



Removal of zinc and lead from aqueous solution by nanostructured cedar leaf ash as biosorbent



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ABSTRACT

In the present study, the adsorption of zinc (Zn^{2+}) and lead (Pb^{2+}) from aqueous solutions by nanostructured cedar leaf ash as biosorbent was investigated in batch tests under different experimental conditions. The chemical and morphological structures of biosorbent were investigated by scanning electron microscopy (SEM), elemental analyzer (CHNSO), particle size analyzer (PSA), X-ray Fluorescence spectroscopy (XRF) and Fourier-transform infrared spectroscopy (FTIR). The effect of different parameters such as solution pH, contact time and adsorbent dosage were investigated on the biosorption of two studied metals by nanostructured cedar leaf ash. The biosorption process was found to be relatively fast and equilibrium was achieved within 30 min for Zn^{2+} and Pb^{2+} . The adsorption data were analyzed using different isotherm models (Langmuir, Freundlich, Redlich–Peterson and Sips (Langmuir–Freundlich)) and kinetic models (pseudo-first-order, pseudo-second-order and intraparticle diffusion). Results revealed that pseudo-second-order kinetic model could well describe the adsorption kinetics of Zn^{2+} and Pb^{2+} biosorption, and Sips (Langmuir–Freundlich) model was found to fit well for Zn^{2+} and Pb^{2+} adsorption. The maximum adsorption capacity from Langmuir model was calculated as 7.23 and 4.79 $mg\ g^{-1}$ for Pb^{2+} and Zn^{2+} , respectively.

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1. Introduction

Water pollution by toxic heavy metals is one of the major environmental problems, because metals are non-biodegradable and harmful to public health, even at very low concentrations [1–4]. Heavy metals are used in numerous industries such as plastics, mining, plating, power generation, pigment, electronic and batteries [5]. Lead and zinc are the most important heavy metals which are used in many industrial applications. However, both metals are well-known toxics and can find their ways to the aquatic environment through wastewater discharge [6]. Lead causes many harmful effects to human health due to its toxicity, accumulation in food chains and persistence in nature [7]. Elevated concentrations of zinc cause severe health problems e.g., vertigo, disharmony, arteriosclerosis, pancreas damage [6]. World Health Organization has determined the allowable concentration of Pb^{2+} ($0.05\ mg\ L^{-1}$) and Zn^{2+} ($4\ mg\ L^{-1}$) [8,9] in drinking water. Various processes exist to remove toxic heavy metal ions, including chemical precipitation/coagulation, membrane technology, electrolytic reduction,

ion exchange and adsorption [10,11]. However, most of these methods have some limitations such as, high operational cost, unaffordable on large scale metals removal from wastewater and ineffective at higher concentrations. Adsorption is generally considered as one of the most efficient technologies due to the advantages of treatment stability, easy operation, lower environmental impacts, and low cost.

Various adsorbents have been used to remove Zn^{2+} and Pb^{2+} ions from water and wastewater such as natural adsorbent [12,13], industrial and/or agriculture wastes [14,15]. Recently, application of nanotechnology has been developed to treat contaminated water to remove diverse pollutants. Unique characteristics of nano particles such as, large specific surface area, has increased their potential for adsorption of toxic heavy metal ions [16–18]. Cedar with the scientific name of *Ziziphus spina-christi* grows in Saudi Arabia, north of Africa and in Iran in provinces of Khuzestan, Fars and Hormozgan. It is used to treat blisters, bruises, chest pains, dandruff, fractures, headache, and mouth problems and of other beneficial applications that include the use of leaves as fodder, branches for fencing, wood as fuel [19]. Furthermore, this plant is adapted to hot and dry climates which make it appropriate for cultivation in an environment characterized by increasing degradation of land and water resources. Lack of research in *Z. spina-christi* prevents its successful improvement and promotion. Also cedar leaf is an

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inexpensive agricultural waste. The major component of *Z. spina-christi* is cellulose ($C_6H_{10}O_5$)_n. The cellulose surface contains functional groups which have been found efficient to bind cations. In our previous work, the adsorption of Cd^{2+} by cedar leaf and cedar leaf ash (using millimeter size) was compared [20]. It was found that cedar leaf ash possesses higher surface area ($20.38 \text{ m}^2 \text{ g}^{-1}$) than cedar leaf ($8.9 \text{ m}^2 \text{ g}^{-1}$). Also, cedar leaf ash showed better adsorption potential for Cd^{2+} (4.27 mg g^{-1}) than cedar leaf (3.91 mg g^{-1}). Further, equilibrium time for Cd^{2+} adsorption by cedar leaf ash was fast (30 min) than cedar leaf (45 min). As cedar leaf ash showed better results for Cd^{2+} adsorption, it was selected in this study to examine its suitability for other metals (Zn^{2+} and Pb^{2+}). Also, in another research, we compared the removal of Cd^{2+} using nano/milli-sized particles of cedar leaf ash [21]. Result of this study showed that cedar leaf ash with nanosize has higher adsorption capacity for Cd^{2+} (7.85 mg g^{-1}) than milli-size (4.33 mg g^{-1}). Therefore, cedar leaf ash in nano form was selected in this study. The equilibrium and kinetic data of adsorption studies were modeled using the adsorption isotherm models Langmuir, Freundlich, Redlich–Peterson and Sips (Langmuir–Freundlich) and the adsorption kinetic models (pseudo-first-order, pseudo-second-order and intraparticle diffusion models).

2. Materials and methods

2.1. Preparation of the adsorbent

Cedar leaves were collected in the area of Khuzestan province, Iran in March 2011. The collected leaves were washed thoroughly using double distilled water to remove impurities. After washing, leaves were dried in the oven at $100 \text{ }^\circ\text{C}$ for 1 h and then were carbonized in the Muffle Furnace (FP6-IRAN KHODSAZ model – made in Iran) at $600 \text{ }^\circ\text{C}$ for 40 min. The reason to select this temperature ($600 \text{ }^\circ\text{C}$) was to establish a balance between carbon content and specific surface area. With the increase in temperature, carbon percentage decreased extensively and the surface area increased because of the removal of volatile matter. The nanostructured cedar leaf ash was prepared by mechanical grinding in a jet mill (D-56070 KOBLENZ model – made in Germany). In this method, the size of material was changed by a mill with metal or ceramic ball. In the mechanical alloying method, no change was observed in the chemical composition of the raw material and only the internal structure and the particle size of the adsorbent was changed.

2.2. Characterization of the adsorbent

A scanning electron microscope (SEM, Leo 1455 VP model, made in Germany) was used to study the morphology of the adsorbent's surface. The specific surface area of the adsorbent was determined by methylene blue method [22]. Particle size was determined using a particle size analyzer (Malvern Zetasizer 3000, UK). Infrared spectra were recorded using FTIR spectrometer (Spectrum GX, PerkinElmer). Also, elemental (C, H, N, S, O) analyses were conducted using a CHNSO analyzer (vario ELIII-elementar – made in Germany). An X-ray Fluorescence Spectroscopy (XRF, BRUKER S4 Pioneer model, made in Germany) was used to determine the metal oxides or nonmetal oxides of adsorbent.

2.3. Determination of point of zero charge (pH_{pzc})

For the determination of pH_{pzc} of the adsorbent, 100 mL 0.01 M NaCl solution was divided into several Erlenmeyer flasks. The initial pH of solutions was adjusted between 3 and 8 by adding 0.1 M HCl or 0.1 M NaOH. Then, 1 g of adsorbent was added to each solution, the mixtures were shaken in controlled temperature for 48 h with a speed of 150 rpm. After completion of the equilibration time, the solutions were filtered and final pH values (pH_{final}) of the filtrates were measured again. The difference between the initial pH (pH_i) and final pH (pH_f)

values ($\Delta\text{pH} = \text{pH}_i - \text{pH}_f$) was plotted against the pH_i. The point of intersection of the resulting curve with abscissa, at which $\Delta\text{pH} = 0$, gave the point of zero charge.

2.4. Adsorption studies

Stock solutions of 1000 mg L^{-1} of Zn^{2+} and Pb^{2+} were prepared from their chloride salts by dissolving them in deionized water. Metals spiked samples at a required concentration range were further prepared by appropriate dilution of the stock solutions with deionized water. The pH of initial solutions was adjusted using 0.1 M NaOH and 0.1 M HCl and recorded using a Mettler Toledo 320 pH meter. The sorption of two metals (zinc and lead) on prepared adsorbent was conducted at room temperature ($20 \pm 2 \text{ }^\circ\text{C}$) by batch experiments. One hundred milliliters of metal solution of varying initial concentrations ($2\text{--}80 \text{ mg L}^{-1}$) in 250 mL capped tubes were shaken (150 rpm) with 1.0 g of adsorbent after adjusting the pH to the desired value, for a specified period of contact time (12 h) in a temperature controlled shaking assembly (THZ-98A mechanical shaker). After equilibrium, the solutions were centrifuged at 12,000 rpm for 20 min and filtered. Reproducibility of the measurements was determined in duplicates and the average values are reported. The initial and the final concentrations of Zn^{2+} and Pb^{2+} in the aqueous solution were measured with an atomic absorption spectrophotometer (Varian 220 FS AA model). Removal efficiency of heavy metal ions was calculated by the following equation:

$$\text{Removal efficiency (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

where C_i and C_e are the initial and final concentrations of Zn^{2+} and Pb^{2+} ions in the solution, respectively. For kinetic studies, metal ions having initial concentration of 10 mg L^{-1} were agitated for different contact times (0, 5, 10, 15, 30, 45, 60, 90, 120 min) with an adsorbent dosage of 10 g L^{-1} at $20 \pm 2 \text{ }^\circ\text{C}$. To study the effect of adsorbent dosage on adsorption of Zn^{2+} and Pb^{2+} , metal solutions having initial concentration of 10 mg L^{-1} were agitated with varying adsorbent dosage (1, 2, 5, 10, 20, 30, 40, 50 g L^{-1}) for 30 min at $20 \pm 2 \text{ }^\circ\text{C}$. Also, for isotherm studies, solutions of metal ions containing varying initial concentration (2, 10, 25, 40, 50 mg L^{-1}) were equilibrated for 30 min with an adsorbent dosage of 10 g L^{-1} at $20 \pm 2 \text{ }^\circ\text{C}$.

2.4.1. Adsorption kinetics

Different adsorption kinetic models have been developed by various researchers to analyze the adsorption kinetics data of heavy metal ions, such as pseudo-first-order, pseudo-second-order, intraparticle diffusion, Elovich and Bangham's models. In this study, adsorption data were analyzed by using three well-known kinetic models namely, pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The nonlinear forms of pseudo-first-order [23] (Eq. (2)), pseudo-second-order [24] (Eq. (3)) and intraparticle diffusion model [25] (Eq. (4)) are expressed below:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (2)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (3)$$

$$q_t = K_p t^{1/2} + I \quad (4)$$

where, q_e and q_t (mg g^{-1}) are the amounts of metal ions adsorbed at equilibrium and at time t , k_1 (min^{-1}) is the constant of the pseudo-first-order kinetics, k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the rate constant of the pseudo-second-order kinetics, K_p is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{ min}^{1/2}$) and I (mg g^{-1}) is the intercept of intraparticle diffusion model.

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