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A pretreated green biosorbent based on Neem leaves biomass for the removal of lead from wastewater

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ABSTRACT

In the present study, *Azadirachta indica* (Neem) leaves biomass (a green biosorbent) was pretreated chemically and physically for possible application in the removal of lead from wastewater. Neem leaves biomass was pretreated chemically with the following chemicals $HgCl_2$, CH_3COOH, CH_3CHO, and Oxalic acid and heating, autoclaving, ultrasonic bath, and boiling were used for physical pretreatment. Among all the pretreatments, boiling, acetic acid, and autoclaving pretreatments were proven to be effective at pH 5. Percentage removal of lead was 93.48% (boiling) > 91.85% (acetic acid) > 86.68% (autoclave) > 82.48% (control) and the maximum adsorption capacity (q) was 91.34 $mg\,g^{-1}$ (boiling) > 89.75 $mg\,g^{-1}$ (acetic acid) > 84.70 $mg\,g^{-1}$ (autoclave) > 80.6 $mg\,g^{-1}$ (control) after 24 h. Langmuir and Freundlich isotherms were used to represent the equilibrium relationship for different initial lead concentrations in order to understand the adsorption process. The Langmuir isotherm model was found to be useful to explain sorption mechanism. Sorption system followed second-order kinetic model, which indicates that the rate-controlling step is chemisorption.

Keywords: Azadirachta indica; Biosorption; Langmuir; Freundlich; Lead; Pretreatments

1. Introduction

Heavy metal ions contribute to a variety of adverse health effects. A very serious problem being faced by public these days is the release of water-soluble metals due to human activity. These metals are frequently accumulated by a majority of organisms causing negative ecological effects on both plants and animals [1]. Lead is one of the toxic heavy metals. In the Dangerous Substances Directive (76/464/EEC) of the European Union, lead has been registered as list 2 dangerous substance with Environmental Quality Standards being set at 25 $g\,L^{-1}$ for estuaries and marine waters [2]. Lead is a potent neurotoxic metal when present above 0.05 $mg\,L^{-1}$ in drinking water [3]. Due to toxic effects of heavy metals, it is important to remove them from wastewater. For this purpose, different conventional methods have been used which include reverse osmosis, electrodialysis, ultra filtration, ion exchange, chemical precipitation, and phytoremediation [4,5]. The use of conventional technologies for this purpose is often inefficient and/or very expensive.

The search for new technologies involving the removal of toxic metals from wastewater as directed attention to biosorption, based on metal binding capacities of various biological materials. The use of various

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parts of plants as biosorbents to remove heavy metals from wastewater is widely reported in literature e.g. Neem leaves and bark [6], rice bran [5,7], *Cicer arietinum* [8], horseradish tree [9], and wheat bran [10]. The researcher also investigated the uptake capacity of other different biosorbents for heavy metals [11–16]. Furthermore, uptake capacity of biomass can be enhanced by pretreatments of biomass [5,7,17,18]. In several papers, it has been found that by modifying agricultural by-products, their capacity can be increased. Common chemical pretreatments include acid, alkaline, ethanol, organic acid, and acetone treatments of the biomass. The success of a chemical pretreatment strongly depends on the cellular components of the biomass itself. In many instances, acidic pretreatment has proved successful; this is because some of the impurities and ions blocking the binding sites can easily be eliminated [19].

Lead is harmful if inhaled or swallowed. Lead is dangerous to human life due to its toxicity, accumulation in food chains and persistence in nature. Lead has both acute and chronic effects in humans. It may cause anemia, headache, chills, diarrhea, and reduction in hemoglobin formation. Lead poisoning causes severe damage to kidneys, nervous system, reproductive system, liver, and brain [20,21].

The Neem tree, *Azadirachta indica* (Meliaceae) is native to South-East Asia and grows in many countries throughout the world [22,23]. The potentiality of Neem has been widely explored for solving various problems related to agriculture, public health, population control, and environmental pollution [23]. Awareness about the Neem-based technology, whether for pest management, public health, family welfare programmes, reforestation, etc. has grown several fold and production and commercialization of various Neem products for domestic use and exports have been taken up aggressively by various agencies [23,24]. Neem leaves have been demonstrated as having good biosorbent activity for the removal of heavy metals from aqueous solution [6,25–27].

The present work aims to develop a non-conventional adsorbent from the pretreated leaves of the *A. indica* (Neem) tree to be used for the removal of lead from aqueous medium. Neem leaves biomass was pretreated chemically with the following chemicals $HgCl_2$, CH_3COOH, CH_3CHO, and Oxalic acid and heating, autoclaving, ultrasonic bath, and boiling were used for physical pretreatment. In this study, efficiency of pretreated Neem leaves in removal of heavy metal lead was investigated in detail. The influence of initial concentration of heavy metal, pH, adsorbent dose, and contact time on biosorption of metal ions was studied.

2. Material and method

2.1. Chemicals

All the chemicals used in this study were of analytical grade and procured from Fluka Chemicals. Many different chemicals used in these findings include $HgCl_2$, CH_3COOH, CH_3CHO, and Oxalic acid. For stock solution (1,000 mg L^{-1}) of lead ion, 1.598 g of $Pb(NO_3)_2$ was dissolved in some distilled water and the final volume was raised to 1,000 mL by adding distilled water. Glassware was washed well with 10% (v/v) HNO_3 solution and then rinsed with distilled water.

2.2. Biomass preparation

Waste Neem leaves were collected from the fields and botanical garden of the University of Agriculture, Faisalabad, Pakistan. Neem leaves were washed with distilled water to remove surface contamination and then dried in open air followed by oven-drying at 60°C for 72 h. Dried Neem leaves were cut into small pieces and ground in a food processor (Moulinex, France) and then sieved through a fine sieve (OCT-Digital 4527-01). This biomass material produced was stored in airtight plastic bottles for further use.

2.3. Pretreatments of biomass

Biomass was dried at 60°C for 12 h in an oven before pretreatments. Forty grams of biomass sample were physically pretreated in four different ways (heating, autoclaving, ultrasonic bathing, and boiling). In heating, biomass was heated at Bunsen burner in a beaker at low heat for 20–25 min. Biomass was autoclaved for 15 min at 121°C and 15 psi and ultrasonic bath at 121°C was used for 15 min. In boiling, biomass was taken in 500 mL of distilled water and then boiled for 15 min. Biomass was pretreated chemically with the following chemicals $HgCl_2$, CH_3COOH, CH_3CHO, and oxalic acid.

2.4. Determination of lead ions in the solution

An atomic absorption spectrophotometer (Perkin-Elmer A Analyst 300) was used to determine the amount of lead in aqueous solutions before and after the equilibrium was established. The hollow cathode lamp was operated at 220 nm for lead.

2.5. Batch study

In all experiments, 100 mL solution of lead was mixed with 0.1 g biosorbent of 0.25 mm size at

130 rpm at room temperature for 24 h. Different conditions of pH, biosorbent dose, initial metal concentration, and contact time were evaluated during the study. The pH of the medium was adjusted with 0.1 M solutions of HCl and NaOH. The flasks were sealed with aluminum foil and constantly shaken on a rotating shaker (PA 250/25 H) for specified time and the solutions were filtered through a (Whatman No. 40, ashless) filter paper.

2.6. Metal uptake

The lead uptake was calculated by the simple concentration difference method using the mass balance equation:

$$q = V(C_i - C_e)/M$$

where V is the volume of the solution (L), C_i and C_e are the initial and final concentrations ($mg\,L^{-1}$) in solution, and M is the mass of the sorbent in g. All data represent the means of three independent experiments.

3. Results and discussion

3.1. Effect of pH and pretreatments

In biosorption process, pH seems to be the most important parameter. It affects the activity of functional groups of biomass and chemistry of metal solutions. The effect of different pH on binding of lead to Neem leaves is shown in Fig .1. The results in Fig. 1 revealed that pH has a significant effect on lead binding to Neem leaves. At pH 5, adsorption capacities were maximum for pretreated Neem leaf biomasses. The chemical pretreatments play an important role to enhance the adsorption capacity of the biomass [28]. They modify the cell surface, either by removing or masking the groups or exposing more metal-binding sites. Keeping this in mind, we investigated the effect of both physical and chemical pretreatments on lead removal using Neem leaves as biomass. The pretreatments (boiling, acetic acid, and autoclave) showed the highest uptake of lead. The percentage removal of lead by pretreated biomass with boiling, acetic acid, autoclave and control was 93.53%, 91.82%, 86.69% and 82.67% respectively and the maximum q values were 91.37 $mg\,g^{-1}$ (boiling) > 89.75 $mg\,g^{-1}$ (acetic acid) > 84.7 $mg\,g^{-1}$ (autoclave) > 80.80 $mg\,g^{-1}$ (control).

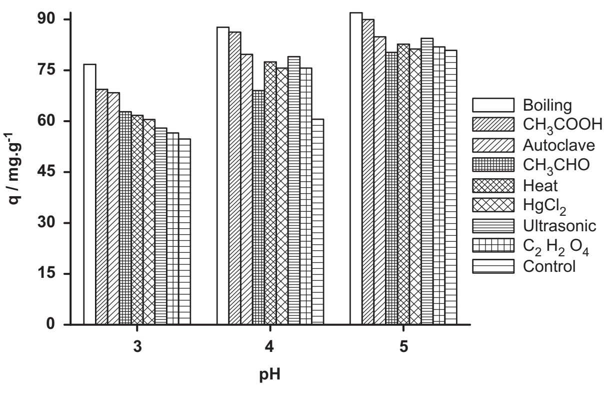

Fig. 1. Effect of pH and pretreatments on biosorption of lead by Neem leaves biomass.

The selection of the optimum pH must take into account the fact that, if too high a pH value is chosen, precipitation of lead would occur. This would defeat the purpose of employing adsorption. Tests showed that precipitation of insoluble salts occurred at pH 6; so adsorption studied was meaningless above pH 5. It was observed that as the pH was lowered, the overall surface charge on the cells became positive and that inhibited the approach of positively charged metal cations. It was likely that protons will then compete with metal ions for the ligands and thereby decrease the interaction of metal ions with the cells of biosorbent at a very low pH [29]. When pH increases, the negative charge density increases on the biomass surface and due to this, the interaction between negative charge and positive charge of metallic ions is increased. Surface charge of adsorbents, the degree of ionization, and the species of adsorbate is mainly affected by the solution pH [5,30]. Performance of a biosorbent can further be improved by various physical and chemical treatments. Among all the pretreatments, boiling, acetic acid, and autoclave pretreatments were proven effective at pH 5. The increase in metal biosorption after pretreatment of biomass may be due to the following reasons. The pretreatments modify the cell surface either by removing or masking the groups or exposing more metal-binding sites. Immobilized biomass of these microbes offer the continuous sorption–desorption system in a fixed-bed reactor. Boiling and autoclaving of biomass may remove mineral matter from biomass and introduce more sorption sites on the surface [18].

This indicates that pretreatment is very useful in improving the adsorption ability of biomass. Removal of surface impurities, rupture of cell membrane and exposure of available binding sites for metal biosorption after treatment may be the reason for the increase in metal biosorption [31,32]. Kuyucak and Volesky showed that treatment of biomass with different chemicals may destroy autolytic enzymes that cause putrefaction of biomass and remove lipids and proteins that mask reactive sites [33].

3.2. Effect of initial metal concentration

Different metals have different adsorption capacities either at low concentration or high concentration. The increase in lead concentration increased the uptake capacity (q) and decreased the percentage removal of lead, except at 100 mg L^{-1} initial metal concentration, at which there was maximum percentage removal of lead. The results are shown in Fig. 2. The maximum percentage removal of lead was 93.53% (boiling) > 91.82% (acetic acid) > 86.69% (autoclave) > 82.71% (control) and uptake capacity (q) was 91.37 mg g^{-1} (boiling) > 89.7 mg g^{-1} (acetic acid) > 84.69 mg g^{-1} (autoclave) > 80.8 mg g^{-1} (control). On increasing metal concentration, the percentage removal decreased after 100 mg L^{-1} concentration due to diminishing loading capacity of the biomass. At lower concentration, adsorption sites are occupied very quickly, so decrease in percent removal with increase in initial concentration is attributed to rapid saturation of the metal-binding sites of the biosorbent. Sorption characteristics indicate that surface saturation depends on initial metal ion concentration. At low concentration, adsorption sites have taken the available metal quickly, while at higher concentration, metal ions need intra particle diffusion to the surface of biosorbent [34]. More metal uptake efficiency occurred by increasing the metal ion concentration.

3.3. Kinetic studies

The experimental results on different time intervals of biosorption of lead on physically and chemically pretreated Neem leaves are shown in Fig. 3. Batch biosorption experiment was carried out at optimum conditions. Kinetic studies revealed that maximum biosorption capacities and metal removal efficiencies for lead were achieved generally in first 15 min of contact, then it decreases significantly. Percentage removal of lead by biosorption process was 93.48% (boiling) > 91.85% (acetic acid) > 86.68% (autoclave) > 82.48% (control) and the maximum uptake capacity (q) were 91.34 mg g^{-1} (boiling) > 89.75 mg g^{-1} (acetic acid) > 84.7 mg g^{-1} (autoclave) > 80.6 mg g^{-1} (control) after 24 h.

Kinetic study revealed that biosorption takes place in two phases, a rapid surface adsorption within 15 min and slow intracellular adsorption up to the end time [35,36]. In the first 15 min, the fast biosorption kinetics observed is typical for biosorption of metals involving no energy-mediated reactions, where metal removal from solution is due to purely physicochemical interactions between biomass and metal solution [5,18].

3.4. Equilibrium isotherm modeling

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

The Langmuir theory considers monolayer coverage of adsorbate over a homogeneous adsorbent surface [37]. If the metal ions were taken up independently on single type of binding site in such a way that the uptake of first metal ions does not affect the sorption of next ion, then the sorption process would follow the

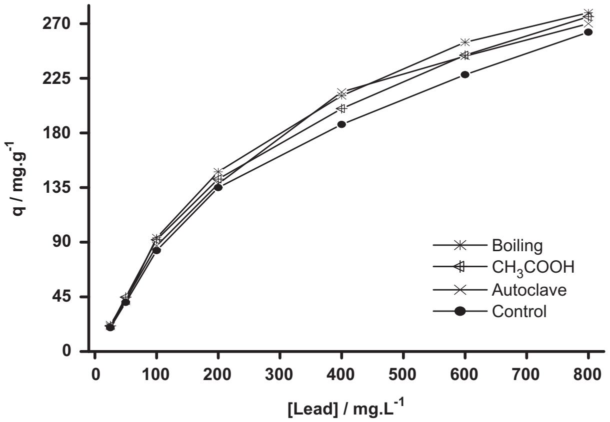

Fig. 2. Effect of concentration on biosorption of lead by pretreated Neem leaves biomass.

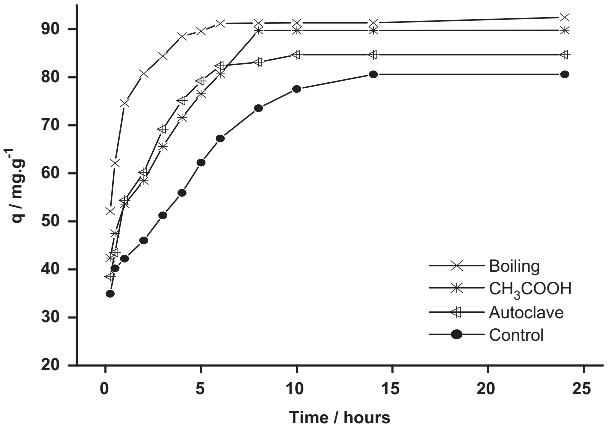

Fig. 3. Effect of kinetics on biosorption of lead by pretreated Neem leaves biomass.

Langmuir adsorption isotherm equation, which was linearized to form:

$$C_e/q_e = 1/q_o \,.\, K_L + C_e/q_o$$

where q_e ($mg\,g^{-1}$) is the equilibrium adsorption capacity, C_e ($mg\,L^{-1}$) is the equilibrium concentration of metal ion solution, q_o ($mg\,g^{-1}$) and K_L ($L\,mg^{-1}$) are the Langmuir constants. The value q_o is the maximum amount of metal ion, which can be taken up by the sorbent molecule and K_L is the sorption equilibrium. The capacity of Neem biomass in binding with lead was determined by plotting C_e/q_e against C_e using the above equation. Fig. 4 shows the data linearized to fit the Langmuir equation. The plots of specific biosorption (C_e/q_e) against equilibrium concentration (C_e) gave the linear isotherm parameters of q_o, $K_{L,}$ and the coefficient of determination and these are presented in Table 1.

The q_o calculated by applying Langmuir equation was 277.27 $mg\,g^{-1}$, 270.27 $mg\,g^{-1}$, 263.15 $mg\,g^{-1}$, and 261.157 $mg\,g^{-1}$ for boiling, acetic acid, autoclave, and control, respectively, which was nearly equal to the experimentally calculated maximum adsorption capacity (q) i.e. 259.61 $mg\,g^{-1}$, 256.35 $mg\,g^{-1}$, 250 $mg\,g^{-1}$, and 243.61 $mg\,g^{-1}$ for boiling, acetic acid, autoclave, and control, respectively with R^2 values (0.989), (0.982), (988), and (0.981) for boiling, acetic acid, autoclave, and control, respectively.

The Freundlich equation is another model, which has been commonly used to describe adsorption isotherm. Freundlich isotherm allows assuming that as the adsorbate level rises, the sorbate concentration on the sorbent surface also increases [38]. Its linearized form is represented by equation.

$$\text{Log}\, q_e = \text{Log}\, K_F + 1/n \,.\, \text{Log}\, C_e$$

where q_e ($mg\,g^{-1}$) is the amount adsorbed per unit mass of adsorbent, C_e ($mg\,L^{-1}$) is the equilibrium concentration of metal ion solution, K_F and $1/n$ are Freundlich constants obtained from regression equation called intercept and slope, respectively. This isotherm is characterized by heterogeneity factor ($1/n$) whereas, K_F ($L\,mg^{-1}$) is adsorption capacity.

The plot of $\log q_e$ vs. $\log C_e$ was linear (Fig. 5) and constants K_F and n can be evaluated from the slopes and intercepts. The Freundlich constants are shown in Table 1. The Freundlich equation is an empirical relationship describing the adsorption of solutes from liquid to the solid surface. It was found that

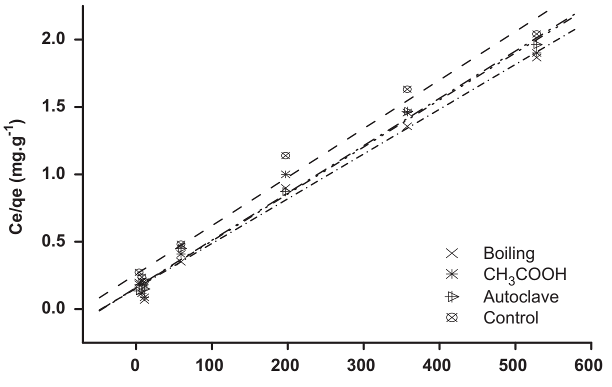

Fig. 4. Langmuir isotherm model for biosorption of lead by pretreated Neem leaves biomass.

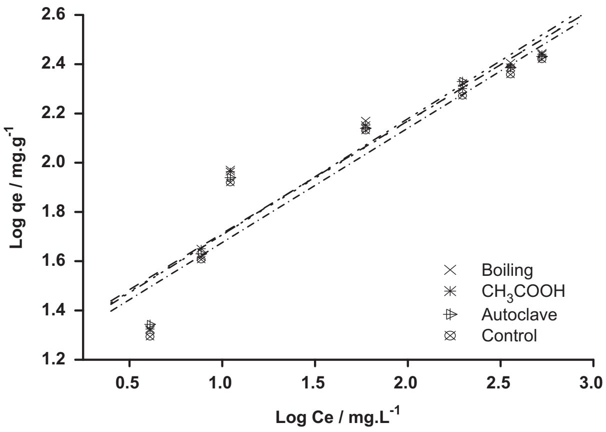

Fig. 5. Freundlich isotherm model for biosorption of lead by pretreated Neem leaves biomass.

Table 1
Langmuir and Freundlich isotherm parameters

Sample	Experimental q_{max} ($mg\,g^{-1}$)	Langmuir isotherm parameters			Freundlich isotherm parameters			
		X_{max} ($mg\,g^{-1}$)	K_L	R^2	q_e ($mg\,g^{-1}$)	K	$1/n$	R^2
Control	243.61	261.16	1.24×10^{-2}	0.979	286.44	10.36	0.51	0.882
Boil	259.61	277.78	1.87×10^{-2}	0.990	294.05	17.56	0.45	0.811
Acetic acid	256.35	270.27	1.70×10^{-2}	0.983	259.73	16.06	0.43	0.819
Autoclave	250.61	263.75	1.52×10^{-2}	0.981	275.37	16.14	0.46	0.931

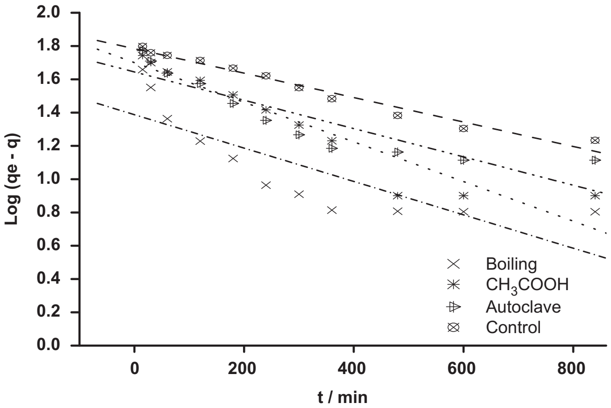

Fig. 6. Pseudo-first-order kinetic model for biosorption of lead by pretreated Neem leaves biomass.

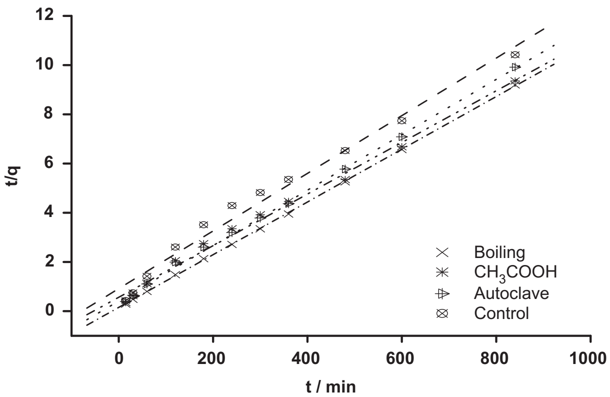

Fig. 7. Second-order kinetic model for biosorption of lead by pretreated Neem leaves biomass.

adsorption equilibrium data were better fitted by the Langmuir isotherm, although they were also modeled by Freundlich isotherm, in the concentration range studied, since it presented the greater coefficient of correlation.

3.5. Kinetics modeling

Kinetic models direct the rates that conclude the residence time defining the efficiency of an adsorbent. Kinetic equations have been used to explain the sorption rate. The order of adsorbate–adsorbent interactions has been described by using various kinetic models. Traditionally, the pseudo-first-order model derived by [39] has found wide application. On the other hand, several authors [40–42] [5] have shown that second-order kinetics can also very well describe these interactions in certain specific cases. The pseudo-first-order rate equation of Lagergren:

$$\text{Log}\,(q_e - q_t) = \log q_e - k_{1,\text{ad}} \times t/2.303$$

where q_e (mg g^{-1}) is the amount of metal ion adsorbed at equilibrium, q_t is the amount of metal ion adsorbed at time t (min), and $k_{1,\text{ad}}$ (min^{-1}) is the Lagergren rate constant of the pseudo-first-order process. Plot of $\log(q_e - q_t)$ vs. t gives a straight line for first-order kinetics (Fig. 6), which allows computation of the adsorption rate constant, $k_{1,\text{ad}}$. The Lagergren first-order rate constant $k_{1,\text{ad}}$, q_e, and R_2 determined from the model indicate that this model had failed to estimate q_e since the experimental value of q_e differs from estimated one.

The best fit for the experimental data of this study was achieved by the application of pseudo-second-order kinetic equation. The second-order model is based on the assumption that biosorption follows a second-order mechanism [42–45]. The pseudo-second-order equation:

$$t/q_t = 1/q_e^2\,.\,k_{2,\text{ad}} + t/q_e$$

where q_e (mg g^{-1} min^{-1}) is the amount of metal ion adsorbed at equilibrium, q_t is the amount of metal ion adsorbed at time t (min), $k_{2,\text{ad}}$ (mg g^{-1} min^{-1}) is the pseudo-second-order rate constant. The plot of t/q_t vs. t gives a linear relationship (Fig. 7), which allows computation of q_e, $k_{2,\text{ad}}$, and h without having to know any parameter beforehand. Table 2 clearly shows the lack of fit in the data for pseudo-first-order

Table 2
Lagergren pseudo-first-order and pseudo-second-order kinetic models parameters

Sample	Experimental $q_{\max}$ (mg g^{-1})	Pseudo-first-order kinetic parameters			Pseudo-second-order kinetic parameters		
		q_e (mg g^{-1})	$K_{1,\text{ad}}$	R^2	q_e (mg g^{-1})	$K_{2,\text{ad}}$	R^2
Control	80.60	55.80	4.38×10^{-3}	0.959	85.47	1.49×10^{-4}	0.982
Boil	91.34	48.19	8.98×10^{-3}	0.990	95.24	4.17×10^{-4}	0.998
Acetic acid	89.75	55.65	3.69×10^{-3}	0.991	92.59	1.63×10^{-4}	0.997
Autoclave	84.70	61.75	6.45×10^{-3}	0.987	90.91	1.87×10^{-4}	0.996

model as indicated by a large scatter of the experimental points from the line of best fit. A high degree of correlation coefficient was obtained for the pseudo-second-order kinetic model. The theoretical q_e values were found to be in good agreement with the experimental q_e values in pseudo-second-order kinetics. The results in Table 2 suggest that the sorption system follows the second-order kinetics, which indicates that the rate-controlling step is the chemisorption.

4. Conclusions

The present study showed that the pretreatments caused an improvement in the sorption capacity of the biosorbent. Chemical and physical pretreatments were used for Neem leaves biomass. Among all the treatments, boiling, autoclave, and acetic acid pretreatments were found more effective for the removal of lead. Maximum sorption was obtained at pH 5. Sorption capacity also increased with rise in initial metal ion level and contact. Lead uptake followed the Langmuir sorption isotherm and obeyed the pseudo-second-order kinetic model. Neem leaves can be used after pretreatments as a new, inexpensive, and environment-friendly biosorbent (green biosorbent) to remove heavy metals on industrial scale and pretreatments of biosorbents can enhance sorption capacity.

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