3.63	1.25	-0.57

the ranges in the Cd(II) concentration range of 36.5 to 218.8 mg L⁻¹:

ΔH	-65.2 to -86.3 kJ mol ⁻¹ (mean -73.7 kJ mol ⁻¹)
ΔS	-0.19 to -0.29 J mol ⁻¹ K ⁻¹ (mean -0.24 J mol ⁻¹ K ⁻¹)
ΔG	-10.10 to -0.67 kJ mol ⁻¹ (293 K, mean -3.63 kJ mol ⁻¹)
	-8.22 to +1.74 kJ mol ⁻¹ (303 K, mean -1.25 kJ mol ⁻¹)
	-6.34 to +4.15 kJ mol ⁻¹ (313 K, mean +0.57 kJ mol ⁻¹)

These values are in agreement with the exothermic and spontaneous nature of the interactions. As the temperature increased, the Gibbs Energy showed a tendency to increase and the interactions became less favourable with a consequent decrease in the extent of adsorption. The entropy changes represented a small decrease indicating that compared to the free Cd(II) ions in solution, the adsorbed ions had an orderly arrangement.

The thermodynamic measurement definitely establish that the equilibrium,



shifts in the forward direction in a spontaneous manner, which results in binding of the Cd(II) ions on to the surface of the NLP particles. Cd(II) is most likely to bind to the surface through the polar functional groups (aldehydes, ketones, acids, phenolic OH, etc.) and two mechanisms are possible:



In which P⁻ and HP are polar groups on the surface of the Neem leaf powder. Such mechanisms have been proposed earlier by Ho et al. [22] for adsorption of Pb(II) on peat. The thermodynamic parameters indicate that adsorbed Cd(II) ions are more stable than the free ions in aqueous solution.

Thermodynamic data on Cd(II) adsorption is scarce. Abou-Mesalam [41] carried out sorption of Cu(II), Zn(II) and Cd(II) on synthesized silico-antimonate ion exchanger and found that in all the cases, the interactions were exothermic with enthalpy change of -8.4 to -12.6 kJ mol⁻¹. These values are very small compared to the values associated with chemical bond formation and the mechanism suggested was that of ion exchange. The same author found that when Ni(II) adsorbed on the same material, ΔH was 15.7 kJ mol⁻¹ and it was inferred that other mechanisms might be oper-

ative along with ion exchange. Boonamnuyvitaya et al. [20] have reported that Cd(II) adsorbs on pyrolyzed coffee residues with heat of adsorption in the range of -2.1 to -21.0 kJ mol⁻¹. These values are less than one third of the values obtained in this work, and obviously point to physical adsorption. Compared to these values, ΔH range of -65.2 to -86.3 kJ mol⁻¹ in the present work indicates comparatively strong bonding between Cd(II) and NLP.

3.6. Desorption study

When washed with double distilled water, NLP loaded with Cd(II) gave off the metal ions at a considerably fast rate up to a water volume of about 100 mL, but it became slow

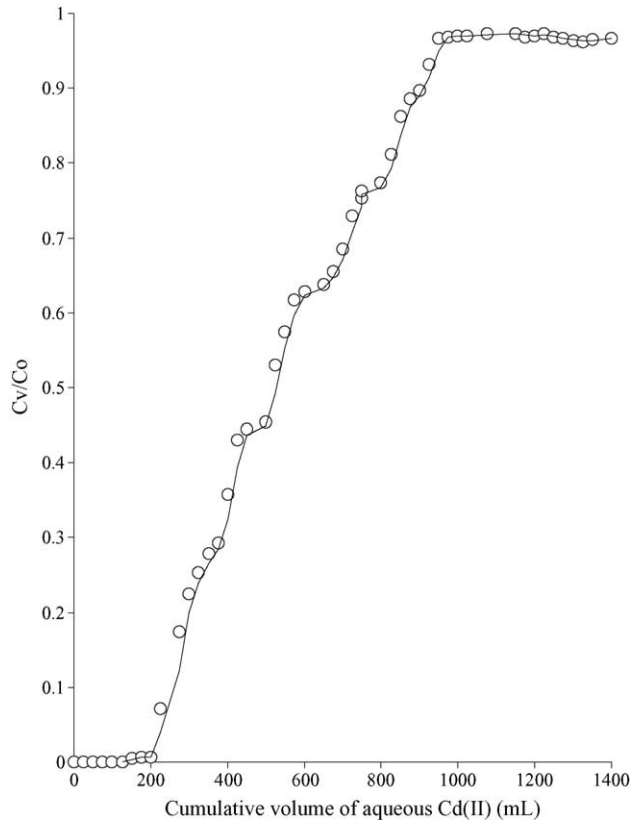


Fig. 13. Breakthrough curve of Cd(II) on NLP at 300 K [C₀ 100 mg L⁻¹, NLP column length 1.5 cm, diameter 1.5 cm].

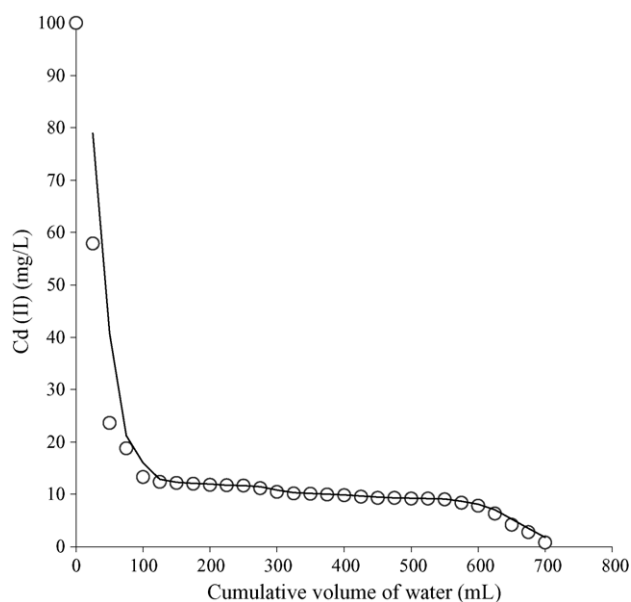


Fig. 14. Desorption of Cd(II) from NLP by washing with double distilled water.

subsequently with an almost constant rate till about 600 mL of water flowed down the column (Fig. 13). Desorption was fast with dilute acid (pH 4.0) or dilute alkali (pH 10.0) as the extractant. The desorption experiments showed that the NLP–Cd(II) linkages were reversible and strong requiring an acid or an alkali to break the adsorbate–adsorbent bonds. The release of Cd(II) by the NLP on washing with dilute acid or alkali showed that the metal ions were held to the NLP surface through ion exchange type of bonding [33,42].

3.7. Column study and breakthrough curve

The breakthrough volume was found to be 200 mL of Cd(II) solution (concentration 100 mg L^{-1}) with C_v/C_o value of 0.071 (Fig. 14). The exhaustion point ($\sim 950 \text{ mL}$ of Cd(II) solution of concentration 100 mg L^{-1}) was approached slowly suggesting a slow mass transfer across the adsorption zone. The lower boundary of the adsorption zone descended slowly to the lower boundary of the NLP column, and the column maintained its capacity to retain Cd(II) till the exhaustion point was reached.

4. Conclusion

From the results, it is possible to conclude that:

- Neem leaf powder (NLP) has very good potential for utilization as an adsorbent for Cd(II) from aqueous medium.
- The kinetics of adsorption of Cd(II) on NLP are complex and while the results were tested with models based on pseudo first order, second order, Elovich equation, liquid film diffusion and intra-particle diffusion, close conformity could be obtained with second order mechanism.

- Application of the intra-particle diffusion model showed very fast initial adsorption followed by one or more slow steps indicating slow diffusion into the internal surface preceded by rapid initial adsorption on external surface.
- The adsorption is influenced by pH of the medium, initial concentration of the metal ions and the amount of the adsorbent.
- The experimental data produces good fits with both Langmuir and Freundlich isotherms and the adsorption coefficients agree well with the conditions supporting favourable adsorption.
- The adsorption process is exothermic and spontaneous at ambient and slightly higher temperatures.

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