Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Özcan, A. Safa , Özcan, Adnan , Tunali, Sibel , Akar, Tamer , Kiran, Ismail and Gedikbey, Tevfik(2007) 'Adsorption Potential of Lead(II) Ions from Aqueous Solutions onto *Capsicum annuum* Seeds', Separation Science and Technology, 42: 1, 137 — 151

To link to this Article: DOI: 10.1080/01496390600956977

URL: http://dx.doi.org/10.1080/01496390600956977

Separation Science and Technology, 42: 137–151, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600956977

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Abstract: The purpose of this work was to evaluate the adsorption potential of *Capsicum annuum* seeds, in a batch system for the removal of lead(II) ions from aqueous solutions. The experimental results showed that this agricultural by-product was effective in removing lead(II) ions. The FT-IR analysis indicated that the mechanism involved in adsorption of lead(II) ions by seeds of *C. annuum* was mainly attributed to lead(II) binding of amino and hydroxyl groups. Adsorption equilibrium approached within 40 min. The adsorption data fitted well to the Langmuir isotherm model. The maximum adsorption capacity ($q_{\max}$) was 1.87×10^{-4} mol g^{-1}. Pseudo-second-order kinetic model was applicable to all the adsorption data over the entire time range. The thermodynamic parameters indicated that the adsorption process is spontaneous since Gibbs free energy values are negative, which are between -26.92 and -30.77 kJ mol^{-1} at the temperature range of 20–50°C.

Keywords: Agricultural by-products, adsorption, heavy metals, isotherm, kinetics, *Capsicum annuum* seeds

Received 14 March 2006, Accepted 20 July 2006

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INTRODUCTION

The release of hazardous substances such as heavy metals and dyes into receiving waters cause a big concern from the environmental point of view. Their removal is one of the important issues in many industrialized countries due to their toxic properties such as being mutagenic and carcinogenic (1, 2). For instance, acute lead poisoning can affect the gastrointestinal tract and the nervous system (3). As a result, many methods have been developed and used for this purpose. These involve a combination of physical and chemical processes such as chemical precipitation, adsorption, ultrafiltration, color irradiation, membrane filtration, ion-exchange, and coagulation. However, their use is restricted because of incomplete removal, low selectivity, high cost, and energy consumption (4, 5).

In recent years considerable attention has been focused on the use of biological materials and their byproducts as adsorbent agent for the removal of heavy metals and organic pollutants from contaminated aqueous solutions. This is because they carry a wide range of adsorption sites such as carboxyl, hydroxyl, amino, sulphydryl, and phosphates groups over their surfaces to biosorp hazardous materials through ion-exchange, complexation, and adsorption. Moreover, they can be cheaply and easily produced in considerably substantial quantities (6, 7). These make them an attractive alternative adsorbent over commonly used adsorbing materials such as activated carbon, which is costly to use for the removal of such dangerous chemicals from polluted industrial wastes (8).

Researchers have reported many biological materials for lead(II) ions removal. These include *Cephalosporium aphidicola* (9), *Neurospora crassa* (10), *Botrytis cinerea* (11), *Aspergillus niger* (12), *Rhizopus arrhizus* (13), *Mucor rouxii* (14), *Marine-algae* (15), *Pinus sylvestris* (16), tree fern (17), crop milling waste (black gram husk) (18), *Phellinus badius* (19), and apple residues (20). One of these materials, which is called *Capsicum annuum* seeds, produced as by-product from sauce production industry. In a recent study, we reported about the ability of *C. annuum* seeds to biosorp copper(II) ions from aqueous solutions (21).

In this study, the removal of lead(II) ions, present in an aqueous solution, using *C. annuum* seeds as the adsorbent agent was investigated. Lead is a very toxic metal and released into water and land-based environment through automobiles and battery manufacturers and may reach high concentration, especially near the discharge site. The effects exerted on ecosystems vary enormously and are of great economic and environmental importance (22). The influence of experimental parameters on the adsorption process, such as pH, contact time, initial lead(II) concentration, and temperature has been examined. Two adsorption isotherm models, the Langmuir and Freundlich, have been used to determine the best-fitting isotherm model for the experimental data. The kinetics and thermodynamic parameters for the adsorption of lead(II) ions onto *C. annuum* seeds were also investigated.

MATERIALS AND METHODS

Adsorbent Preparation

The *C. annuum* seeds used in this study were purchased from a local market. The seeds were separated, extensively washed with deionized water, and then dried at 80°C in an oven. This was followed by crushing and sieving the dried adsorbent to select the particle size of 300 μm by using ASTM standard sieve and stored in a desiccator for further use.

Lead(II) Solutions

A stock solution of lead(II) was prepared by dissolving an accurate quantity of $Pb(NO_3)_2$ in deionized water. Other concentrations varied between 75 and 300 mg dm^{-3} were prepared from stock solution by dilution. The pH of the working solutions was adjusted to desired values by the addition of either 0.1 M HNO_3 or 0.1 M NaOH solutions. Fresh dilutions were prepared and used for each experiment. All chemicals were of analytical grade.

Adsorption Experiments

Adsorption experiments were performed at different pH values, adsorbent feeds, initial lead(II) concentrations, and various temperatures. The batch experiments were carried out in a beaker (100 cm^{-3}) closed with parafilm to avoid evaporation at an agitation speed of 200 rpm on a magnetic stirrer.

Firstly, the effect of the solutions pH on the adsorption capacity of lead(II) ions onto *C. annuum* by-product was examined by equilibrating the adsorption mixture with dried adsorbent (0.1 g) and 50 cm^{-3} of 100 mg dm^{-3} lead(II) solution, adjusting the pH value between 1 and 5.5. The effect of adsorbent concentration on lead(II) adsorption was also determined using adsorbent samples ranging from 0.4 to 6.0 g dm^{-3} at 50 cm^{-3} of 100 mg dm^{-3} lead(II) solution and pH of 5.0 for 1 h at 20°C. Then, the binding capacity of the adsorbent was assessed, varying the lead(II) concentration within the range of 75–300 mg dm^{-3}. The optimum pH and adsorbent concentrations were determined as 5.0 and 4.0 g dm^{-3}, respectively and used throughout all adsorption experiments. When the adsorption procedure was completed, the solutions were centrifuged at 4500 rpm for 2 min and the supernatants were then analyzed for residual lead(II) ion concentrations.

Finally, kinetic experiments were carried out as follows: a constant adsorbent concentration of 4.0 g dm^{-3} was taken and mixed with 100 mg dm^{-3} lead(II) solution at various time intervals between 10 and 90 minutes and temperatures of 20, 30, 40, and 50°C. The remaining concentration of lead(II) ions was determined as described above.

Analytical Methods

The final lead(II) concentrations of the solutions were analyzed using an atomic absorption spectrophotometer (Hitachi 180-70, Japan) with an air-acetylene flame. Deuterium background correction was used. Infrared spectra of dried and lead(II) loaded *C. annuum* seeds prepared as KBr discs were recorded in a Bruker Tensor 27 infrared spectrophotometer.

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR spectra of dried unloaded and lead(II)-loaded *C. annuum* seeds in the range of 400–4000 cm^{-1} were taken and compared with each other to obtain information on the nature of the possible adsorbent-metal ion interactions and presented in Fig. 1. The broad stretching absorption bands at 3280–3303 cm^{-1}, represent –NH and bonded –OH groups. The intensities of these bands decreased only in the FTIR spectrum of lead(II)-loaded *C. annuum* seeds. The changes in the intensities decrease of the amino and hydroxyl groups in FTIR spectrum indicated that these two groups were possibly involved in the lead(II) adsorption. The bands observed at 2865 and 2927 cm^{-1} are assigned to the symmetric and asymmetric stretching vibrations of the $-CH_3$ and $-CH_2$ groups and their bending vibrations are 1371 and 1445 cm^{-1} for unloaded and lead(II)-loaded *C. annuum* seeds. Carbonyl stretching band of un-ionized carboxylates of adsorbent was observed at 1745 cm^{-1}. The bands at 1650 cm^{-1} and 1540 cm^{-1} correspond to carbonyl stretching vibration of amide considered to be due to the combined

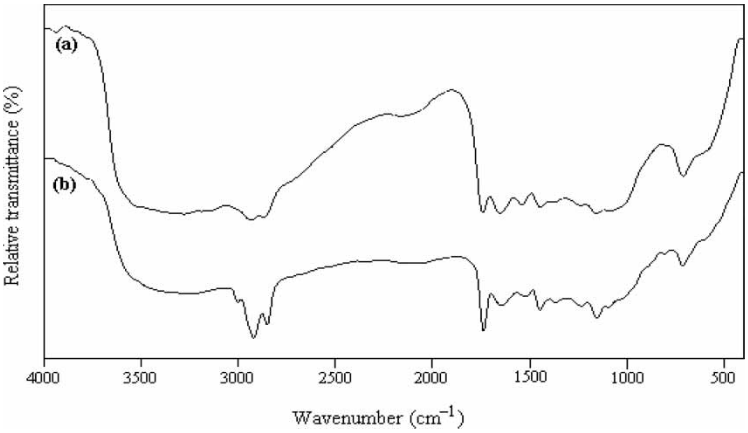

Figure 1. FTIR spectra of (a) unloaded and (b) lead(II) loaded *C. annuum* seeds.

effect of double-bond stretching vibrations (23) and –NH deformation band for unloaded and lead(II)-loaded *C. annuum* seeds, respectively. Their intensities in the spectrum of unloaded adsorbent decrease and separately the –NH deformation band shifts to 1526 cm^{-1}in the lead(II)-loaded adsorbent. This behavior reflects the interaction between the amino groups and metal ions. Therefore, *C. annuum* seeds provide more adsorption sites for lead(II) ions.

The 1085 cm^{-1} band is due to C-O stretching of carbonyl groups and the bending vibration of hydroxyl groups for unloaded *C. annuum* seeds but the disappearance of this band after the lead(II)-loaded *C. annuum* seeds suggests that this type of functional group is likely to participate in metal binding.

Effect of pH

As can be easily seen from Fig. 2, the uptake of lead(II) ions by *C. annuum* seeds is directly related to the pH of the solution. There was no lead(II) adsorption onto the adsorbent in the pH range of 1–2. The reason could be that the adsorbent surface was completely protonated, resulting in repulsion of positively charged lead(II) ions from interacting with the functional groups on the adsorbent surface (12). The adsorption capacity was then

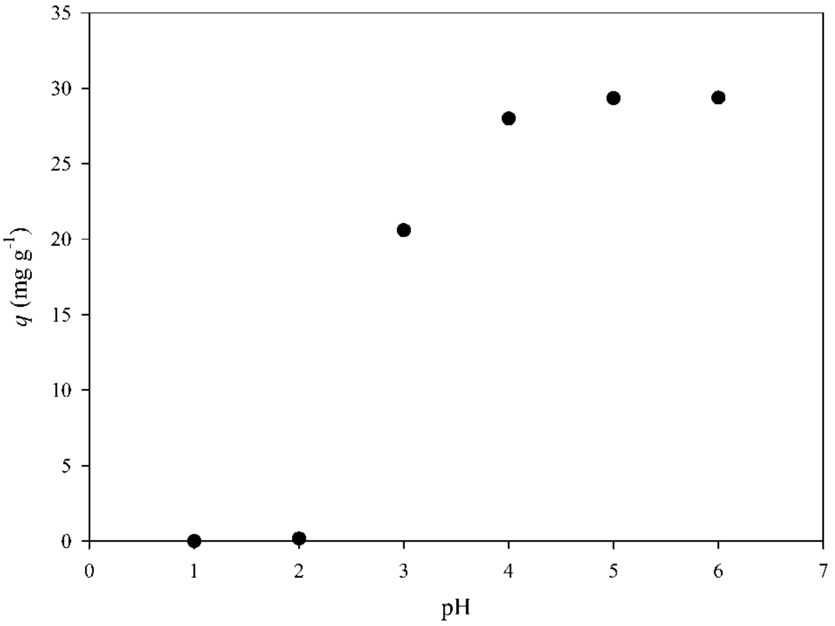

Figure 2. Effect of pH for lead(II) ions adsorption onto *C. annuum* seeds at 20°C.

sharply increased after pH 2 and reached the maximum level at pH 5 and then it stayed constant until pH 5.5. This could be attributed to an electrostatic interaction between the negatively charged adsorbent and the positively charged lead(II) ions. Experiments were not conducted beyond pH 5.5 due to the fact that lead(II) precipitation appears at higher pH values and interferes with the accumulation or adsorbent deterioration (24, 25).

Effect of Adsorbent Concentration on Lead(II) Removal

Figure 3 presents the effect of adsorbent concentration for lead(II) ions adsorption onto *C. annum* seeds. As can be seen from the figure, the application of different adsorbent dosage has a direct effect on the lead(II) uptake. Varying the adsorbent mass from 0.4 to 3.0 g dm^{-3} increases the percentage lead(II) removal at equilibrium from 10 to 85% and reaches a maximum point of 90% at 4.0 g dm^{-3} adsorbent concentration. Further increase in the adsorbent concentration does not change the adsorption ratio which stays constant up to 6.0 g dm^{-3} adsorbent concentration. This may be attributed to the number of possible binding sites increasing as the adsorbent concentration rises and then reaching a saturation point after

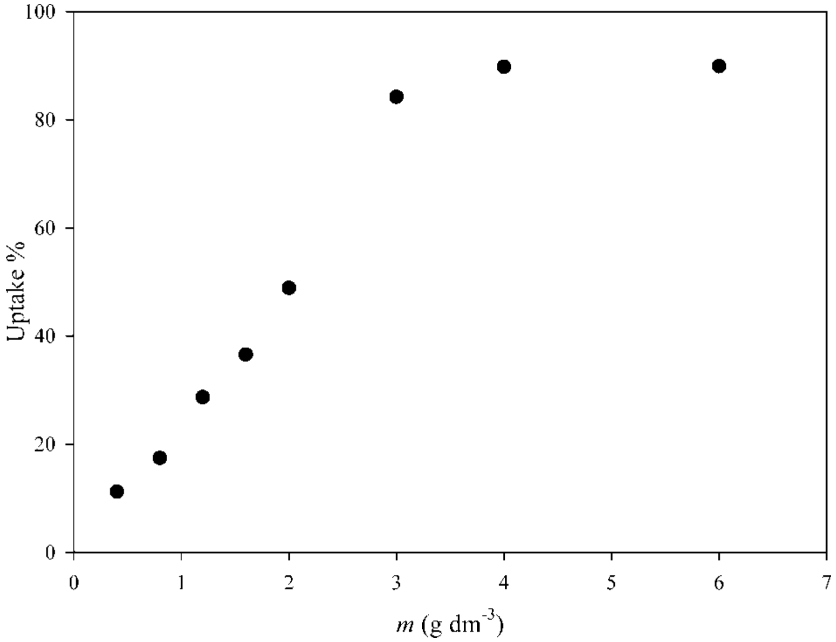

Figure 3. Effect of adsorbent concentration for lead(II) ions adsorption onto *C. annuum* seeds at 20°C.

which no further lead(II) ions adsorption occurs (16). Therefore, 4.0 g dm^{-3}- adsorbent concentration was selected as the optimum value for the adsorption experiments.

Effect of Equilibrium Contact Time

The adsorption capacity of lead(II) ions removed by *C. annuum* seeds versus contact time is depicted in Fig. 4. It can be seen that the adsorbed amount of lead(II) ions increased with contact time up to 40 min, after that a maximum removal is attained. For this reason, the optimum contact time was chosen as 40 min for further experiments.

Effect of Temperature on Metal Uptake

The equilibrium adsorption capacity of lead(II) ions onto *C. annuum* seeds was favored at higher temperatures. This may show that adsorption of lead(II) ions onto adsorbent is in endothermic nature. When the temperature increases from 20 to 50°C, the adsorption capacity goes up from 21.56 to 24.10 mg g^{-1} at an equilibrium time of 40 min. Below equilibrium time, an

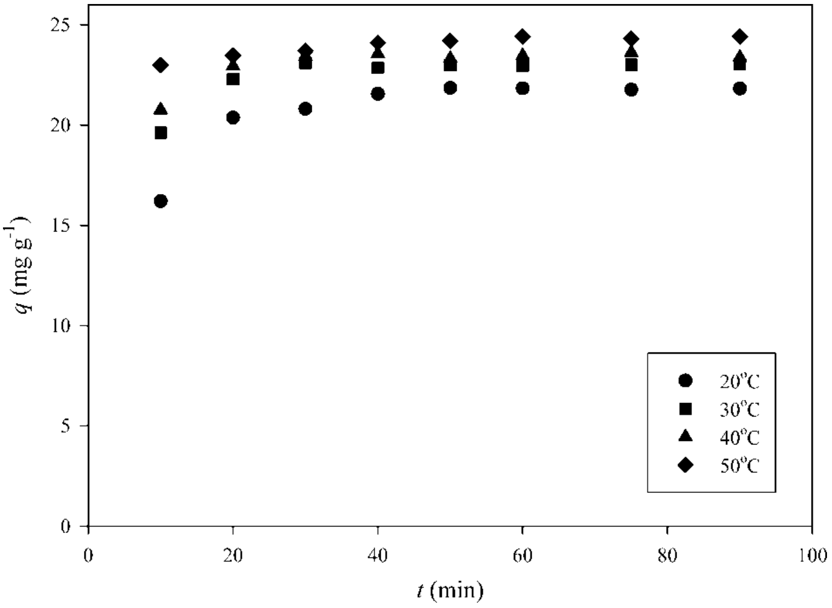

Figure 4. The effect of contact time for lead(II) ions adsorption onto *C. annuum* seeds at various temperatures.

increase in the temperature leads to an increase in the lead(II) ions adsorption, which indicates a kinetically controlling process. After reaching the equilibrium, the uptake increases with increasing temperature. This effect may be explained by the availability of more active sites of adsorbent at higher temperatures.

Adsorption Isotherms

Two linear isotherm model equations; Langmuir (26) and Freundlich (27), are used for the estimation of adsorption mechanism between lead(II) ions and *C. annuum* adsorbent.

Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{q_{\max} K_L}\right)\frac{1}{C_e} \tag{1}$$

Freundlich equation:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{2}$$

where $q_{\max}$ is the maximum amount of adsorption (mol g^{-1}), q_e is the equilibrium adsorption capacity (mol g^{-1}) and C_e is the equilibrium solution concentration (mol dm^{-3}), K_L is the Langmuir adsorption constant (dm^3 mol^{-1}) related to the free energy of adsorption, K_F (dm^3 g^{-1}) and n (dimensionless) are the Freundlich isotherm constants. The plots of the linear form of the Langmuir and Freundlich adsorption isotherms for the removal of lead(II) ions onto *C. annuum* seeds obtained at the temperatures of 20–50°C are illustrated in Figs. 5 and 6 and isotherm model parameters are listed in Table 1. These results showed that the surface of *C. annuum* seeds is made up of homogeneous adsorption patches. In other words, Langmuir isotherm model fits very well when the r^2 values are compared in Table 1.

The maximum adsorption capacity ($q_{\max}$) of adsorbent calculated from Langmuir isotherm equation defines the total capacity of the adsorbent for lead(II) ions. The adsorption capacity of the adsorbent increased with increasing the temperature. The highest value of $q_{\max}$ obtained at 50°C is 1.87×10^{-4} mol g^{-1}. It appears to be the highest in comparison with the uptake obtained at the other temperatures (Table 1).

The Langmuir isotherm can also be expressed by means of a dimensionless constant, R_L, which is referred as a separation factor or equilibrium parameter (28). It provides information about whether the adsorption process is spontaneous or nonspontaneous and is calculated by using the following equation,

$$R_L = \frac{1}{1 + K_L C_o} \tag{3}$$

where C_o is the highest initial lead(II) ions concentration (mol dm^{-3}).

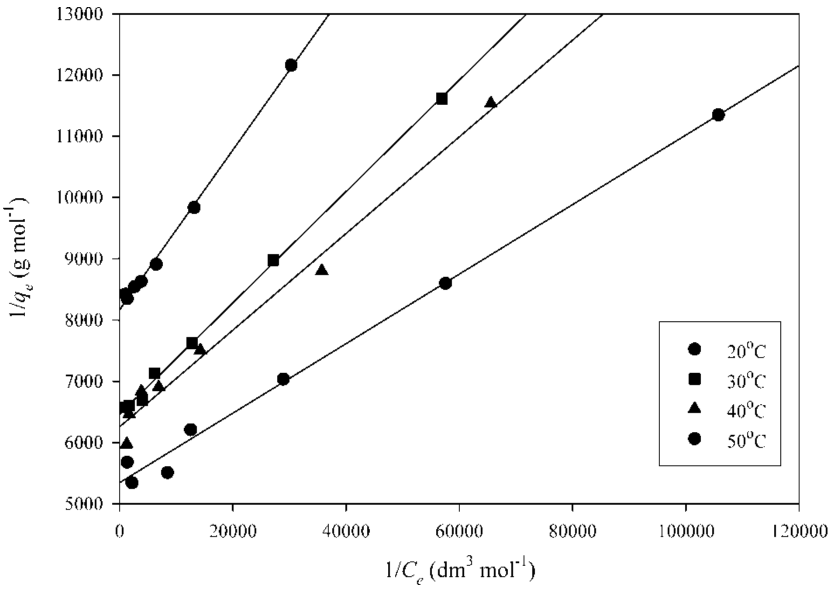

Figure 5. Langmuir plots for lead(II) ions adsorption onto *C. annuum* seeds at various temperatures.

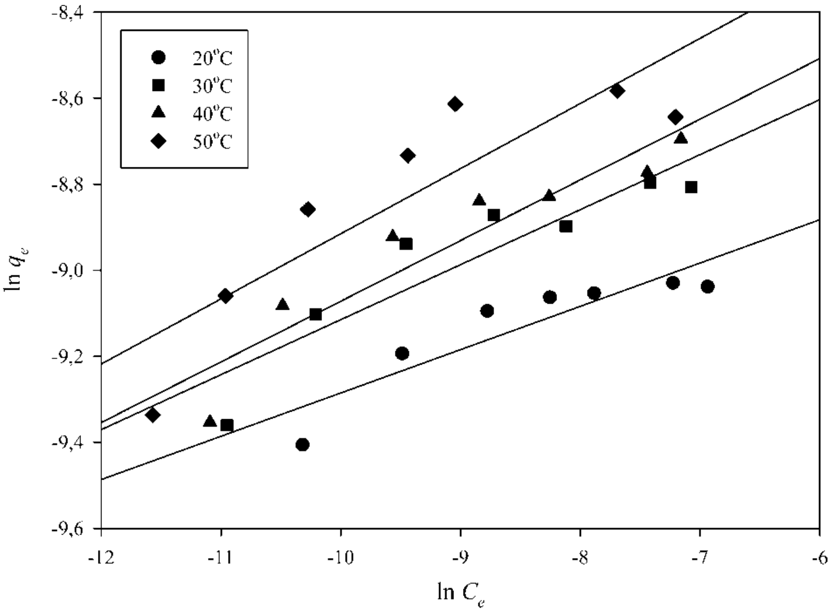

Figure 6. Freundlich plots for lead(II) ions adsorption onto *C. annuum* seeds at various temperatures.

Table 1. Isotherm constants for the adsorption of lead(II) ions onto *C. annuum* seeds at various temperatures

	Langmuir				Freundlich		
t(°C)	q_{max} (mol g^{-1})	K_L (dm^3 mol^{-1})	r_L^2	R_L	n	K_F (dm^3 g^{-1})	r_F^2
20	1.22×10^{-4}	6.26×10^4	0.997	1.09×10^{-2}	9.931	2.54×10^{-4}	0.811
30	1.55×10^{-4}	7.10×10^4	0.998	9.64×10^{-3}	7.819	3.95×10^{-4}	0.837
40	1.60×10^{-4}	7.92×10^4	0.985	8.65×10^{-3}	7.092	4.70×10^{-4}	0.879
50	1.87×10^{-4}	9.41×10^4	0.993	7.29×10^{-3}	6.605	6.10×10^{-4}	0.782

The values of R_L calculated from equation (3) are tabulated in Table 1. As the R_L values lie between 0 and 1, the adsorption process is favorable (28). Further, the R_L values for this study at all temperatures studied are between 1.09×10^{-2} and 7.29×10^{-3}, therefore, the adsorption is spontaneous.

Adsorption Kinetics

The pseudo-second-order kinetic model (29) (Equation (4)) was used to elucidate the mechanism of the adsorption process.

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \tag{4}$$

where q_2 is the maximum adsorption capacity (mg g^{-1}) for the pseudo-second-order adsorption, q_t is the amount of lead(II) ions adsorbed at equilibrium at time t (mg g^{-1}), k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). Values of k_2 and q_2 can be calculated by plotting t/q_t values versus t (Fig. 7).

The pseudo-second-order kinetic parameters for the adsorption of lead(II) ions onto *C. annuum* seeds are given in Table 2. As can be seen from Table 2, the adsorption of lead(II) ions onto *C. annuum* seeds follows

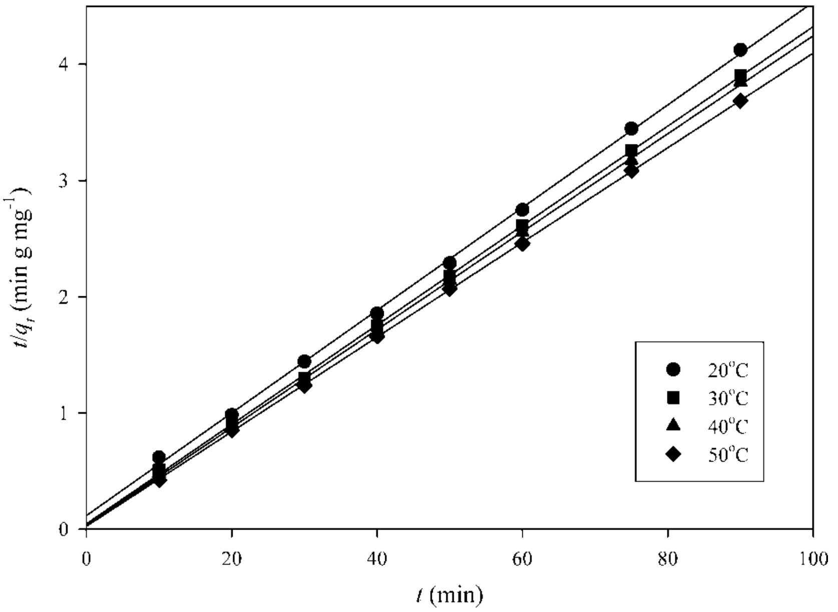

Figure 7. Pseudo-second-order kinetic plots for lead(II) ions adsorption onto *C. annuum* seeds at various temperatures.

Table 2. Pseudo-second-order kinetic parameters for the adsorption of lead(II) ions onto *C. annuum* at various temperatures

t (°C)	k_2 (g mg^{-1} min^{-1})	q_2 (mg g^{-1})	r_2^2
20	1.67×10^{-2}	22.63	0.999
30	3.92×10^{-2}	23.37	0.999
40	5.47×10^{-2}	23.73	0.999
50	6.56×10^{-2}	24.62	0.999

the pseudo-second-order kinetic model with the high correlation coefficients of 0.999 at all the temperatures studied.

The pseudo-second-order rate constants indicate a steady increase from 1.67×10^{-2} to 6.56×10^{-2} g mg^{-1} min^{-1} with an increase in the solution temperatures from 20 to 50°C (Table 2), indicating that the adsorption of lead(II) ions onto *C. annuum* seeds is rate-controlled.

Thermodynamic Parameters

The values of the equilibrium constants required for the calculation of the Gibbs free energy (ΔG^o), the enthalpy (ΔH^o) and the entropy (ΔS^o) changes are estimated by solving the Langmuir isotherm equation for the parameter K_L. The thermodynamic parameters were estimated using the following equations.

$$\Delta G^o = -RT \ln K_L \tag{5}$$

$$\ln K_L = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{6}$$

The values of $\Delta H^o$and ΔS^o, calculated from the slope and the intercept of the straight line from Fig. 8 obtained by plotting ln K_L against $1/T$. The results of the Gibbs free energy (ΔG^o) obtained are -26.92 kJ mol^{-1} at 20°C, -28.15 kJ mol^{-1} at 30°C, -29.37 kJ mol^{-1} at 40°C and -30.77 kJ mol^{-1} at 50°C. The negative values of ΔG^oat all temperatures studied are due to the fact that the adsorption process is spontaneous. The positive value of ΔH^o(+10.44 kJ mol^{-1}) suggests the endothermic nature of adsorption. The positive value of ΔS^o(+127.34 J K^{-1} mol^{-1}) suggests increased randomness at the solid/solution interface during the adsorption of lead(II) ions onto *C. annuum* seeds.

CONCLUSIONS

This study has conducted the adsorption of lead(II) ions onto one of the agricultural by-products *C. annuum* seeds from aqueous solutions. The maximum

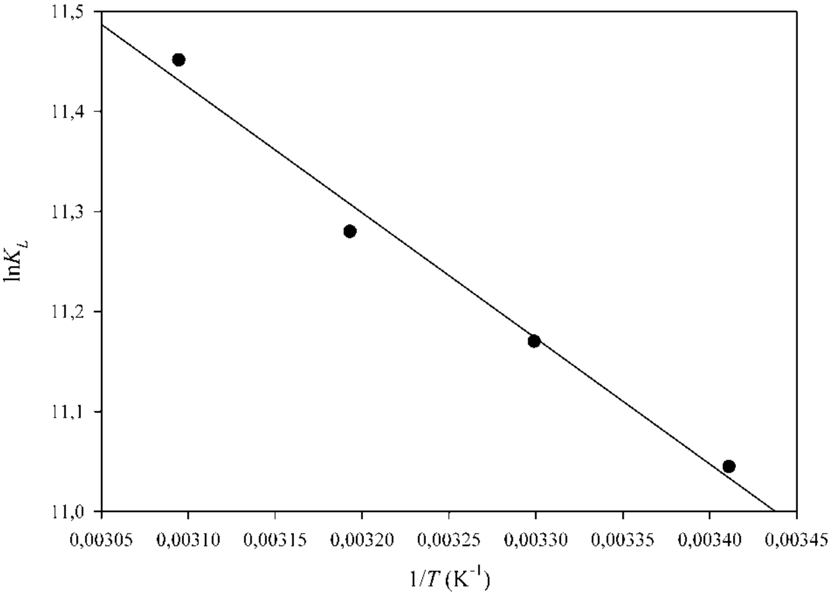

Figure 8. Plot of $K_L$versus $1/T$ for estimation of thermodynamic parameters for lead(II) ions adsorption onto *C. annuum* seeds.

adsorption capacity of *C. annuum* seeds for the removal of lead(II) ions was obtained at pH 5. Experiments were performed as a function of pH, contact time and temperature.

The Langmuir and Freundlich isotherm models were used for the mathematical description of the adsorption of lead(II) ions onto *C. annuum* seeds depending on temperature and the isotherm constants were deduced from these isotherm models. Results indicated that the adsorption equilibrium data fitted very well to Langmuir isotherm model in the concentration range at all temperatures studied. The kinetics of lead(II) ions adsorption onto *C. annuum* seeds was based on the assumption of the pseudo-second-order mechanism. The negative values of ΔG^o confirm a favorable adsorption of lead(II) onto *C. annuum* seeds and the positive value of ΔH^o leads to an endothermic nature of adsorption. It may be concluded from the above results that *C. annuum* seeds can be used for the elimination of heavy metal pollution from wastewater due to the fact that it is a low-cost, abundant, and locally available adsorbent.

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