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ORIGINAL ARTICLE

Evaluation of *Acacia nilotica* as a non conventional low cost biosorbent for the elimination of Pb(II) and Cd(II) ions from aqueous solutions

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Abstract In the present study a biomass derived from the leaves of *Acacia nilotica* was used as an adsorbent material for the removal of cadmium and lead from aqueous solution. The effect of various operating variables, viz., adsorbent dosage, contact time, pH and temperature on the removal of cadmium and lead has been studied. Maximum adsorption of cadmium and lead arises at a concentration of 2 g/50 ml and 3 g/50 ml and at a pH value of 5 and 4, respectively. The sorption data favored the pseudo-second-order kinetic model. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were applied to describe the biosorption isotherm of the metal ions by *A.* nilotica biomass. Based on regression coefficient, the equilibrium data found were fitted well to the Langmuir equilibrium model than other models. Thermodynamic parameters such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) have been calculated, respectively revealed the spontaneous, endothermic and feasible nature of adsorption process. The activation energy of the biosorption (Ea) was estimated as 9.34 kJ mol^{-1} for Pb and 3.47 kJ mol^{-1} for Cd from Arrhenius plot at different temperatures.

1. Introduction

Heavy metals are the major pollutants in marine, ground, industrial and even treated wastewaters (Valdman et al., 2001). Sources of lead include folk medicines, cosmetics, lead-glazed ceramics and leaded crystals, imported candies or foods, imported food in cans, soil, paint, car batteries, radiators, some inks, etc. Cadmium metal is produced as a by-product from the extraction, smelting and refining of the nonferrous metals zinc, lead and copper. Contribution of trace metals into ecosystem is large as a result of mining operations, refining ores, sludge disposal, fly ash from incinerators, processing of radioactive materials, metal plating, or manufacturing of electrical equipment, paints, alloys, batteries, pesticides and preservatives (Goyer, 1997). Lead is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems. Cadmium toxicity cause

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dry throat, cough, headache, vomiting, chest pain, pulmonary edema, inflammation of lungs, muscle weakness, leg pain, and cadmium may be carcinogenic (NA, 1965). Chronic cadmium exposure may cause damage to the liver and kidneys (Gupta et al., 2003). Several methods have been devised for the treatment and removal of heavy metals. The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation and ion exchange (Benito and Ruíz, 2002). Traditional metal removal method has certain disadvantages like incomplete metal removal, high reagent and energy requirements generation of toxic sludge or other waste products that require careful disposal have made it of vital importance for a cost-effective treatment method that is capable of removing heavy metals from aqueous effluents (Gupta et al., 2002). A number of workers have used different adsorbent systems, developed from various industrial waste materials, for the removal of heavy metals (Reddad et al., 2002). There still exists a need to develop a low cost and efficient adsorbent for the removal of lead and cadmium from water. The aim of the present research work is to evaluate the biosorption capacity of *Acacia nilotica* to remove Pb(II) and Cd(II) ions from aqueous solution in a batch procedure. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were applied to describe the sorption behavior of the Pb(II) and Cd(II) ions by *A. nilotica*. Spontaneity and feasibility of the sorption process are confirmed by determining the thermodynamical parameters such as ΔG, ΔH and ΔS.

2. Methods

2.1. Materials

All chemicals used were of analytical reagent grade which were purchased from Fluka Chemicals. All solutions were prepared using Milli-Q water. Lead(II) and cadmium(II) stock solutions of 1000 mg l^{-1} were prepared by dissolving $Cd(NO_3)_2{\cdot}4H_2O$ and $Pb(NO_3)_2$, respectively. All metal solution used in the experiments were obtained by stock solution dilution.

2.2. Biomass preparation

Adsorbent material leaves of *A.* nilotica (non UDA certified plant) were collected from the Botanical garden, (Punjab University, Lahore). Leaves of *A.* nilotica were washed with distilled water and placed in sunlight and then in an electric oven at 50 °C until adsorbent material was completely dried. Then it was ground by using electric grinder (Philips) and sieved which gave particle size of 100 μm suitable for adsorption process. The material was stored in a vacuum desiccator for further analysis.

2.3. Adsorption studies

Batch adsorption experiments were carried out in a series of Erlenmeyer flasks of 250 ml capacity covered with aluminum foil to prevent contamination. The effect of adsorbent dose (0.5–5 g), contact time (5–50 min), pH (1.0–9.0), and temperature (30–80 °C) was studied. Isotherms were obtained by adsorbing different concentrations of metal ions. After prescribed contact times, the solutions were filtered. A Pekin–Elmer 2380 Atomic Absorptions Spectrophotometer with air-acetylene flame was used for the determination of Pb(II) and Cd(II) ions concentration.

2.4. Batch sorption experiments

To evaluate the performance of adsorbent material, batch experiments were carried out. The adsorbent material (0.5–5.0 g) was placed in 250 ml flasks containing 50 ml of standard solutions of Pb and Cd (50 ppm).

Then, adjusted (pH 1–9) by adding 0.01 M HCl or 0.01 M NaOH solutions. The flasks were shaken at different temperatures (30–80 °C) on an electrical shaker at 100 rpm for a designated time intervals (5–50 min). The time required for reaching the equilibrium condition was estimated by analyzing the samples at regular intervals of time. The biomass was separated from the solution by filtration and resulting solutions were analyzed. The final concentration of lead and cadmium in solutions was determined by atomic absorption spectrometer (Perkin–Elmer A Analyst 100). The percent sorption of metal ions were calculated as follows:

$$\%\quad \text{adsorption} = \frac{C_o - C_e}{C_e} \times 100 \tag{1}$$

where C_o and C_e are the initial and final concentrations of metal ions. The amount of Pb and Cd adsorbed at equilibrium per unit mass of the adsorbent material (mg/g) was calculated by using the following equation:

$$q_e(\text{mg/g}) = \frac{(C_o - C_e)V}{m} \tag{2}$$

where C_o and C_e are the initial and equilibrium Pb and Cd ion concentrations, respectively. V is the volume of the solution in liter; m is the mass of the dry adsorbent material in gram.

3. Results and discussion

3.1. Effect of adsorbent dosage

The percent removal of lead increased up to 91.3% when the dosage of adsorbent material was increased from 0.5 to 3 g/50 ml, whereas further increase in adsorbent material dosage up to 5 g/50 ml has no effect on the percent removal of lead. Minimum adsorption was 80.72% at 0.5 g/50 ml and maximum adsorption was 91.3% for dose at 3 g/50 ml. Hence, for further experiments 3 g/50 ml of adsorbent material was selected as the optimum dosage for Pb(II) removal.

The percent removal of cadmium increased up to 75.96% when the dosage of adsorbent material was increased from 0.5 to 2 g/50 ml, whereas further increase in adsorbent material dosage up to 5 g/50 ml has decreased the percent removal of cadmium. Minimum adsorption of Cd(II) was 73.3% at 0.5 g/50 ml and maximum adsorption was 75.96% for dose at 2 g/50 ml. When the initial metal concentration and the volume of solution are fixed, the removal of metal ions is enhanced, which is obvious because of the increase in the number of active sites (Sen and De, 1987) but after the establishment of equilibrium, increase in adsorbent had no effect. Hence, for further experiments 2 g/50 ml of adsorbent material was selected as the optimum dosage for Cd(II) removal.

3.2. Effect of contact time

For Pb(II), the minimum adsorption was 92% at 5 min and maximum adsorption was 97% at 20 min, which indicate the availability of the adsorption sites. Further increase in time up to 30 min, the adsorption was constant and after that increase in time contact decreased the removal of Pb(II). Therefore, further adsorption experiments for lead were carried out for a contact time of 20 min. For Cd(II), the minimum adsorption was 63.5% at 5 min and maximum adsorption was 72.45% at 25 min, which indicate the availability of the adsorption sites. Further increase in time contact decreased the removal of Cd(II). Therefore, further adsorption experiments for Cd(II) were carried out for a contact time of 25 min.

3.3. Effect of pH

The heavy metal ions adsorption is strictly pH dependent. The distribution of Pb(II) and Cd(II) ions in aqueous water is mainly dependent on pH conditions. pH dependent behavior for removal of lead from waste water using bagasse Fly Ash also has been reported earlier by Gupta (Gupta et al., 1998). The uptake of Pb(II) by adsorbent material was increasing from pH 1 to 3 and maximum at pH 4, and after that became constant, when the pH value was exceeded to 5 shown in Fig. 1a. Maximum removal efficiency was 100% at pH 4. Hence, for further experiment pH 4 was selected as an optimum pH value.

The uptake of Cd(II) by adsorbent material was increasing from pH 1 to 4 and maximum at pH 5, after that adsorption decreased, when the pH value was exceeded to 6 as in Fig. 1a. Maximum removal efficiency was 75.95% at pH 5. Hence, for further experiment pH 5 was selected as an optimum pH value. The decrease in adsorption at a higher pH may be attributed due to the hydrolysis of lead and cadmium. A similar behavior has been reported earlier (Sen and De, 1987) for the adsorption of Hg(II) and also by Gupta et al., for the removal of Pb(II) by fly ashes (Gupta et al., 1998). So, finally it was concluded that, adsorbent functional groups on which adsorption of lead and cadmium ions takes place provide the active sites for the binding of the metal ions when solutions were acidic.

3.4. Effect of temperature

In lead solutions maximum adsorption was observed at 50 °C and removal efficiency was 96% and in case of cadmium solutions, maximum adsorption was obtained at 70 °C and removal efficiency was 83%. But once the equilibrium has been established it remains constant or decreases. Increase in temperature increases the kinetic energy and as a result metal adsorption increases. The increase in adsorption with increasing temperature indicated endothermic nature of the adsorption process (Ho et al., 2002). Effect of temperature on the adsorption of Pb(II) and Cd(II) was studied and the results are given in Fig. 1b.

3.5. Adsorption isotherms

The principle of adsorption isotherm is to find the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration in the solution at equilibrium C_e. Isotherm studies provide information about the capacity of the adsorbent material or the amount required to remove a unit mass of pollutants like Pb(II) and Cd(II) from water. The adsorption data have been subjected to Freundlich and Langmuir isotherm models.

Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface (Langmuir, 1916). Langmuir's isotherm has been used by various workers for the sorption of a variety of compounds, and the linear form of this isotherm is given by the following equation:

$$\frac{1}{q_e} = \left[\frac{1}{b.q_{\max}}\right] \cdot \frac{1}{C_e} + \frac{1}{q_{\max}} \tag{3}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l) and $q_{\max}$ and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When $1/q_e$ was plotted

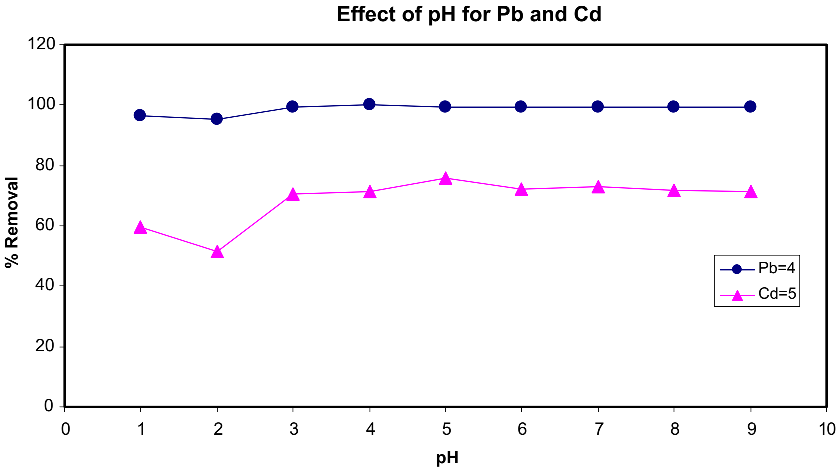

Figure 1a Effect of pH on for sorption of Pb(II) and Cd(II) on *A. nilotica*.

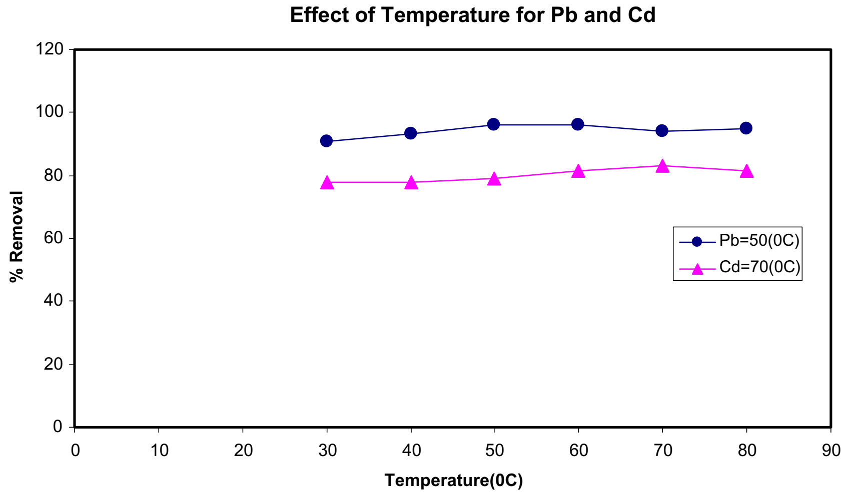

Figure 1b Effect of temperature on for sorption of Pb(II) and Cd(II) on *A. nilotica*.

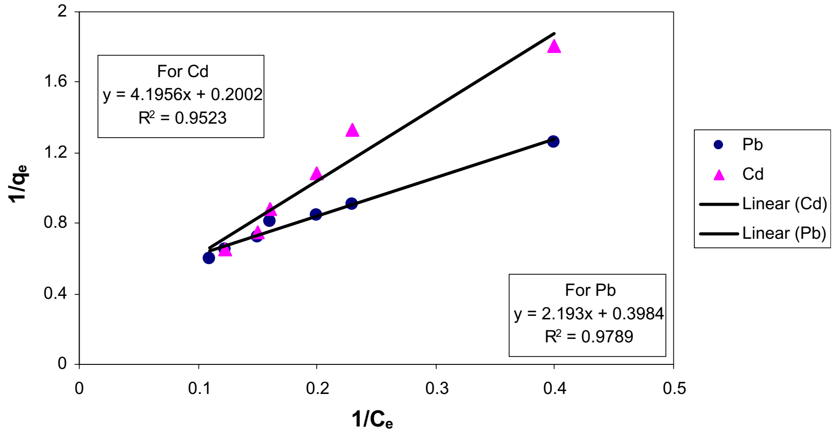

Figure 2a Langmuir adsorption isotherm for sorption of Pb(II) and Cd(II) on *A. nilotica*.

against $1/C_e$, straight lines with slopes $1/b{\cdot}q_{max}$ were obtained for lead and cadmium respectively). Fig. 2a indicating that the adsorption of lead and cadmium on biomass of *A. nilotica* leaves followed the Langmuir isotherm. The Langmuir constants for lead and cadmium were calculated and results are given in Table 1.

The specific surface area of *A. nilotica* for monolayer sorption of Pb(II) and Cd(II) ions was determined using the following equation:

$$S_L = \frac{q_{max}.N_A.A}{M} \tag{4}$$

where q_{max} is the biosorption capacity (mg/g), N_A is Avogadro's number (6.022×10^{23}), A is the cross sectional area of metal ion (A^2) and M the molecular mass of metal ion. The molecular mass of Pb(II) is 207 and the cross sectional area is 5.56 A^2 (the radius of Pb(II) ions for close packed monolayer is 1.33 Å). The specific surface area for Pb(II) ions was found to be 1.456 m^2/g. The molecular mass of Cd(II) is 112 and the cross sectional area is 3.70 A^2 (the radius of Cd(II) ions for close packed monolayer is 1.09 Å). The specific surface area for Cd(II) ions was found to be .097 m^2/g (U. Farooq et al., 2010).

The adsorption data of lead and cadmium were also fitted into the Freundlich model (Freundlich, 1906). The logarithmic form of Fruendlich model is given by the following equation:

$$\log q_e = \log K_F + 1/n \log C_e \tag{5}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l) and K_f and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. When $\log q_e$ was plotted against $\log C_e$, straight lines with slopes '$1/n$' were obtained for lead and cadmium, respectively, Fig. 2b shows that the adsorption of lead and cadmium followed the Freundlich isotherm also.

The equilibrium data were also subjected to the D–R isotherm model to determine the nature of biosorption processes as physical or chemical. The D–R sorption isotherm is more general than Langmuir isotherm, as its derivation is not based on the ideal assumptions such as equipotent of the sorption sites, absence of steric hindrance between sorbed and incoming particles and surface homogeneity on microscopic level (M.M.

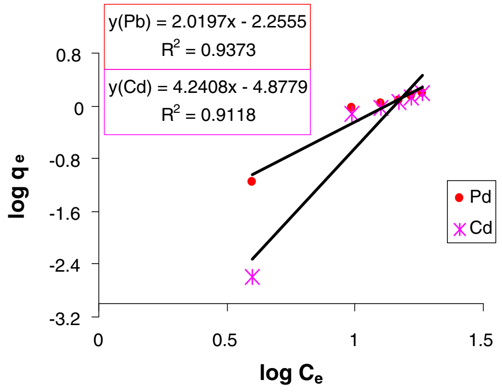

Figure 2b Freundlich adsorption isotherm for sorption of Pb(II) and Cd(II) on *A. nilotica*.

Dubinin, 1947). The linear presentation of the D–R isotherm equation is expressed by:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{6}$$

where q_e is the amount of metal ions adsorbed on per unit weight of biomass (mol/L), q_m the maximum biosorption capacity (mol/g), β the activity coefficient related to biosorption mean free energy (mol^2/J^2) and ε is the Polanyi potential.

$$\varepsilon = \mathrm{RT}\ln\left(1 + \frac{1}{C_e}\right) \tag{7}$$

where ε, the Polanyi potential, is a constant related to the biosorption energy, R is the gas constant (8.314 kJ/mol) and T is the absolute temperature (K). q_m and β are the D–R isotherm constants in mg/g and mol^2/kJ^2, respectively.

The D–R isotherm model was not well fitted to the equilibrium data since the R^2 value was found to be 0.841 for Pb(II) and 0.447 for Cd(II). The (D–R) constants for Pb(II) and Cd(II) were calculated from Fig. 2c and results are given in Table 1. The biosorption mean free energy *Es* (kJ/mol (Bukallah et al., 2007) is as follows:

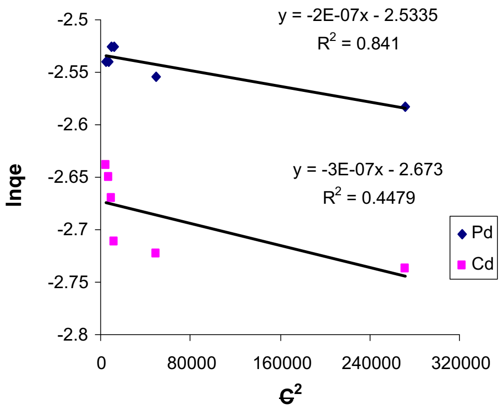

Figure 2c Dubinin–Radushkevich (D–R) adsorption isotherm for sorption of Pb(II) and Cd(II) on *A. nilotica*.

$$Es = \frac{1}{\sqrt{2\beta}} \tag{8}$$

Physical and chemical adsorption can be predictable form the magnitude of biosorption mean free energy (Milmile et al., 2011).

a. The values of *Es* below 8 kJ/mol indicate the physical adsorption.
b. A magnitude of *Es* between 8 and 16 kJ/mol reveals the adsorption process follows chemical ion exchange.

From Fig. 2c the magnitude of biosorption mean free energy Es was found to be 1.587 kJ/mol for Pb(II) and 1.291 kJ/mol for Cd(II) which is related to the physical adsorption.

3.6. Adsorption kinetics

The prediction of biosorption rate gives important information for designing batch biosorption systems. Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full-scale batch process. In order to clarify the biosorption kinetics of Cd(II) and Pb(II) ions onto *A. nilotica* biomass two kinetic models, which are Lagergren's pseudo-first-order and pseudo-second-order models, were applied to the experimental data.

The linear form of the pseudo-first-order rate equation by Lagergren (S. Lagergren, 1889) is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{9}$$

where q_t and q_e (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively and k_1 is the rate constant of the equation (min^{-1}). The biosorption rate constants (k_1) can be determined experimentally by plotting ln ($q_e - q_t$) versus t.

The plots of ln ($q_e - q_t$) versus t for the pseudo-first-order model were shown as Fig. 3a. It can be concluded from the R^2 values in Table 2 that the biosorption mechanisms of Cd(II) and Pb(II) ions onto *A. nilotica* biomass does not follow the pseudo-first-order kinetic model.

Experimental data were also tested by the pseudo-second order kinetic model which is given in the following form (Ho and McKay, 1999):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

where k_2 (g/mg min) is the rate constant of the second-order equation, q_t (mg/g) is the amount of biosorption time t (min) and q_e is the amount of biosorption equilibrium (mg/g).

This model is more likely to predict kinetic behavior of biosorption with chemical sorption being the rate-controlling step (Ho, 2006). The linear plots of t/q_t versus t for the pseudo-second order model for the biosorption of Cd(II) and Pb(II) ions onto *A. nilotica* were shown in Fig. 3b. The rate constants (k_2), the R^2 and q_e values are given in Table 2. It is clear from these results that the R^2 values are very high in the range of 0.996–0.942 for the Pb(II) and Cd(II) biosorption, respectively. In the view of these results, it can be concluded that the pseudo-second-order kinetic model provided a good correlation for the biosorption of Cd(II) and Pb(II) onto *A. nilotica* in contrast to the pseudo-first-order model.

Table 1 Equilibrium isotherm parameters of sorption of Pb(II) and Cd(II) on *A. nilotica*.

Adsorption isotherm metals ions	Constant parameters			
Langmuir isotherm	q_{max}	b		R^2
Pb	2.51	0.18		0.987
Cd	4.99	0.015		0.952
Freundlich isotherm	K_f	n		R^2
Pb	2.7×10^{-3}	0.49		0.937
Cd	1.3×10^{-5}	0.235		0.911
Dubinin–Radushkevich (D–R) isotherm	β	$\ln q_m$	Es (kJ mol^{-1})	R^2
Pb	2×10^{-07}	0.079	1.587	0.841
Cd	3×10^{-07}	0.069	1.291	0.447

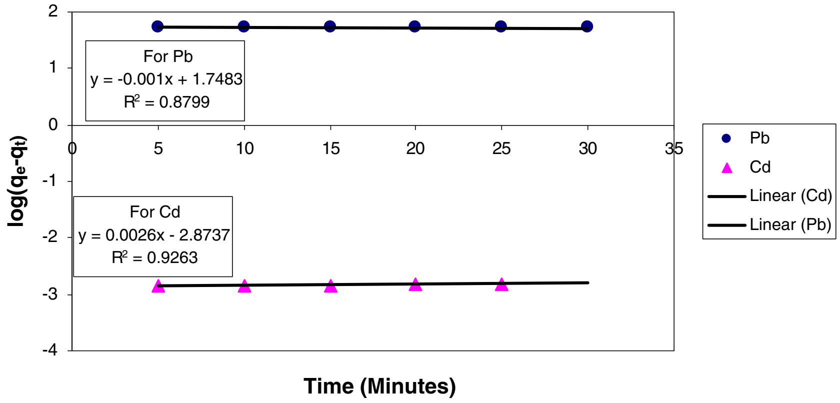

Figure 3a Pseudo-first-order kinetics for sorption of Pb(II) and Cd(II) on *A. nilotica*.

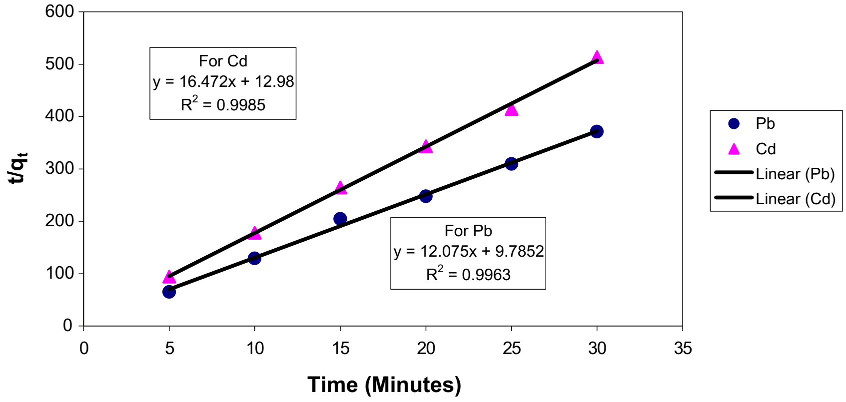

Figure 3b Pseudo-second-order kinetics for sorption of Pb(II) and Cd(II) on *A. nilotica*.

Table 2 Kinetics parameters for sorption of Pb(II) and Cd(II) on *A. nilotica*.

Pseudo-second-order kinetic				Pseudo-first-order kinetic		
Metal ions	q_e (mg/g)	K_2 (mg/g min)	R^2	q_e (mg/g)	K_1 (min^{-1})	R^2
Lead	0.0808	1.28	0.996	4.25	0.002303	0.879
Cadmium	0.0548	1.29	0.998	0.060375	0.004606	0.946

Table 3 Thermodynamical and activation parameters for sorption of Pb(II) and Cd(II) on *A. nilotica*.

Thermodynamically activated parameters (283–333 K)	Results (kJ mol^{-1})	Conclusion
ΔG		
Pb	−(5.91–8.35)	Spontaneous and feasible process
Cd	−(3.76–5.04)	
ΔH		
Pb	9.39	Endothermic process
Cd	4.85	
ΔS		
Pb	0.52	Increase in randomness at solid/solution interface
Cd	0.028	
Ea		
Pb	9.34	Physical adsorption
Cd	3.47	

4. Thermodynamic studies

In order to describe the thermodynamic properties of the adsorption of Pb and Cd ions onto adsorbent material, enthalpy change ($\Delta H°$), Gibbs free energy change ($\Delta G°$) and entropy change ($\Delta S°$) were calculated. $\Delta G°$ was calculated by using equations:

$$\Delta G^{\circ} = -\mathrm{RT}\ln K_D \quad (11)$$

$$K_D = \frac{q_e}{C_e} \quad (12)$$

$$lnK_D = \frac{-\Delta G^{\circ}}{\mathrm{RT}} = \frac{-\Delta \mathrm{H}^{\circ}}{\mathrm{RT}} + \frac{\Delta S^{\circ}}{\mathrm{R}} \quad (13)$$

where R is the universal gas constant (8.314 J/mol K), T the temperature (K) and K_D (q_e/C_e) is the distribution coefficient (Sari et al., 2009). The Gibbs free energy indicates the degree of spontaneity of the sorption process and the higher negative value reflects more energetically favorable sorption. The values of $\Delta G°$ for Pb and Cd were given in Table 3 (Figure not shown). The values of ($\Delta G°$) free energy decreased with an increase in temperature thereby indicating an increase in adsorption at higher temperature and endothermic nature of the adsorption process (Anayurt et al., 2009). A similar behavior for $\Delta G°$ has been reported earlier (Gupta et al., 1998) for the removal of cadmium and nickel from waste water using bagasse fly ash–a sugar industry waste. So, it was concluded that an increase in temperature favors the removal process. The negative values of $\Delta G°$ confirm the thermodynamic feasibility of the process and spontaneous nature of adsorption. The positive value of $\Delta H°$ indicated the endothermic nature of the adsorption. While the positive values of $\Delta S°$ reflected the affinity of the adsorbent material for metal Pb(II) and Cd(II) ions. A similar behavior for $\Delta G°$ and $\Delta S°$ has been reported by (Mohan and Singh, 2002) for single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse.

The kinetic parameters at different temperatures were plotted in terms of Arrhenius Eq. (14)

$$lnk_2 = lnk_0 - \frac{E_a}{RT} \quad (14)$$

where k_2 is the rate constant pseudo-second order of adsorption (gmg^{-1} min^{-1}), k_0 is the independent temperature factor (gmg^{-1} min^{-1}), R is the gas constant (J mol^{-1} K^{-1}), and T is the solution temperature (K). A plot of ln k_2 versus $1/T$ gives a straight line and the corresponding activation energy was determined from the slope of linear plot shown in Fig. 4. The activation energy for the biosorption of Pb(II) and Cd (II) on *A. nilotica* was found to be 9.34 and 3.47 kJ mol^{-1}. From the values of activation energy it appears that the biosorption of Pb(II) and Cd(II) on *A. nilotica* is a physical adsorption process. This is confirmed from the fact that the activation energy for chemical adsorption is usually more than 4–6 kJ mol^{-1} (T.S. Anirudhan, 2008).

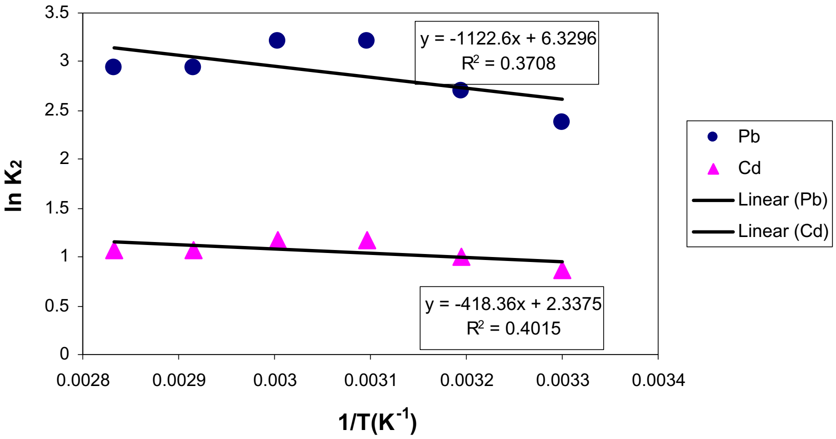

Figure 4 Activation energy by Arrhenius plot for sorption of Pb(II) and Cd(II) on *A. nilotica*.

5. Conclusion

It can be concluded that *A*. nilotica is an effective and low cost adsorbent for the removal of lead and cadmium from aqueous water. Adsorption follows both Langmuir and Freundlich models. The adsorption was found to be spontaneous and endothermic in nature. Nearly 100% removal of lead was possible at a pH value of 4 and 80.05% removal of cadmium was possible at a pH value of 5 under the batch test conditions. The adsorption capacity increased with the rise in temperature indicating that the adsorption was a spontaneous, endothermic process. This was also supported by the thermodynamic parameters calculated at different temperatures ($\Delta G°$, $\Delta H°$, $\Delta S°$). The adsorption data showed that the pseudo-second-order kinetic model is rate controlling for Pb(II) and Cd(II) ions adsorption process.

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