Adsorption of Pb(II) from aqueous solution by *Azadirachta indica* (Neem) leaf powder

Krishna G Bhattacharyya*, Arunima Sharma

Department of Chemistry, Gauhati University, Guwahati 781014, Assam, India

Abstract

An adsorbent was developed from the mature leaves of the Neem (*Azadirachta indica*) tree for removing Pb(II) from water. Adsorption was carried out in a batch process with several different concentrations of Pb(II) by varying amount of adsorbent, pH, agitation time and temperature. The uptake of the metal was very fast initially, but gradually slowed down indicating penetration into the interior of the adsorbent particles. Both first-order and second-order kinetics were tested and it was found that the latter gave a better explanation. The experimental data closely followed both Langmuir and Freundlich isotherms. The adsorbent had a considerably high Langmuir monolayer capacity of 300 mg/g. A small amount of the adsorbent (1.2 g/L) could remove as much as 93% of Pb(II) in 300 min from a solution of concentration 100 mg/L at 300 K. The adsorption continuously increased in the pH range of 2.0–7.0, beyond which the adsorption could not be carried out due to the precipitation of the metal. The adsorption was exothermic at ambient temperature and the computation of the parameters, ΔH, ΔS and ΔG, indicated the interactions to be thermodynamically favourable.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Lead; Adsorption; Neem leaf powder; Kinetics; Isotherms

1. Introduction

Lead enters into the human system through a number of processes like breathing workplace air (lead smelting, refining, and manufacturing industries), eating lead-based paint chips, drinking water that comes from lead pipes or lead-soldered fittings, breathing or ingesting contaminated soil, dust, air, or water near waste sites, breathing tobacco smoke, eating contaminated food grown on soil containing lead or food covered with lead-containing dust, breathing fumes or ingesting lead from hobbies that use lead (leaded-glass, ceramics). The health hazards due to the presence of lead in water are of extreme concern to the public, government and industry. Lead has toxic effects on the neuronal system and on the function of brain cells [1,2]. This underlines the need for developing methods for effective removal of lead from water at least below the regulatory level.

Heavy metals in aqueous solution are usually removed by adsorption, ion exchange, coagulation, floatation, hyper-filtration, chemical precipitation, reverse osmosis, etc. Use of ion exchange resins requires considerable cost and adsorption on activated carbon is beset with problems related to regeneration of the adsorbent and recovery of the contaminants. These technologies, apart from being expensive, create secondary problems with metal-bearing sludge [3]. This has initiated research in new, low-cost materials for possible use as adsorbents (Table 1). Such materials can be broadly classified into three categories: (i) natural minerals and similar materials like coal, peat, clays (kaolinite, wollastonite, sepiolite, etc.), red mud, sand, hydrous ferric oxide, etc., (ii) industrial wastes like fly ash, saw dust, biogas slurry, chrome sludge, electric furnace slag, etc., and (iii) biological materials like coconut shell, banana pith, beech leaves, orange peel, waste tea, water hyacinth, moss, algae, chitin, bagasse, tree fern, soya cake, olive cake, almond shells, cactus leaves, fly larva, cypress, chinchona and pine leaves, and in many cases their carbonized products. The efficiency of various bacteria, yeast, fungi, algae and bioadsorbents for heavy metal uptake has been observed

---

* Corresponding author. Tel.: +91-361-2571529.
E-mail address: krishna2604@sify.com (K.G. Bhattacharyya).

Table 1
Low-cost adsorbents and their typical applications (plant-based adsorbents are shown in bold type)

Type	Typical removal	Reference
Giridih coal and coconut shell	Cd(II)	[36]
Fly ash/wollastonite	Cr(VI)	[37]
Fly ash	Cu(II)	[38]
Peat	Cu(II), Cd(II), Ni(II), Zn(II)	[7]
Hydrous ferric oxide	Cd(II)	[39]
Fly ash	Victoria Blue	[40]
Wollastonite	Fe(II)	[41]
Peat	Pb(II)	[12]
Fly ash and impregnated fly ash	Phenol, *o*-cresol, *m*-cresol, *p*-cresol, *o*-nitrophenol, *m*-nitrophenol and *p*-nitrophenol	[42]
Fly ash	Fluoride	[43]
Peat	CN⁻, Cr(VI), Ni(II)	[44]
Wollastonite	Ni(II)	[45]
China clay	Ni(II)	[46]
Groundnut husk carbon	Cr(VI)	[47]
Banana pith	Acid Violet	[48]
Beech leaves	Cd(II)	[49]
Coconut shell carbon	Cr(VI)	[50]
Biogas residual slurry	Congo red	[51]
Biogas residual slurry	Rhoda mine-B, Acid Brilliant Blue, Direct Red 12B, Cr(VI), Pb(II)	[52]
Peanut hull carbon	Hg(II), Cd(II), Pb(II), Ni(II), Cu(II)	[53]
Waste tea, Turkish coffee, Exhausted coffee, Nut shell and Walnut shell	Cr(VI), Cd(II), Al(III)	[54]
Leaf mould	Cr(VI)	[8]
Water hyacinth roots	Methylene Blue	[55]
Moss and copper-coated moss	Cr(III), Cr(VI)	[56]
Algae	Lauryl benzyl sulphonate	[57]
Orange peel	Congo Red, Procion Orange, RhodamineB	[58]
Chrome sludge	Acid Blue 29, Reactive Blue 2	[56]
Chitin	Acid Blue 193, Acid Blue 40, Direct yellow 44, Direct Blue 78	[59]
Red mud	Congo Red	[60]
Fishery wastes (chitosans)	Cu(II), RR222	[31]
Bagasse pith	Hg(II)	[61]
Tree fern	Zn(II), Cu(II), Pb(II)	[62]
Used tea leaves	Pb(II)	[34]
Kaolinite	Mn(II), Co(II), Ni(II), Cu(II)	[63]
Soya cake	Cr(VI)	[64]
Crab shell	Pb(II), Cd(II), Cu(II), Cr(VI)	[65]
Goethite-coated sand	Cd(II)	[66]
Wool, olive cake, sawdust, pine needles, almond shells, cactus leaves, charcoal	Cr(VI)	[28]
Fly larva shells	Mn(II), Zn(II), Ni(II), Cu(II), Fe(III)	[67]
Chitosans	Zn(II), Ni(II), Cu(II)	[68]
Chitin	Cd(II)	[69]
Sepiolite	Co(II)	[70]
Electric furnace slug	Pb(II), Cu(II)	[32]
Cypress, cinchona, pine leaves	Pb(II)	[34]

over two decades [4]. The interesting features of the newly developed bioadsorbents are their high versatility, metal selectivity, high uptake, no concentration dependence, high tolerance for organics and regeneration [5]. These properties coupled with rapid kinetics of the biosorption systems have allowed engineering of new and highly effective yet simple industrial biosorbents for heavy metal removal processes. The present work has used an easily available plant-based renewable resource, dry Neem leaf powder, as an adsorbent for removal of toxic heavy metals such as Pb(II).

2. Experimental

2.1. Reagents and materials

All the chemicals used in the experiments were of analytical grade and they were used without further purification. Pb(NO$_3$)$_2$ (Qualigens Fine Chemicals, Mumbai; minimum assay 99%) was used as the source of Pb(II) and all the solutions were made in double-distilled water. The solutions of Pb(II) were made from a stock solution containing 1000 mg

of Pb(II) in 1 L. The pH of the aqueous solution was ∼6.0, which did not change much with dilution. For experiments at different pH, the acidity of Pb(II) solutions were adjusted by addition of drops of 0.1 M HNO$_3$ and 0.1 M NaOH solutions.

2.2. Preparation of adsorbent

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 and were allowed to dry at room temperature in a shade. The leaves were then kept in an air oven at 333–343 K for 30 h till the leaves became crisp. The dried leaves were then converted into fine powder (Neem leaf powder, NLP) by grinding in a mechanical grinder. The powder was sieved and the 53–74 μm fraction was separated. This fraction was washed several times with double-distilled water till the washings were free of color and turbidity. After drying for several hours at room temperature, the powder was preserved in glass bottles for use as an adsorbent.

2.3. Adsorption experiments

The adsorption experiments were carried out in a batch process under the following experimental conditions:

Initial Pb(II) concentration (mg/L)	50, 75, 100, 125, 150
Amount of adsorbent (mg/L)	0.2, 0.4, 0.6, 0.8, 1.2
pH	2.0–7.0
Agitation time (min)	20, 40, 60, 120, 180, 240, 300
Adsorption temperature, T (K)	308, 313, 318
Particle size (μm)	53–74

The adsorption was carried out in 100 mL borosil conical flasks by agitating a pre-weighed amount of the powder with 50 mL of the aqueous Pb(II) solution in a constant temperature, water bath shaker (NSW, Mumbai) for a pre-determined time interval at a constant speed. After adsorption, the mixture was centrifuged (Remi Research Centrifuge, R24) when the adsorbent settled quickly and Pb(II) remaining unabsorbed in solution was determined with atomic absorption spectrometry (Varian SpectrAA 220, Lamp current 5 mA, air-acetylene oxidizing flame, 217.0 nm, slit width 1.0 nm, working range 0.1–30 μg/mL).

The amount of Pb(II) adsorbed per unit mass of the adsorbent (q in mg/g) was computed by using the following expression:

$$q = \frac{C_0 - C_t}{m}$$

where C_0 and C_t are Pb(II) concentrations in mg/L before and after adsorption for time t, and m (g) is the amount of

NLP taken for 1 L of Pb(II) solution. The extent of adsorption in percentage is found from the relation

$$\text{adsorption (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

2.4. Kinetics of adsorption

The mechanism of adsorption often involves chemical reaction between functional groups present on the adsorbent surface and the metal ions. This involves, in most cases, formation of metal-organic complexes or cation exchange reactions due to high cation exchange capacity of the adsorbents. Other possible mechanisms involve mass-transport processes, bulk transport in the liquid phase, diffusion across the liquid film surrounding the solid particles, and diffusion into micropores and macropores. The important characteristics of the adsorbent that determine equilibrium capacity and rate are the surface area, the physicochemical nature of the surface, the availability of that surface to adsorbate molecules or ions, the physical size and form of the adsorbent particles. System parameters such as temperature and pH can also markedly influence adsorption as they affect one or more of the above parameters.

The order of adsorbate–adsorbent interactions has been described by using various kinetic models. Traditionally, the pseudo-first-order model derived by Lagergren [6] has found wide application. On the other hand, several authors [7–10] have shown that second-order kinetics can also very well describe these interactions in certain specific cases.

In the case of adsorption preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo-first-order rate equation of Lagergren:

$$\frac{dq_t}{dt} = k_{ad}(q_e - q_t) \tag{1}$$

where q_t and q_e are the amount adsorbed at time t and at equilibrium, and k_{ad} is the rate constant of the pseudo-first-order adsorption process. The integrated rate law, after applying the initial condition of $q_t = 0$ at $t = 0$, is

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_{ad}}{2.303}\right)t \tag{2}$$

Plot of $\log(q_e - q_t)$ versus t gives a straight line for first-order kinetics, which allows computation of the adsorption rate constant, k_{ad}. If the experimental results do not follow Eqs. (1) and (2), they differ in two important aspects: (i) $k_{ad}(q_e - q_t)$ then does not represent the number of available adsorption sites, and (ii) $\log q_e$ is not equal to the intercept of the plot of $\log(q_e - q_t)$ against t. In such cases, pseudo-second-order kinetics [2,11] given by

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{3}$$

where k is the second-order rate constant, is applicable. For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of the equation is

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \tag{4}$$

which can also be written as

$$q_t = \frac{1}{1/kq_e^2} + \frac{t}{q_e} \tag{5}$$

or, in the linear form,

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \tag{6}$$

where $h = kq_e^2$ can be regarded as the initial sorption rate as $t \to 0$. If the pseudo-second-order kinetics is applicable, the plot of t/q_t versus t gives a linear relationship, which allows computation of q_e, k and h without having to know any parameter beforehand.

The adsorption data may also be analyzed using the Elovich equation, which has the form:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{7}$$

where α is the initial sorption rate constant and β is the desorption rate constant during any one experiment. The Elovich equation can be simplified by assuming [12] that $\alpha\beta t \gg 1$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, when the equation becomes

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \tag{8}$$

The constants can be obtained from the slope and the intercept of the plot of q_t versus $\ln(t)$. The variation in the amount of adsorption with time at different initial metal ion concentrations can be used to evaluate the role of diffusion in the adsorption process. The intra-particle diffusion rate constant (k_p) is given by the equation

$$q_t = k_p t^{0.5} \tag{9}$$

If a linear relation is observed between q_t and $t^{0.5}$ [13,14], k_p is given by the slope.

2.5. Adsorption isotherms

The fractional coverage, θ, on an adsorbent surface at constant temperature is represented by Langmuir isotherm, the most widely used two-parameter equation for a single component system. This isotherm has the simple form

$$\theta = \frac{q_e}{q_m} = \frac{bC_e}{1 + bC_e} \tag{10}$$

where C_e is the concentration of the adsorbate at equilibrium, q_e is the amount adsorbed at equilibrium in unit mass of the adsorbent, q_m is the monolayer capacity, and b is the equilibrium constant, given by the ratio k_a/k_d, k_a and k_d being the rate constants of the adsorption and desorption processes respectively. Eq. (10) can be rearranged to

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \left(\frac{1}{q_m}\right)C_e \tag{11}$$

and a plot of (C_e/q_e) versus C_e should give a straight line. The slope and the intercept of this line give the values of q_m and b.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L [15] or the separation factor, defined as

$$R_L = \frac{1}{1 + bC_{ref}} \tag{12}$$

where C_{ref} is any equilibrium liquid-phase concentration of the solute. For favorable adsorption, $0 < R_L < 1$, while $R_L > 1$ represents unfavorable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$.

The empirical isotherm due to Freundlich is also used to describe adsorption. This has the form

$$q_e = K_f C_e^n \tag{13}$$

where K_f and n are known as Freundlich coefficients obtainable from the plots of $\log q_e$ versus $\log C_e$ on the basis of the linear form of the equation

$$\log q_e = \log K_f + n \log C_e \tag{14}$$

2.6. Thermodynamics of adsorption

Adsorption is usually an exothermic process and as the temperature increases, the amount adsorbed at a given concentration decreases in accordance with Le Chatelier's principle. The thermodynamic criteria for the adsorption process were evaluated through computation of Gibbs energy (ΔG), enthalpy of adsorption (ΔH), and entropy of adsorption (ΔS) by carrying out the adsorption experiments at three different temperatures and using the following equations [16]:

$$\Delta G = \Delta H - T\Delta S \tag{15}$$

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{16}$$

where (q_e/C_e) is called the adsorption affinity and is the ratio of q_e, the amount adsorbed per unit mass at equilibrium to C_e, the equilibrium concentration of the adsorbate. The values of ΔH and ΔS were determined from the slope and the intercept of the plots of $\log(q_e/C_e)$ versus $1/T$. The ΔG values were calculated using Eq. (15).

2.7. Desorption and regeneration

For carrying out desorption and regeneration studies, NLP was first saturated with Pb(II) by taking 4 g of NLP in a pyrex glass column (1.5 cm internal diameter) and continuously passing a solution of Pb(II) (60 mg/L) through it while keeping a constant head of 2 cm till the concentration at the outlet equaled the initial concentration. Desorption was carried out by passing successively (i) deionised water (pH 7.0) and (ii) dilute nitric acid (pH 4.0) through the column till Pb(II) could not be detected in the outlet in each case.
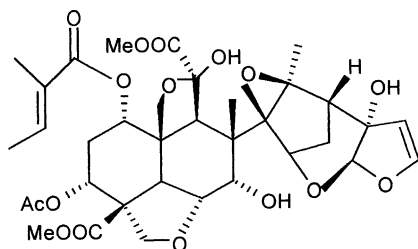
Fig. 1. Structure of azadirachtin.

3. Results and discussion

3.1. Characterization of the adsorbent

The Neem tree (*Azadirachta Indica*) is well known in India and neighbouring countries for more than 2000 years. The Neem is a fast growing, usually evergreen plant, which reaches a height of 15–20 m and a trunk girth of 1.5–3.5 m [17]. The unpaired, pinnate leaves are 20–40 cm long containing about 30 leaflets on both sides. The leaflets are 5–8 cm long with dark green colour and are asymmetrical in nature. The importance of Neem has been recognized by the US National Academy of Sciences, resulting in a 1992 report entitled "Neem – a tree for solving global problems" [17]. The Neem tree survives in the city atmosphere contaminated with pollutants emitted by vehicles [18]. The tree helps growing of other trees in barren land by improving soil fertility [17,19] and it prevents the loss of valuable topsoil by wind-erosion, especially during the winter.

The main chemical ingredients, present in various segments of the Neem tree, consist of a few related compounds belonging to the "triterpene", or more specifically "limonoid" group of natural products. The main components in Neem are azadirachtin, salannin, meliantriol, nimbin and nimbidin. The structure of azadirachtin, which was the first active ingredient isolated from Neem and which has been projected as the main agent in Neem for fighting insects, is shown in Fig. 1 [20]. Other important constituents of Neem include a number of fatty acids like oleic acid, steric acid, palmitic acid, linoleic acid, etc. [21]. The presence of polar groups on the surface [2,9,11] is likely to give considerable cation exchange capacity to Neem leaf powder.

The physicochemical characteristics of fresh Neem leaves have been reported [22] as follows:

Moisture (%)	59.4
Fat (%)	1.0
Carbohydrates (%)	22.9
Calcium	510 mg/100 g
Iron	17 mg/100 g
Niacin	1.40 mg/100 g
Carotene	1998 μg/100 g
Glutamic acid	73.30 mg/100 g
Aspartic acid	15.50 mg/100 g
Proline	4.00 mg/100 g
Proteins (%)	7.1
Fiber (%)	6.2
Minerals (%)	3.4
Phosphorous	80 mg/100 g
Thiamine	0.04 mg/100 g
Vitamin C	218 mg/100 g
Calorific value (kcal/kg)	1290
Tyrosine	31.50 mg/100 g
Alanine	6.40 mg/100 g
Glutamine	1.00 mg/100 g

FTIR measurements (Perkin Elmer Spectrum RX I) for the Neem leaf powder showed the presence of a large number of functional groups, notably –OH (3597–$3600\,cm^{-1}$), –NH_2 ($3399\,cm^{-1}$), $\equiv CH$ ($3297\,cm^{-1}$), $>C=N-$ ($1656\,cm^{-1}$), $\equiv C-C\equiv$, $\equiv C-N<$ and $\equiv C-O-$ ($1160\,cm^{-1}$), $>C=O$ (1633, 1656, 1672, 1688, $1714\,cm^{-1}$), $>C=C<$ ($1656\,cm^{-1}$), and $>C=S$ ($1105\,cm^{-1}$). This is in conformity with the presence of various constituents of Neem leaves. Further, it was observed that if NLP was agitated with water for 6–8 h, dried and IR spectra taken again, no significant change in peak distribution and intensity was observed. The surface structure of the NLP particles thus remained stable through long periods of agitation with water.

XRF analysis of the dried Neem leaf powder (Philips PW 1480, Rh anode and LiF 200 Crystal Analyzer) showed the presence of Ca, Cu, Fe, K, and Mn. However, due to absence of suitable standard, quantitative estimation could not be done.

Determination of the surface area of the Neem leaf powder by the methylene blue adsorption method [23] yielded a value of $21.45\,m^2\,g^{-1}$ for the specific surface area (average monolayer capacity for methylene blue adsorption on Neem leaf powder was $8.76\,mg\,g^{-1}$, cross-sectional area of the dye molecule $1.30 \times 10^{-18}\,m^2$). With respect to Pb(II) (average monolayer capacity 300 mg/g on Neem leaf powder at 300 K, cross-sectional area of Pb(II) ion $5.56 \times 10^{-20}\,m^2$ [24]), the specific surface area was computed to be $48.50\,m^2\,g^{-1}$.

Scanning electron microscopy (SEM, JEOL JSM-35CF) of the Neem leaf powder (Fig. 2) showed that the powder was an assemblage of fine particles, which did not have regular, fixed shape and size. The particles were of various dimensions and all of them contained a large number of steps and kinks on the external surface, with broken edges.

3.2. Effect of pH

pH is an important factor controlling the process of adsorption. In the present work, adsorption could not be carried out beyond pH 7.0 due to precipitation of Pb(OH)$_2$ and therefore, the experiments were done in pH range 2.0–7.0. For a typical experiment with Pb(II) solution of concentration 100 mg/L, adsorbent dose of 0.4 g/L, and agitation time of 3 h, the extent of adsorption at 300 K increased from 0.92 to 78.56% in the pH range of 2.0–7.0 (Fig. 3). It was seen
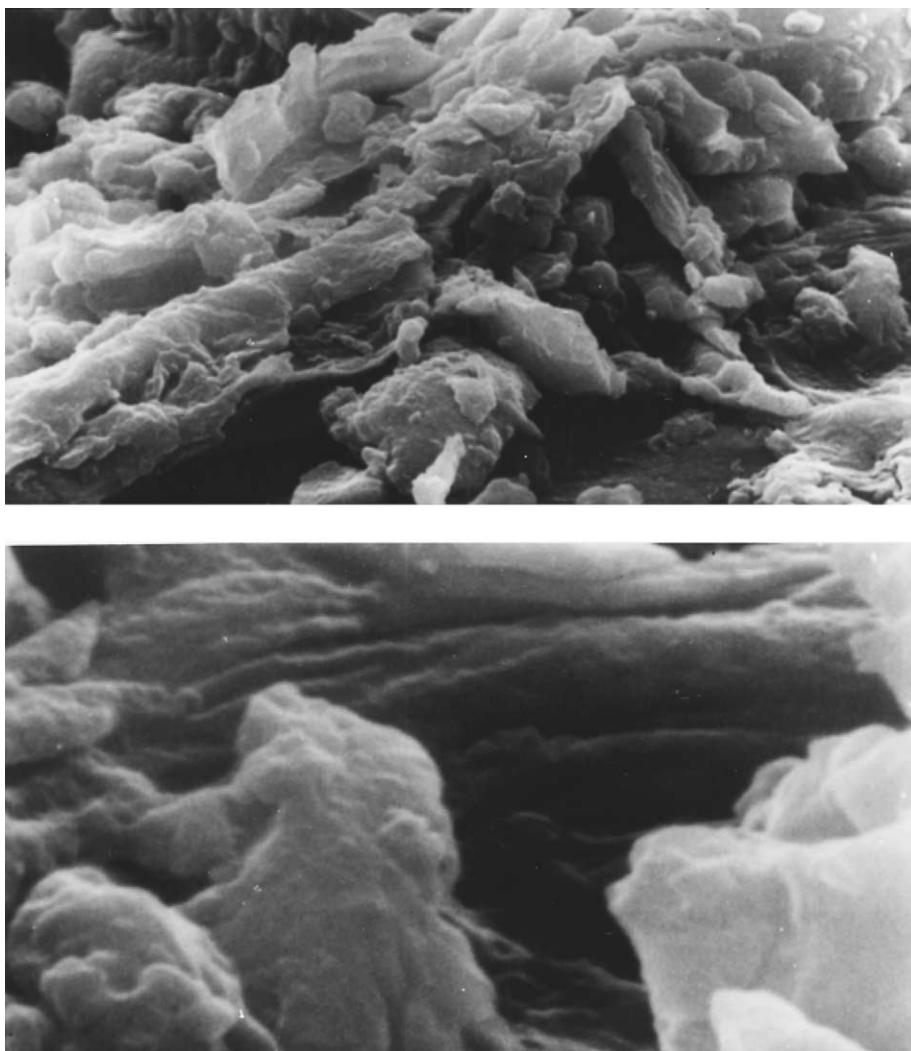
Fig. 2. SEM photographs of Neem leaf powder at $4000\times$ (top) and $20\,000\times$ (bottom) magnification.

that adsorption increased continuously with decrease in acidity till it reached an almost constant value between pH 4.5 and 5.5, after which the extent of removal of Pb(II) again showed an increase which might be due to onset of precipitation. Low pH depresses adsorption of Pb(II), which may be due to competition with H^+ ions for appropriate sites on the adsorbent surface. However, with increasing pH, this competition weakens and Pb(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 ion may take place through binding of both Pb^{2+} and $Pb(OH)^+$ ions to the adsorbent surface [25].

Similar trend was reported for adsorption of Pb(II) on silica gel [26] when the extent of adsorption 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.

3.3. Effect of agitation time and kinetics

The kinetics were investigated with a constant Pb(II) concentration of 100 mg/L at 300 K with five different NLP amounts of 0.2, 0.4, 0.6, 0.8 and 1.2 g/L in the interaction time intervals of 20–300 min. A gradual increase in the extent of adsorption with time was observed (Fig. 4). Pb(II) adsorption increased from 16.1 to 60.8% and 67.7 to 93.0% in the given time interval for NLP amounts of 0.2 and 1.2 g/L respectively. Such behaviour is expected in a batch reactor with either constant adsorbent amount and varying initial adsorbate concentration or vice versa [27]. An increase in the adsorbent amount should result in a decrease in the agitation time to reach apparent equilibrium while the fraction of the metal removed from the aqueous phase should increase with an increase in the adsorbent amount. The nature of the adsorbent and its compactness affected the time needed to reach equilibrium. In the present case, the adsorbate–adsorbent
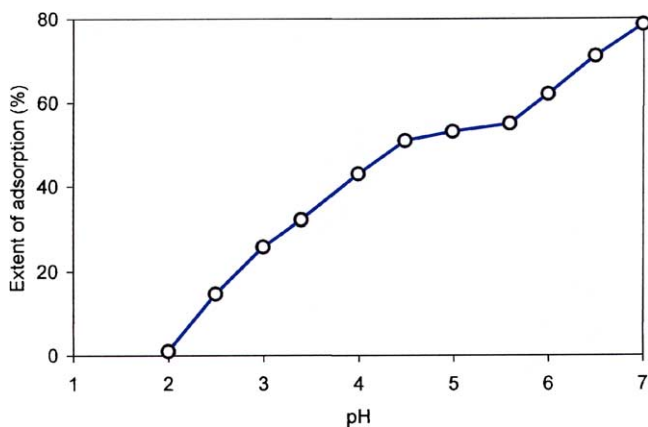
Fig. 3. Effect of pH on adsorption of Pb(II) on Neem leaf powder at 300 K (Pb(II): 100 mg/L, adsorbent: 0.4 g/L, agitation time: 3 h).

Fig. 5. Lagergren plots for adsorption of Pb(II) on Neem leaf powder at 300 K (powder amount: 0.8 g/L).

interactions approached pseudo-equilibrium at around 300 min.

Lagergren plots (Fig. 5) of $\log(q_e - q_t)$ versus agitation time for adsorption of Pb(II) (NLP 0.8 g/L) at 300 K for six different Pb(II) concentrations were linear in nature. The rate constants, calculated from the slopes of the best-fit lines (correlation coefficient, $R = 0.99$ in all the cases), were in the range of 8.75×10^{-3} to 13.82×10^{-3} min^{-1} with a mean value of 12.10×10^{-3} min^{-1}. Ho and McKay [9] have found first-order rate constant for adsorption of Pb(II) on peat in the range of $(3.66–4.40) \times 10^{-2}$ min^{-1}. Dakiky et al. [28] 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}).

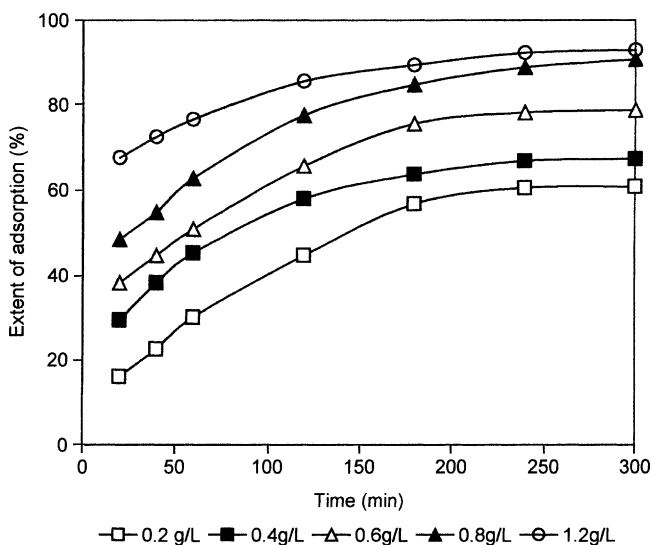The pseudo-first-order equation of Lagergren has been adequate to describe the adsorption process in a large num-

ber of cases [9,12] despite its failure to provide a concrete mechanism of the adsorption process. It was observed in the present work that $\log q_e$ values computed from the experimental q_e values did not agree with $\log q_e$ values obtained from Lagergren plots. This indicates that pseudo-first-order kinetics might not be sufficient to describe the mechanism of Pb(II)–NLP interactions [2,11]. The pseudo-second-order model based on Eq. (6), which considers the rate-limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the adsorbate and the adsorbent, was therefore applied. The plot of t/q_t versus t (Fig. 6) yields very good straight lines (correlation coeffi-

Fig. 4. Effect of agitation time on adsorption of Pb(II) on Neem leaf powder at 300 K (Pb(II) concentration: 100 mg/L).

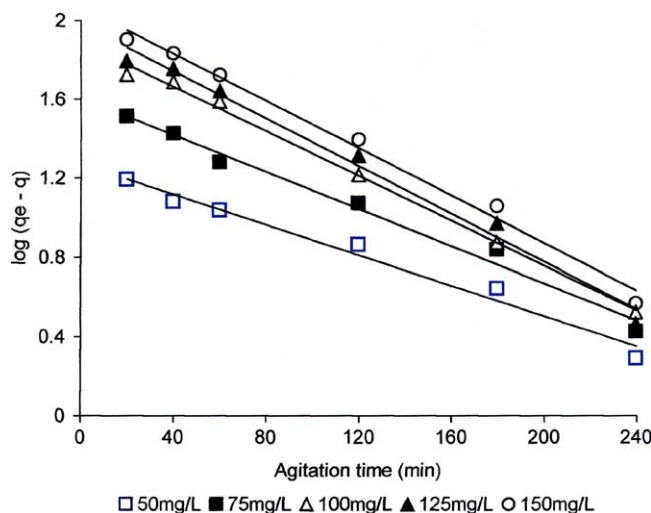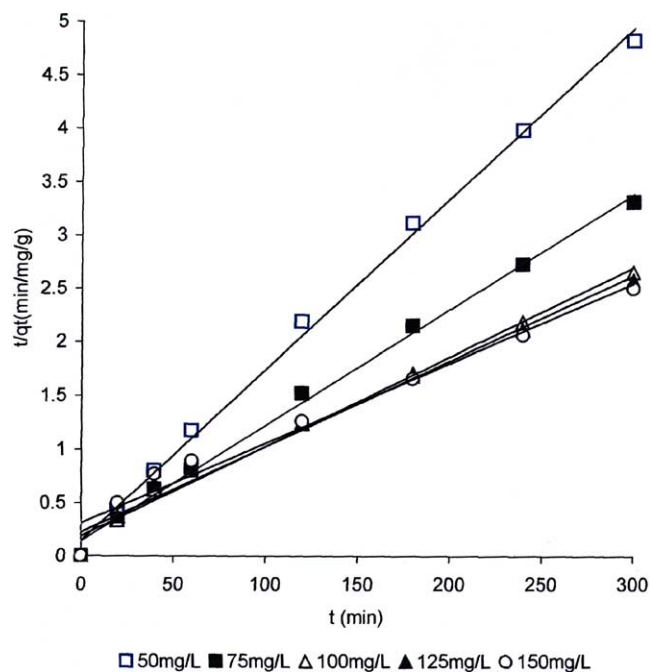Fig. 6. Pseudo-second-order plots for adsorption of Pb(II) on Neem leaf powder at 300 K (powder amount: 0.8 g/L).

Table 2

Kinetic order of interaction between different adsorbents and metal ions

Adsorbent	Adsorbate	Order	Reference
Peat	Pb(II)	Second	[2,44]
Peanut hull carbon	Pb(II)	First	[71]
Granular activated carbon	Pb(II)	First	[71]
Biogas residual slurry	Pb(II)	First	[72]
Kaolinite clay	Pb(II)	First	[73]
Biopolymers	Pb(II)	First	[74]
Peat	Cu(II)	Second	[29]
Peanut hull carbon	Ni(II)	First	[71]
Peat	Ni(II)	Second	[75]
Leaf mould	Cr(VI)	Second	[8]
Peanut hull carbon	Cd(II)	First	[77]
Biogas residual slurry	Cr(VI)	First	[72]
Peat	Cu(II)	Second	[7]
	Cd(II)		
	Ni(II)		
	Zn(II)		

cient, $R = 0.99$). The second-order rate constant was in the range of 1.78×10^{-4} to 1.80×10^{-3} g mg^{-1} min^{-1}.

Success with the second-order kinetics suggests chemisorption as the rate-controlling step [12]. Second-order kinetics was earlier reported for adsorption of Pb(II), Cu(II), and Ni(II) on peat [11] with rate constants 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 1.75×10^{-1} g mg^{-1} min^{-1}, respectively. Table 2 shows a few systems of metal ion-adsorbent systems showing both first-order and second-order kinetics. The kinetics are not specific to the type of materials used while in many cases, the kinetics might not have been explored beyond pseudo-first-order.

Kinetics of adsorption of Pb(II) on Neem leaf powder also followed the Elovich equation with the plots of q_t versus $\ln t$ yielding straight lines (Fig. 7) with high correlation coefficient of 0.99 in all the cases. The Elovich equation does not predict any definite mechanism, but it is useful in describing adsorption on highly heterogeneous adsorbents [29] similar to the Neem leaf powder. Applicability of the Elovich equation shows the adsorption of Pb(II) on NLP to be predominantly chemical in nature [29,30]. The Elovich constants computed from the plots are given in Table 3.

An adsorption process is normally controlled by three diffusion steps: (i) transport of the solute from the bulk solution to the film surrounding the adsorbent, (ii) transfer from

Table 3

Calculated values of α and β in the Elovich equation for the sorption of Pb(II) on Neem leaf powder

Pb(II) (mg/l)	α (mg g^{-1} min^{-1})	β (g/mg)	R
50	34.604	5.58	0.99
75	0.453	12.22	0.99
100	0.028	21.90	0.99
125	0.013	25.56	0.99
150	0.005	32.02	0.99

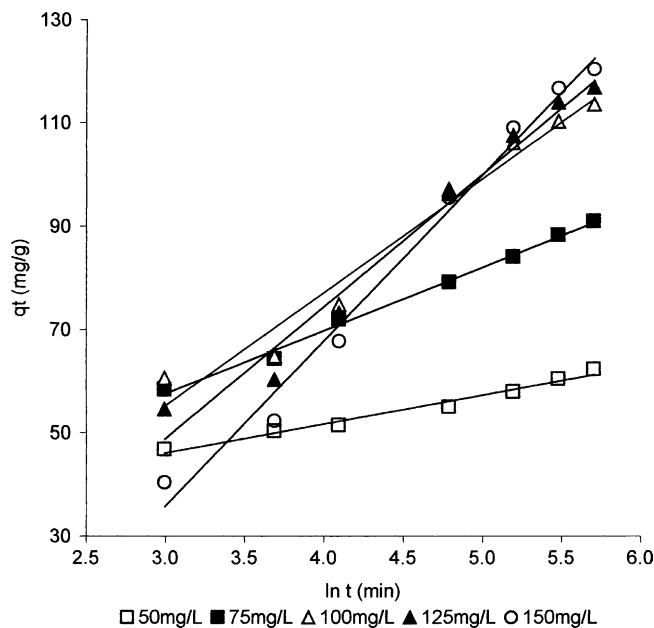Fig. 7. Plots of Elovich equation for adsorption of Pb(II) on Neem leaf (powder amount: 0.8 g/L).

the film to the adsorbent surface leading to surface adsorption, and (iii) diffusion from the surface to the internal sites followed by binding of the adsorbate on the active sites. The slowest of these steps determines the overall rate of the adsorption process. If intra-particle diffusion has significant presence in the adsorption process [13], the approach towards equilibrium is governed by the function $(Dt/r^2)^{0.5}$, where r is the radius of the particle and D is the diffusivity within the particle. The initial rates of intra-particle diffusion are obtained with the help of the Eq. (9) by plotting q_t versus $t^{0.5}$ (Fig. 8). The plots show multi-linearity [31] with two or more steps. The first, sharper portion represents adsorption on the external surface, which is almost instantaneous. The second portion indicates a comparatively slower adsorption when the adsorbate diffuses gradually into the interior surfaces of the particles and the adsorption becomes intra-particle diffusion controlled [31]. In a few of the curves, a third portion could also be distinguished as the final equilibrium stage when the intra-particle diffusion starts to slow down due to saturation of most of the adsorption sites. The multi-linear curves might be due to adsorption on the irregular, non-uniform sites in the steps and edges of the particles as evidenced by SEM photographs.

3.4. Effect of adsorbent amount and Pb(II) concentration

The variation in the extent of adsorption with the amount of adsorbent for a constant Pb(II) concentration (100 mg/L) at 300 K is presented in Table 4. The adsorption increased rapidly as more and more of the adsorbent was added. The adsorption increased from 16.1 to 67.7% when the adsorbent
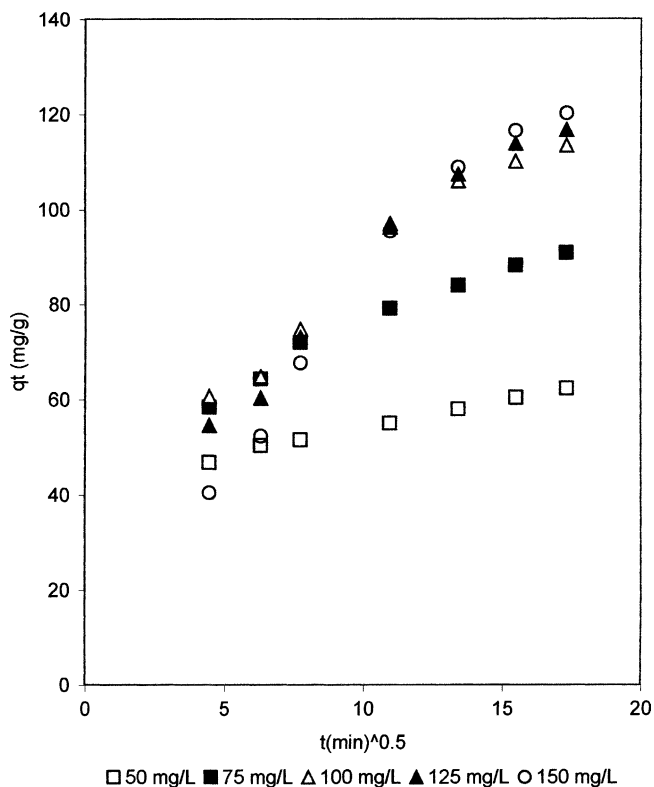
Fig. 8. Plots of q_t vs. $t^{0.5}$ for adsorption of Pb(H) on Neem leaf powder at 300 K (powder amount: 0.8 g/L).

amount was increased from 0.2 to 1.2 g/L for an agitation time of just 20 min. Increasing the amount of the adsorbent makes a large number of sites available leading to an increase in adsorption.

With an increase in the concentration of Pb(II) at constant amount of adsorbent, the adsorption came down for the same agitation time (Table 5). The extent of adsorption decreased from 88.0 to 50.9% (time: 120 min) as Pb(II) concentration was increased from 50 to 150 mg/L for NLP amount of 0.8 g/L. Considering the heterogeneities of NLP surface and the possibility of multi-layer adsorption, these results could be explained on the basis of water–Pb(II), Pb(II)–NLP, and water–NLP interactions.

Table 4
Variation in the extent of adsorption of Pb(II) at 300 K on different amounts of Neem leaf powder (Pb(II) concentration 100 mg/L)

Time (min)	Extent of adsorption (%) for adsorbent amount of				
	0.2 g/L	0.4 g/L	0.6 g/L	0.8 g/L	1.2 g/L
20	16.1	29.4	38.2	48.5	67.7
40	22.6	38.2	44.7	54.8	72.5
60	30.0	45.2	50.8	62.8	76.6
120	44.7	58.0	65.7	77.6	85.6
180	56.7	63.7	75.7	84.8	89.4
240	60.5	66.9	78.3	88.9	92.3
300	60.8	67.3	78.8	90.7	93.0

Table 5
Variation in the extent of adsorption of Pb(II) at 300 K for different concentrations of Pb(II) (Neem leaf powder 0.8 g/L)

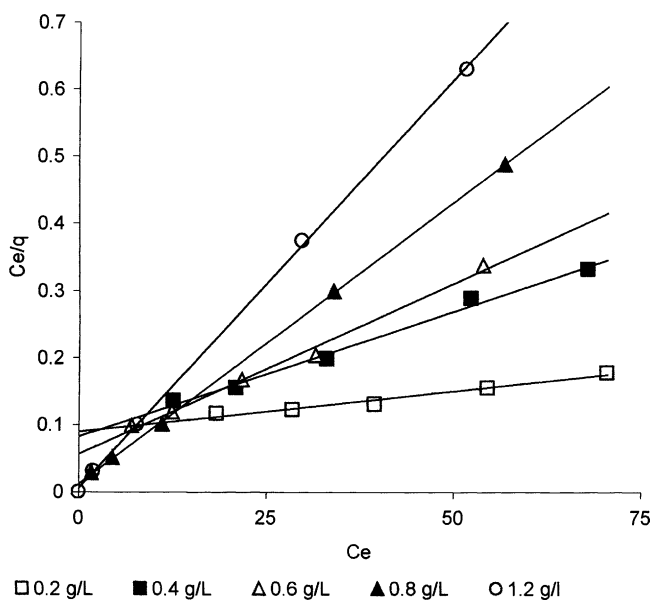| Time (min)	Extent of adsorption (%) for Pb(II) concentration of				
	50 mg/L	75 mg/L	100 mg/L	125 mg/L	150 mg/L
20	74.9	62.2	48.5	34.9	21.6
40	80.5	68.6	54.8	38.6	27.9
60	82.3	76.7	62.8	46.8	36.1
120	88.0	84.4	77.6	61.6	50.9
180	92.7	89.6	84.8	68.7	58.1
240	96.6	94.1	88.9	72.8	62.2
300	99.7	96.9	90.7	74.7	64.1

Fig. 9. Langmuir plots for adsorption of Pb(II) on Neem leaf powder (five different amounts) at 303 K (Pb(II) concentration of 50, 75, 100, 125 and 150 mg/L for each adsorbent concentration, agitation time: 4 h).

3.5. Adsorption isotherms

Langmuir and Freundlich plots for the present work are shown in Figs. 9 and 10 and the adsorption coefficients computed from these are given in Table 6. All the curves

Table 6
Adsorption coefficients for Pb(II)–NLP interactions at 303 K (agitation time: 240 min, Pb(II) concentration: 50, 75, 100, 125, 150 mg L^{-1} for each different amount of NLP)

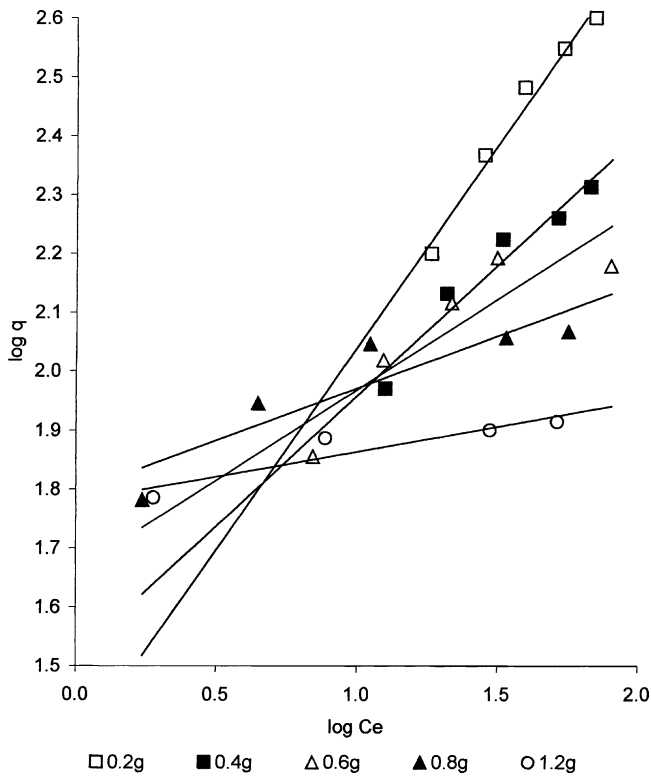| NLP (g L^{-1})	Langmuir Isotherm				Freundlich Isotherm			
	R	q_m (mg g^{-1})	K_d (L mg^{-1})	R_L	R	K_f (L g^{-1})	n
0.2	0.99	833.3	0.013	0.43	0.99	22.7	0.68
0.4	0.99	270.3	0.045	0.18	0.98	32.9	0.44
0.6	0.99	196.1	0.091	0.10	0.89	46.0	0.31
0.8	0.99	119.0	0.700	0.01	0.91	62.4	0.18
1.2	0.99	82.0	2.104	0.01	0.93	60.1	0.09
Mean	0.99	300.1	0.591	0.15	0.94	44.8	0.34

Fig. 10. Freundlich plots for adsorption of Pb(II) on Neem leaf powder (five different amounts) at 303 K (Pb(II) concentration of 50, 75, 100, 125 and 150 mg/L for each adsorbent concentration, agitation time: 4 h).

Table 7
Monolayer adsorption capacity for adsorption of Pb(II) on various adsorbents [76]

Materials	q_m (mg/g)
Waste slurry	1380
Amberlite IR-120	1039
Focus vesiculosus	600
Ascophyllum nodosum	478
Sargassum fluitans	378
Absidia orchidis	351
Oxidized anthracite	259
Ascophyllum nodosum	257
Algae	251
Spruce sawdust	224
Rhizopus nigiricans	166
Peat	150
Zoogloea ramigera	110
Resting cells	110
Blast furnace sludge	79.9
Inactivated cells	79.5
Tea leaves	78.7
Montmorillonite	71.8
Penicillium chrysogenum	63
Sphagnum moss peat	61.9
Rhizopus arrhizus	55
High carbon content sludge	55.0
Groundnut husks	39.4
Sphagnum moss peat	30.7
Coke	19.1
Spruce sawdust	15
Illite clay	14.1
Soil	12.6
Linden saw dust	12
Kaolinite	9.37
Kaolinite	6.46
Kaolinite	3.93
Wollastonites	1.68
China clay	0.411
Fly ash	0.368
Peat	122
NLP (this work)	300.1

had good linearity (correlation coefficient, $R \approx 0.99$) indicating strong binding of Pb(II) ions to the surface of NLP particles. Langmuir monolayer adsorption capacity (q_m) decreased from 833.3 to 82.0 mg/g when NLP amount was varied from 0.2 to 1.2 g/L. The adsorption equilibrium parameter, b, showed an increasing trend of 0.013–2.104 L/mg in the same range of adsorbent amount. The dimensionless parameter, R_L, remained between 0.01 and 0.43 ($0 < R_L < 1$) for the whole range of amounts of adsorbent.

Values of Langmuir coefficients obtained in the present work are in general agreement with values reported by other authors for a variety of materials. Curkovic et al. [32] have reported Langmuir monolayer capacity (q_m) and equilibrium coefficient (b) values of 33.78–37.04 mg/g and (2.68–4.79) $\times 10^{-3}$ L/mg respectively for adsorption of Pb(II) on electric furnace slag in the temperature range of 293–313 K. Ghoul et al. [33] reported q_m values of 82.64 and 50.76 mg/g and b values of 2.80 and 1.78 mL/mg for adsorption of Pb(II) on silica gel coated with polyethyleneimine and crosslinked with glutaraldehyde. NLP had similar values for q_m, but considerable differences exist for the values of b. Values of q_m for a few unconventional adsorbents are presented in Table 7 from which it is seen that the value for NLP (mean value: 300.1 mg/g) is better than most of the adsorbents reported in the literature.

Freundlich plots (Fig. 10) have high linearity ($R = 0.89$–0.99) indicating the process to have conformed to the empirical Freundlich pattern of adsorption on non-specific, energetically non-uniform, heterogeneous surface. Freundlich coefficient, n, remained between 0.09 and 0.69 (mean value 0.34), fulfilling the condition of $0 < n < 1$ for favourable adsorption. The other Freundlich coefficient, K_f, representing adsorption capacity, increased from 22.7 to 62.4 L/g with an increase in NLP amount. The values showed a trend similar to that of Langmuir coefficient, b. For adsorption of Pb(II) on electric furnace slag in the temperature range 293–313 K, the Freundlich coefficients were reported as $n = 0.42$–0.56 and $K_f = 0.57$–1.82 L/g [32]. NLP had similar n values, but its K_f values were larger. For adsorption of Pb(II) on leaves of cypress, cinchona and pine trees, Al-Subu [34] has found Freundlich coefficients, n and K_f, to have values of 0.97, 0.61, and 1.57, and of 0.42, 1.35, and 0.02 respectively. Again, with respect to n, NLP appears to be a better adsorbent than cypress, cinchona and pine leaves.
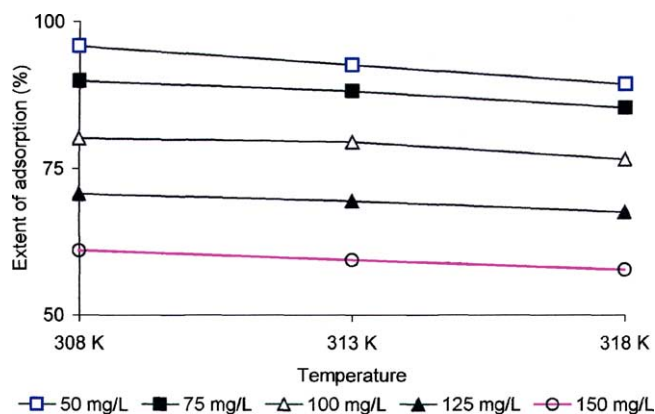
Fig. 11. Variation of extent of adsorption of Pb(II) on Neem leaf powder with temperature for different concentrations (adsorbent amount: 0.8 g/L, agitation time: 2 h).

3.6. Thermodynamic studies

Adsorption of Pb(II) on NLP decreased when the interaction temperature was increased from 308 to 318 K (Fig. 11). The process was thus exothermic in nature. The plots of $\log q_e/C_e$ versus $1/T$ (Fig. 12) were used to compute the values of the thermodynamic parameters (Table 8). The enthalpy change, ΔH, varied from -82.5 to $-10.9 \, kJ \, mol^{-1}$ in Pb(II) concentration range of 50–150 mg/L while the entropy change, ΔS, varied from -240.3 to $-29.6 \, J \, mol^{-1} \, K^{-1}$. The decrease in enthalpy was in conformity with exothermic and spontaneous nature of the adsorption process. The distribution of Pb(II) ions in solution was obviously more chaotic compared to Pb(II) ions bound to NLP surface, and this resulted in a net decrease in entropy.

Spontaneity of the adsorption process was demonstrated further by the decrease in Gibbs energy, ΔG (values varied from -4.69 to $-3.96 \, kJ \, mol^{-1}$ in the temperature range 308–318 K). The negative values of ΔG indicate that the equilibrium

$$Pb(II) \, (aqueous) + NLP \rightleftharpoons Pb(II) \cdots NLP$$

shifts to the forward direction in a spontaneous manner leading to binding of Pb(II) ions on to surface constituents of NLP. Pb(II) is most likely to bind on polar functional groups (–CHO, >CO, –COOH, –OH (phenolic), etc.) by either of
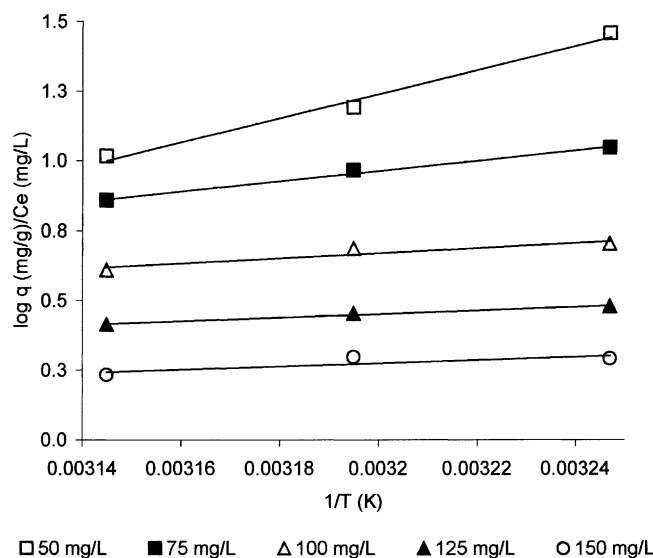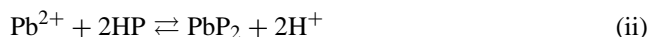

Fig. 12. Plots of $\log(q/C_e)$ for adsorption of Pb(II) on Neem leaf powder against $1/T$ for different concentrations (adsorbent amount: 0.8 g/L, agitation time: 2 h).

the two mechanisms:

$$Pb^{2+} + 2P^- \rightleftharpoons PbP_2 \qquad (i)$$

or

$$Pb^{2+} + 2HP \rightleftharpoons PbP_2 + 2H^+ \qquad (ii)$$

in which P^- and HP are polar groups on the surface of NLP. Such mechanisms have been proposed earlier by Ho et al. [2] for adsorption of Pb(II) on peat. However, since XRF measurement showed the presence of a number of metal ions (Ca, Cu, Fe, K, and Mn) on NLP surface, interaction of Pb(II) through an ion-exchange mechanism can also be simultaneously operative.

ΔG decreased less with increasing temperature (e.g. ΔG varied from -8.5 to $-6.8 \, kJ \, mol^{-1}$ in the temperature range of 308–318 K for Pb(II) 50 mg/L), which indicated that the adsorption of Pb(II) on NLP became less favourable at higher temperature.

Adsorption of Pb(II) on chemically treated used tea leaves was reported to be endothermic with ΔH of $+10.0 \, kJ/mol$, although the process had ΔG values of -11.55, -11.77, -12.00 and $-11.50 \, kJ \, mol^{-1}$ at 298, 313, 333 and 343 K

Table 8
Thermodynamic parameters for adsorption of Pb(II) on Neem leaf powder (0.8 g dm^{-3}) after agitating for 120 min

Pb(II) (mg dm^{-3})	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1} K^{-1})	$-\Delta G$ (kJ mol^{-1}) at temperature		
			308 K	313 K	318 K
50	82.49	240.28	8.49	7.28	6.80
75	34.72	92.70	6.17	5.71	5.24
100	17.39	42.86	4.19	3.98	3.76
125	12.07	30.00	2.83	2.68	2.53
150	10.90	29.61	1.78	1.63	1.48
Mean	31.51	87.09	4.69	4.26	3.96

respectively and ΔS values of 72.3, 69.6, 66.1 and 62.7 J/mol [35]. Curcovic et al. [32] also showed endothermic adsorption ($\Delta H = 24.15 \, \text{kJ mol}^{-1}$) of Pb(II) on electric furnace slag with ΔS of $14.18 \, \text{J mol}^{-1}$ and ΔG of approximately $-14.0 \, \text{kJ mol}^{-1}$ in the temperature range 293–313 K. Compared to these results, the exothermic adsorption of Pb(II) on Neem leaf powder had more potentiality for practical application.

3.7. Regeneration of the adsorbent

Desorption experiments showed that 80% of Pb(II) could be recovered simply by washing Pb(II)-loaded NLP with deionised water (pH 7.0) and the rest with dilute nitric acid (pH 4.0). The washed NLP after being thoroughly dried first in air and then in an air oven at 333 K for 4 h could be reused as an adsorbent with nearly equal activity. The results of desorption are an indication that most of Pb(II) were held on NLP surface by comparatively weak adsorptive interactions while the rest might be held through strong chemisorptive or ion-exchange type of binding.

4. Conclusions

Although the Neem is an evergreen tree, it sheds the mature leaves in the months of February and March every year and the leaves can be collected at no cost. The conversion of the leaves to powder form requires an air oven for operation at about 35° above ambient temperature followed by the use of an electrical grinder, and therefore does not involve much energy consumption. The leaves can even be dried to crispness in strong sunshine easily available in a tropical country like India and could be powdered in a traditional mechanical grinder. Thus, NLP can truly be termed as a low-cost adsorbent. Based upon the results of this work, the following advantages can be seen for using it as an adsorbent for removal of toxic metals like Pb(II):

(i) Neem leaf powder (NLP) could very efficiently remove Pb(II) from an aqueous solution and the adsorption process had the support of appropriate thermodynamic parameters. The adsorption process was exothermic and spontaneous at ambient and slightly higher temperatures.

(ii) NLP particles have a large number of polar and non-polar functional groups on the surface and some of these groups can bind metal ions to the surface through the formation of strong chemisorptive bonds or through ion exchange mechanism.

(iii) The kinetics of the adsorption of Pb(II) on NLP can be better described with second-order kinetics. Intra-particle diffusion might also have a significant role in the adsorption process slowing down the approach towards equilibrium.

(iv) The experimental data gave good fits with both Langmuir and Freundlich isotherms and the adsorption coefficients agreed well with the conditions of favourable adsorption. NLP had a higher monolayer capacity than a large number of similar plant-based, low-cost adsorbents.

(v) Adsorbed Pb(II) could be recovered and the adsorbent could be regenerated by washing the Pb(II)-loaded NLP with deionised water and dilute acid successively.

References

[1] R. Freedman, L. Olson, B.J. Hoffer, Environ. Health Persp. 89 (1990) 27.
[2] Y.S. Ho, J.C.Y. Ng, G. MacKay, Sep. Sci. Technol. 36 (2001) 241.
[3] D. Brady, A. Stoll, F.R. Duncan, Environ. Technol. 15 (1994) 428.
[4] N. Kuyuck, B. Volesky, Biotechnol. Lett. 10 (1988) 137.
[5] B. Voleasky, in: B. Voleasky (Ed.), Biosorption of Heavy Metals, CRC press, Boston, 1990, p. 7.
[6] S. Lagergren, Handlingar 24 (1898) 1.
[7] T. Gosset, J.L. Trancart, D.R. Thevenot, Water Res. 20 (1986) 21.
[8] D.C. Sharma, C.F. Foster, Bioresource Technol. 49 (1994) 31.
[9] Y.S. Ho, G. McKay, J. Environ. Sci. Health A34 (1999) 1179.
[10] C.T. Tien, C.P. Huang, in: J.P. Vernet (Ed.), Trace Metals in the Environment, Elsevier, Amsterdam, 1991, p. 295.
[11] Y.S. Ho, G. McKay, Water Air Soil Pollut. 124 (2000) 141.
[12] Y.S. Ho, G. McKay, Trans. IChemE 76B (1998) 332.
[13] W.J. Weber, J.C. Morris, J. Sanit. Eng. Div. ASCE 89 (1963) 31.
[14] G. McKay, S.J. Allen, Can. J. Chem. Eng. 32 (1980) 521.
[15] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Ind. Eng. Chem. Fund. 5 (1966) 212.
[16] S.A. Khan, R. Rehman, M.A. Khan, Waste Manage. 15 (1995) 271.
[17] H. Schmutterer, in: H. Schmutterer (Ed.), The Neem Tree, VCH, Weinheim, 1995, p. 1.
[18] K.R.T. Raju, T.V. Reddy, C. Gonda, in: H. Schmutterer (Ed.), The Neem Tree, VCH, Weinheim, 1995, p. 86.
[19] S.A. Radwanski, G.E. Wickends, Econ. Bot. 35 (1981) 398.
[20] W. Kraus, Biologically active ingredients, in: H. Schmutterer (Ed.), The Neem Tree, VCH, Weinheim, 1995, p. 35.
[21] J.H. Skellon, S. Thorburn, J. Spence, S.N. Chatterjee, J. Sci. Food Agric. 13 (1962) 639.
[22] Neem Foundation, http://www.neemfoundation.org, 1997.
[23] A. Mudroch, J.M. Azcue, P. Mudroch (Eds.), Manual of Physico-Chemical Analysis of Aquatic Sediments, CRC Lewis Publishers, Boca Raton, 1997, p. 37.
[24] Y.S. Ho, C.T. Huang, H.W. Huang, Process Biochem. 37 (2002) 1421.
[25] G.N. Manju, K. Krishnan, V.P. Vinod, T.S. Anirudhan, J. Hazard. Mater. 91 (2002) 221.
[26] H.H. Tran, F.A. Roddick, J.A. O'Donnel, Water Res. 33 (1999) 2992.
[27] K.H. Chu, J. Hazard. Mater. 90 (2002) 77.
[28] M. Dakiky, M. Khamis, A. Manassra, M. Mereb, Adv. Environ. Res. 6 (2002) 533.
[29] Y.S. Ho, J.F. Porter, G. McKay, Water Air Soil Pollut. 141 (2002) 1.
[30] C. Aharoni, M. Ungarish, Chem. Soc. Faraday Trans. 73 (1977) 456.
[31] F.-C. Wu, R.-L. Tseng, R.-S. Juang, J. Hazard. Mater. 73 (2000) 63.
[32] L. Curkovic, S. Cerjan-Stefanovic, A. Rastovean-Mioe. 35 (2001) 3436.
[33] M. Ghoul, M. Bacquet, Water Res. 37 (2003) 729.
[34] M.M. Al-Subu, Adv. Environ. Res. 6 (2002) 569.
[35] D.K. Singh, D.P. Tiwari, D.N. Saksena, Indian J. Environ. Health 35 (1993) 169.
[36] A.K. Bhattacharya, C. Venkobachar, J. Environ. Eng. ASCE 110 (1984) 110.

[37] K.K. Panday, G. Prasad, V.N. Singh, J. Chem. Technol. Biotechnol. A: Chem. Technol. 34 (1984) 367.

[38] K.K. Panday, G. Prasad, V.N. Singh, Water Res. 19 (1985) 869.

[39] D.A. Dzombak, F.M.M. Morel, J. Colloid Interf. Sci. 112 (1986) 588.

[40] S.K. Khare, K.K. Panday, V.N. Srivastava, R.M. Singh, J. Chem. Technol. Biotechnol. A: Chem. Technol. 38 (1987) 99.

[41] A.K. Singh, D.P. Singh, K.K. Pandey, V.N. Singh, J. Chem. Technol. Biotechnol. 42 (1998) 39.

[42] B.K. Singh, N.S. Rawat, J. Chem. Technol. Biotechnol. 61 (1994) 57.

[43] A.K. Chaturvedi, K. Yadava, K.C. Pathak, V.N. Sing, Water Air Soil Pollut. 49 (1990) 51.

[44] Y.S. Ho, G. McKay, Resources Conserv. Recycl. 25 (1999) 171.

[45] Y.C. Sharma, G.S. Gupta, G. Prasad, D.C. Rupainwar, Water Air Soil Pollut. 49 (1990) 69.

[46] Y.C. Sharma, G. Prasad, D.C. Rupainwar, Int. J. Environ. Studies 37 (1991) 183.

[47] K. Periasamy, K. Srinivasan, P.K. Murugan, Indian J. Environ. Health 33 (1991) 33.

[48] C. Namasivayam, N. Kanchana, Chemoshere 25 (1992) 1691.

[49] R. Salim, M.M. Al-Subu, E. Sahrhage, J. Environ. Sci. Health A: Environ. Sci. Eng. 27 (1992) 603.

[50] P.S. Rao, S.R. Mise, G.S. Manjunatha, J. Environ. Sci. Health A: Environ. Sci. Eng. 27 (1992) 2227.

[51] C. Namasivayam, R.T. Yamuna, Water Air Soil Pollut. 65 (1992) 101.

[52] R.T. Yamuna, C. Namasivayam, Toxicol. Environ. Chem. 38 (1993) 131.

[53] C. Namasivayam, K. Periasamy, Water Res. 27 (1993) 1663.

[54] Y. Orhan, H. Buyukgungor, Water Sci. Technol. 28 (1993) 247.

[55] K.S. Low, C.K. Lee, K.K. Tan, Bioresource Technol. 35 (1995) 79.

[56] C. K Lee, K.S. Low, K.L. Kek, Bioresource Technol. 54 (1995) 183.

[57] N.A. Fernadez, E. Chacin, E. Gutierrez, N. Alastre, B. Llamoza, C.F. Forster, Bioresource Technol. 54 (1995) 111.

[58] C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani, K. Ranganathan, Bioresource Technol. 17 (1996) 1023.

[59] C.Y. Kim, H.M. Choi, H.T. Cho, J. Appl. Polym. Sci. 63 (1997) 725.

[60] C. Namasivayam, D.J.S.E. Arasi, Chemosphere 34 (1997) 401.

[61] K. Anoop Krishnan, T.S. Anirudhan, J. Hazard. Mater. 92 (2002) 161.

[62] Y.S. Ho, C.T. Huang, H.W. Huang, Process Biochem. 37 (2002) 1421.

[63] O. Yavuz, Y. Altunkaynak, F. Guzel, Water Res. 37 (2003) 948.

[64] N. Daneshvar, D. Salari, S. Aber, J. Hazard. Mater. 94 (2002) 49.

[65] H.K. An, B.N. Park, D.S. Kim, Water Res. 35 (2001) 3551.

[66] C.-H. Lai, C.-Y. Chen, B.-L. Wei, S.-H. Yeh, Water Res. 36 (2002) 4943.

[67] O. Gyliene, R. Rekertas, M. Salkauskas, Water Res. 36 (2002) 4128.

[68] R.S. Juang, H.J. Shao, Water Res. 36 (2002) 2999.

[69] B. Benguella, H. Benaissa, Water Res. 36 (2002) 2463.

[70] M. Kara, H. Yuzer, E. Sabah, M.S. Celik, Water Res. 37 (2003) 224.

[71] K. Periasamy, C. Namasivayam, Sep. Sci. Technol. 30 (1995) 2223.

[72] C. Namasivayam, R.T. Yamuna, Environ. Pollut. 89 (1995) 1.

[73] F.F.O. Orumwense, J. Chem. Technol. Biotechnol. 65 (1996) 363.

[74] H. Seki, A. Suzuki, Ind. Eng. Chem. Res. 35 (1996) 1378.

[75] Y.S. Ho, D. Wase, C.F. Forster, Water Res. 29 (1995) 1327.

[76] C. Namasivayam, K. Periasamy, J. Chem. Technol. Biotechnol. 61 (1994) 57.

[77] Y.S. Ho, G. McKay, Trans IChemE 77B (1999) 165.