Batch sorption of lead from aqueous solutions using Reed as an adsorbent: Equilibrium and kinetic studies

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Abstract

Kinetic and equilibrium sorption experiments concerning the removal of lead (II) ions from aqueous solutions by Reed were carried out on in order to assess its potential use as an efficient sorbent. The effects of contact time, initial lead (II) concentration, sorbent dose and ionic strength were investigated and discussed.

Results of batch experiments showed that this sorbent exhibited high sorption capacities toward lead (II). Experimental data were analyzed using pseudo-first order and pseudo-second order kinetics. It was found that kinetics followed a pseudo-second order equation.

The equilibrium results were modelled and evaluated using Langmuir and Freundlich model isotherms. The Langmuir model provided the best fit of equilibrium data of lead (II) ions with a maximum sorption capacity for lead (II) ions of 79 mg g^{-1}.

This study revealed that Reed was an effective sorbent for the removal of lead (II) from aqueous solutions.

Keywords *Reed; Sorption; Lead (II); Langmuir isotherm; Pseudo-second-order model.*

I. Introduction

Human activities introduce heavy metals to the hydrosphere in many ways such as burning of fossil fuels, smelting of ores, municipal sewage, industrial effluent, mining activities, landfill, mineral weathering, underground toxic waste disposal, etc. [1, 2]. Regardless of their sources these contaminants, are easily dispersed into the aquatic system, and tend to accumulate in living organisms, resulting in various disorders and diseases in the ecosystem.

Lead is a metal which is considered to be of an environmental concern. The problem of Pb(II) pollution is due to its use in service pipes and particularly in soft water is the first recognized metal pollutant. Other sources of Pb(II) pollution are the battery industry, auto exhaust, paints, ammunition, and the ceramic glass industries [3]. The permissible level of lead in drinking water is 0.05 mg^3 L^{-1}. The permissible limit of Pb(II) in wastewater, given by the Environmental Protection Agency (EPA) is 0.05 mg^3 L^{-1}, and that of the Bureau of Indian Standards (BIS) is 0.1 mg^3 L^{-1} [4].

Various treatment technologies have been used for the clean-up of waters contaminated with trace toxic metals in aquatic environments. Conventional techniques usually involve the application of physico-chemical processes such as precipitation, oxidation, reduction, solvent extraction, electrolytic extraction, adsorption, (electro) dialysis, filtration, flocculation, sedimentation, evaporation, osmosis, ion-exchange, chelation, Biosorption, etc. Among the available techniques, it is known that sorption plays an important role in controlling the fate and transport of metal contaminants in ecosystem. Moreover, it is also important to select an appropriate sorbent for a successful application. Large-scale sorption processes for water treatment require inexpensive, non toxic, available sorbents of known kinetic parameters and sorption characteristics. To date, a number of researchers have focused on the development of low cost effective materials and have examined the effectiveness of various natural inorganic and organic materials on metal sorption: agricultural wastes such as tea waste [5] and coffee [6], Leaves of Date Trees [7], peanut hull [8], sawdusts [9] pine cone shell [10], palm kernel shell [11] and coconut husk [12,13], modified cellulosic materials [14, 15] chemically modified banana peels [16] corncobs [17] and modified corncob [18] rice husks [19], activated carbon developed from coffee residue [20] pine bark [21] cellulose cotton fibers [22] tea leaves [23] and peel waste [24], modified lignocellulose-biomass jute fiber [14], chemically modified orange peel [25] sunflower, potato, canola and walnut shell residues [26] banana peels, sugarcane bagasse and watermelon rind [27] and different waste fruit cortexes [28] have been used and investigated.

Reed is a large-leafed grass, about 1.5 to 5 m tall, with feathery flower clusters and stiff, smooth stems. Dried reed stems have been used for millennia as thatching and construction material, in basketry, for arrows and pens, and in musical instruments. They are also cultivated for their cellulose content. This material which is produced in great quantity in our country can represent a real source for the sorbent preparation.

The present work considered the sorption of lead (II) ions from aqueous solution using reed and focussed on its sorption capacity by means of batch experiments. The influence of operating parameters such as contact time, initial lead concentration, adsorbent dose and ionic strength were investigated and the obtained experimental data were fitted and exploited for the determination of the sorbent equilibrium isotherms and kinetic model types.

II. EXPERIMENTAL SECTION

II.1 Adsorbent and Characterization

The reed used in the present study was collected from the Toudja region in the north of Algeria. The collected reed was washed with distilled water several times to remove dirt particles and water-soluble materials. The washing process was continued until the wash water was colourless. The washed materials were then completely dried in an oven at 110°C, then ground, sieved, dried again in an air circulating oven at 110 °C and stored in a desiccator ready for use.

A measurement of the specific area was by nitrogen adsorption at 77 K using a Brunauer-Emmett-Teller (BET) surface analyzer (Nova Station A). The scanning electron microscopy was carried out on a Phillips SEM 501 electron microscope. The nature of surface groups of reed was performed by IR analysis. Fourier transform infrared transmission spectra of biomaterial were obtained through potassium bromide technique on FTIR spectrometer in the wave number range of 4000–400 cm^{-1}. Reed was mixed with potassium bromide at a ratio of roughly 1/1000. The amount of acidic and basic groups on the reed was analyzed by Boehm titration method [29].

II.2 Adsorbate and analytical measurements

All the compounds used to prepare reagent solutions are of analytic reagent grade. The mother solution of Pb(II) (1000 mg L^{-1}) was prepared by dissolving a weighed quantity of lead nitrate in distilled water. The concentration of metals solutions ranged from 10 to 90 mg L^{-1}. Before mixing with the biosorbent, the pH of each solution was adjusted to the required value by adding 0.1 M NaOH or 0.1 M HNO_3. SCHIMADZU AA6500 atomic absorption spectrophotometer (AAS) equipped with a Zeeman atomizer and a SSC-300 auto sampler was used to determine the concentration of unabsorbed Pb(II) ions in the solution. All the instrumental conditions were optimized for maximum sensitivity as indicated by the manufacturer.

II.3 Batch sorption procedure

Batch experiments of sorption were performed in a batch reactor (3L) placed in a temperature-controlled shaker (RCS LAUDA), at 25±2 °C. A known weight of biosorbent was left in contact with 1000 mL of each solution (10-90 mg/L) stirred at 200 rpm during 2 h. The initial pH value of the solution was adjusted with nitric acid (0.1 mol L^{-1}) or sodium hydroxide (0.1 mol L^{-1}). The pH value was chosen so that metallic species were present in their divalent form (5.8). Small-volume liquid samples were withdrawn at different time intervals. Samples were filtered through glass-filter paper to remove adsorbent particles. The evolution of the adsorbed quantities of Pb(II) ions was evaluated using the following equation:

$$q_e = \frac{(C_0 - C_e)\ V}{m} \qquad (1)$$

where q_e is the amount of ions adsorbed per mass unit of biosorbent, C_0 is the initial metal ions concentration (mg L^{-1}), C_e the equilibrium metal ions concentration (mg L^{-1}), V the volume of the aqueous phase (L) and m is the weight of used biosorbents (g).

II.4 Sorption isotherms

Langmuir and Freundlich models were tested for equilibrium description. Langmuir equation, based on a theoretical model, assumes monolayer sorption over an energetically homogeneous sorbent surface. It does not take into consideration interactions between sorbed ions. It can be represented by the equation [31]:

$$q_e = q_{mon} \frac{K_L C_e}{1 + K_L C_e} \tag{2}$$

where C_e and q_e as defined just above, q_{mon} and K_L are Langmuir constants related to sorption capacity (mg g^{-1}) and the energy of sorption, respectively.

Freundlich equation is an empirical model based on heterogeneous sorption over independent sites and is given by [32]:

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F (mg $^{1-1/n}$ $L^{1/n}$ g^{-1}) and $1/n$ are the Freundlich constants related to sorption capacity and sorption intensity, respectively.

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution.

II.5 Sorption kinetics

The controlling mechanism of the metal sorption process was investigated by fitting first and second-order kinetic models to the experimental data. The linear first-order kinetic model is given as [32]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{4}$$

where q_e as defined previously, q_t is the amount of sorbate sorbed at time t (mg g^{-1}), k_1 is the pseudo-first-order rate constant (min^{-1}) and t is the contact time (min). The linear form of the second-order kinetic model is [33]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where k_2 is the equilibrium rate constant of pseudo-second-order model (g mg^{-1} min^{-1}).

III. Results and Discussion

III.1 Sorbent characteristics

The structural characteristics of the reed with average particle size of 356 µm were measured as: BET surface area of 57 m^2 g^{-1} and bulk density of 0.701 (Table 1). Results obtained from the Boehm's method are presented in Table 1. It is seen that the amount of acidic and basic groups are as follows: acidic > basic.

Table 1. Physical and chemical characteristics of the Reed

Surface area ($m^2.g^{-1}$)	57
Porosity (%)	0.236
Particle size (µm)	356
Bulk density	0.701
Basic surface functional groups ($mmol.g^{-1}$)	0.97
Acidic surface functional groups ($mmol.g^{-1}$)	1.36

Figure 1 shows the SEM micrograph of reed sample before lead (II) ions sorption. It is clear that reed had considerable numbers of heterogeneous layer of pores where there was a good possibility for metal to be sorbed. The FTIR spectrum of the reed (Figure 2) displays a number of absorption peaks, indicating the complex nature of the reed. The main chemical groups of the reed are given in Table 2.

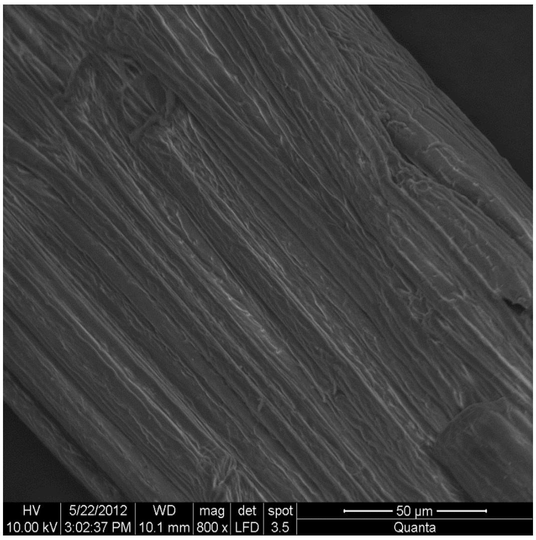

Figure 1. SEM micrograph of Reed

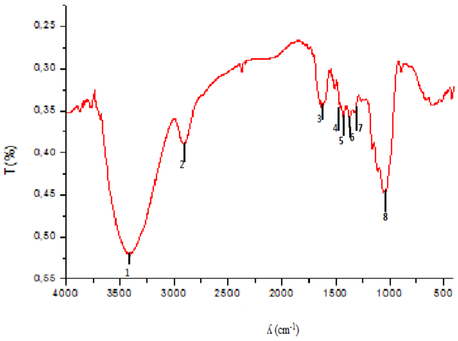

Figure 2. FTIR spectra of the Reed

Table2. Main chemical groups of the reed

Bond (cm^{-1})	Associated Structure
3409	OH bond
2919	CH_2 bond
1732	C=O bond of lactones structures
1634	C=O bond and C-N of protein
1606	C=C bond of woody structures or C=O of carboxylic acids
1515	C-N bond or N-H of protein
1161	C-O-C of polysaccharides
<1000	Functional groups of phosphate and sulfur

III.2 Effect of initial concentration on the sorption of Pb (II) ions

The effect of the initial Pb(II) ions concentration was examined by preparing sorbent–sorbate solution with fixed sorbent dose and different initial Pb(II) ions concentration for different time intervals and shaken until equilibrium was reached. The percentage removal of Pb(II) ions was highly dependent on the initial amount of lead ions concentration. The effect of the initial Pb(II) ions concentration factor depended on the immediate relation between the concentration of the metallic ions and the available binding sites on the sorbent surface. Generally the percentage of Pb(II) ions removal decreased with an increase in the initial concentration, which might be due to the saturation of sorption sites on the sorbent surface. At a low concentration there would be vacant active sites on the sorbent surface, the number of which decreased with the increase of the initial Pb(II) ions concentration, inducing even a deficit. Also the increase in the initial lead (II) ions concentration would cause an increase in the loading capacity of the sorbent and this might be due to the high mass transfer driving force at a high initial Pb(II) ions concentration.

Figure 3 shows the effects of agitation time and Pb(II) ions concentration on sorption capacity. It can be seen that the sorption of Pb(II) ions increased with an increase in agitation time and reached the equilibrium in 15 min, and this at different lead concentrations.

This result is interesting because equilibrium time is one of the parameters for economical wastewater treatment plant applications. According to these results, the agitation time was fixed at 120 min for the rest of the batch experiments to make sure that equilibrium was reached. It also shows that increases in lead (II) ions concentration increased the amount of lead (II) ions uptake per unit weight of reed (mg/g). The increase in loading capacity of the reed related to lead (II) ions concentration was due to a high mass transfer driving force.

It could also be noted during the experiments that the measured pH values of solutions at equilibrium decreased throughout to the end. This reduction in pH was due to the dissociation of the acid functional groups located at the surface of the reed biosorbent, hence partially inducing an ion exchange with Pb(II).

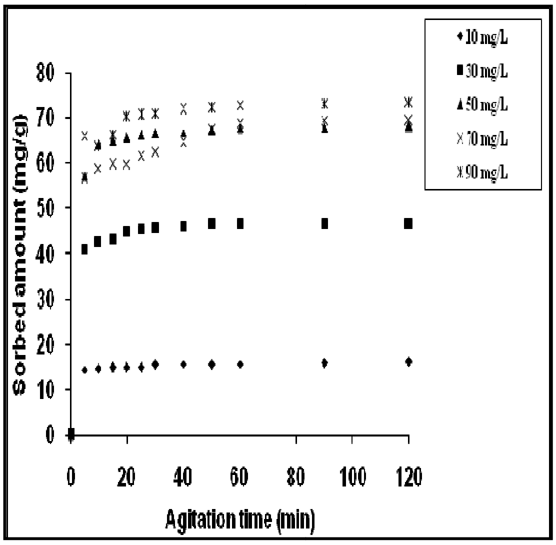

Figure 3. Effect of agitation time and initial concentration of Pb(II) on its sorption onto Reed.

III.3 Effect of sorbent concentration

The dose of sorbent was varied from 0.5 to 1.5g/1000 mL keeping all the other experimental variables, viz. pH 5.8, initial concentration (50 mg L^{-1}) and agitation speed (120 rpm) constant. Figure 4 presents the sorbent dose profile versus sorbed Pb(II) ions amount. It may be observed that on increasing the sorbent dose, the sorbed amount of Pb(II) ions decreased, due to concentration gradients between solute concentrations in the solution and on the sorbent surface. But the removal of Pb(II) ions increased with an increase in sorbent dosage. The increase in Pb(II) ions removal was due to the increase of the available sorption surface, hence providing a greater availability of sorption sites.

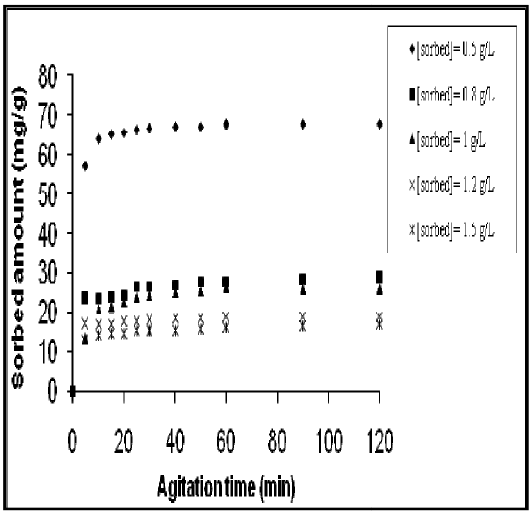

Figure 4. Effect of sorbent dosage on the sorption of lead (II) ions by Reed.

III.4 Effect of ionic strength

Wastewaters from electroplating industries, textiles, tanneries, oil refineries, mining, and smelters industries contain various types of suspended solids and salts. The presence of ions leads to high ionic strength, which may significantly affect the performance of the sorption process. Figure 5 presents the effect of ionic strength on the uptake of lead (II) ions. It was observed that the sorption potential decreased with increased concentration of NaCl in the medium. The adverse effect of ionic strength on lead (II) ions suggests the possibility of ion exchange mechanisms being in operation in the sorption process (competitive effect between lead ions and cations from the salt (Na^+) for the sites available for the sorption process). Another reason is the influence of the great ionic strength on the activity coefficient of lead which reduced its transfer to the sorbent surface.

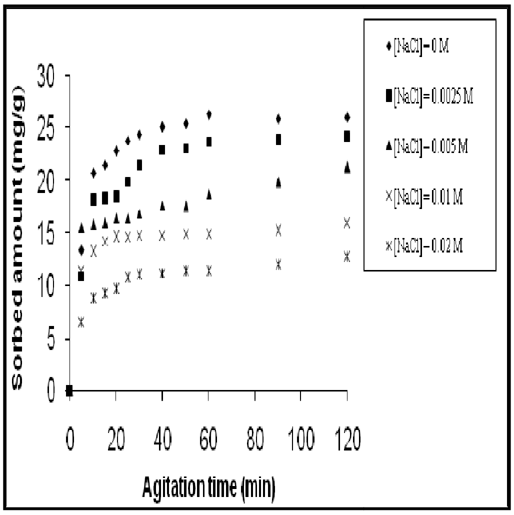

Figure 5. Effect of ionic strength on the sorption of lead (II) ions by Reed.

III.5 Sorption kinetics

In most cases, the first-order equation did not apply well throughout the whole range of contact times and was generally applicable over only the initial 20–30 min of the sorption process. The plotting of $log(q_e - q_t)$ versus time (curves not shown) deviated considerably from the theoretical. The plots and intercepts of curves were used to determine the first-order constant k_1 and equilibrium capacity q_e. The calculated values of $q_{e(\mathrm{cal})}$ (Table 3) from the first-order kinetic model were lower than the experimental. So, the sorption system did not follow a first-order reaction. The ratio t/q_t was plotted versus t at different adsorbate concentrations and the second order sorption rate constant (k_2) and q_e values were determined from the slopes and intercepts of the plots. The correlation coefficients for the linear plots were greater than 0.999 in all the cases. The values of these parameters and the correlation coefficients are presented in Table 3. The theoretical $q_{e\ (\mathrm{cal})}$ values agree perfectly with the experimental $q_{e(exp)}$ ones. This suggests that the sorption system was not a first-order reaction and that a pseudo-second-order model could be considered. The latter is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. It provided the best correlation of the data.

III.6 Sorption isotherm (Non-linear Method)

The analysis and design of sorption separation process require the relevant equilibrium sorption, which is the most important piece of information in understanding the sorption process. In the present study, the sorption capacity and equilibrium isotherm for lead (II) ions onto Reed were estimated using Langmuir and Freundlich isotherms equations.

Mathematically the non-linear used the original form of the equation. The constants of the Langmuir and Freundlich models were determined by minimizing the error function using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel. The used error function was as follows:

$$\sum_{i=1}^{P} \left(q_e - q_{cal}\right)_i^2 \qquad (6)$$

where P is the number of experimental data.

The q_{mon}, K_L, n, K_F and R^2 values calculated from isotherms are presented in Table 4. The determination of the correlation coefficients (R^2)

suggests that the Langmuir isotherm provides a good fit to the isotherm data for the sorption of Pb(II) ions. The calculated maximum sorption capacity from this isotherm was equal to79 mg.g^{-1}.

The equilibrium data were further analyzed using the Freundlich model. The calculated Freundlich isotherm constants and the corresponding coefficients of determination are shown in Table 4.

The magnitude of the exponent *n* gives an indication on to what extent the sorption process is favourable where generally values of *n* in the range 2–10, in 1-2 or less than 1 represent good, moderately difficult or poor sorption characteristics, respectively [29]. The results show that the value of *n* was superior to 2 indicating that the sorption is favourable.

In order to check the validity of these models, it is interesting to recalculate the sorbed amount using the calculated constant parameters determined using the non linear forms. The simulated curves at 25°C determined using Freundlich and Langmuir model isotherms are given in Figure 6. The Langmuir model isotherms generate a best fit of equilibrium data than Freundlich isotherm (Figure 6).

Table 3. Kinetic parameters for sorption of lead (II) ions onto Reed.

C_0 (mg L^{-1})	Pseudo-first-order			
	k_1	q_e (cal) mg g^{-1}	R^2	q_e (exp) mg g^{-1}
10	0.017	2.11	0.365	16.24
30	0.036	4.79	0.482	46.80
50	0.033	6.63	0.533	68.01
70	0.032	16.83	0.701	69.26
90	0.032	10.21	0.635	73.54
C_0 (mg L^{-1})	Pseudo-second-order			
	k_2	q_e (cal) mg g^{-1}	R^2	q_e (exp) mg g^{-1}
10	0.047	16.39	0.999	16.24
30	0.026	47.62	1	46.80
50	0.021	71.44	1	68.01
70	0.006	71.43	0.999	69.26
90	0.012	76.92	0.999	73.54

Table 4. Langmuir and Freundlich constants for sorption of lead (II) ions by Reed using the non-linear method.

Langmuir	q_{mon}	79.17
	K_L	0.408
	R^2	0.998
Freundlich	K_F	24.48
	$1/n$	0.315
	R^2	0.834

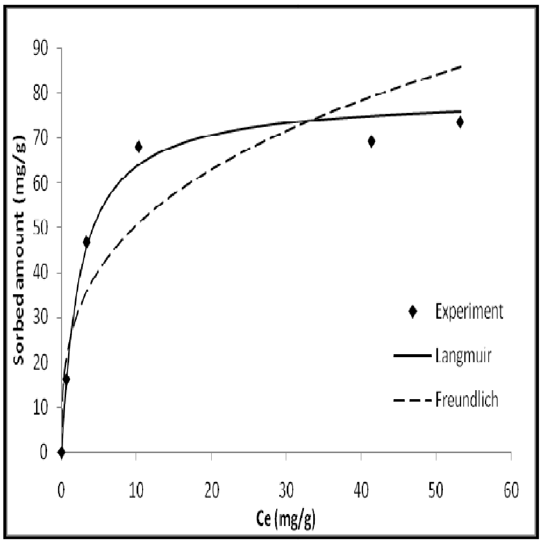

Figure 6. Sorption isotherms of PB (II) ions onto Reed.

IV. Conclusions

The results revealed the potential of Reed, an agricultural material, to be a low-cost sorbent for removing Pb(II) ions from aqueous solutions. The sorption process was found to be contact time, initial concentration, ionic strength and adsorbent dose dependent. The kinetic study of the sorption of Pb(II) showed that the pseudo-second-order model provided better correlation of the sorption data than the pseudo-first-order model. This suggested that the rate-limiting step might be chemical sorption rather than diffusion.

The Freundlich and Langmuir isotherm models were used to represent the equilibrium data. Obtained results indicated that the sorption equilibrium data fitted well by the Langmuir isotherm model in the studied concentration range. Maximum sorption capacity calculated from the Langmuir isotherm was equal to 79 mg.g^{-1} at an initial pH of 5.8. These results showed that this very low commercial value adsorbent might be effectively used for removal of Pb(II) ions from aqueous waste systems in favour of environmental protection purposes.

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