Calligonum crinitum as a novel sorbent for sorption of Pb(II) from aqueous solutions: Thermodynamics, kinetics, and isotherms

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Abstract

Calligonum crinitum, a desert plant, was used as a natural adsorbent for the removal of Pb(II) ions from aqueous solutions. The sorption capacity of the sorbent was investigated through batch adsorption, as a function of contact time, metal ion concentration, and pH. The surface chemistry of the sorbent was probed using Fourier transform infrared spectroscopy, allowing an understanding of the key functionalities involved in binding the Pb(II) ions to the sorbent. Textural characteristics, including surface area and pore volume, showed higher surface areas relative to other natural adsorbents previously reported. Surface morphological analysis, observed via SEM images and EDX analysis, confirmed adsorption of Pb(II) ions, up to 71% on the surface of calligonum crinitum. Isothermal analysis, using Langmuir, Freundlich and Temkin models with nonlinear regression, showed the Langmuir model to best represent adsorption within this system, yielding a maximum adsorption capacity of 337 mg g⁻¹ (pH 5.5, 30 °C). The Freundlich constant of <10 indicates that adsorption of Pb(II) ions is favourable onto calligonum crinitum. Adsorption kinetics were modelled using pseudo-first-order, pseudo-second-order and intra-particle diffusion models; the results indicate that the kinetics are pseudo-second-order, suggesting a degree of chemical influence in the adsorption process. While thermodynamic analysis shows the process to be exothermic in nature with an ordering of solute within the adsorption process. Calligonum crinitum has, therefore,

1 been proven as an effective sorbent for the removal of Pb(II) ions from aqueous solutions, with
2 potential in water remediation processes.

3 **Keywords:** Sorption, Pb(II) ions, calligonum crinitum, kinetics, isotherms

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1. Introduction

Heavy metals are non-biodegradable and persist in water bodies long after release. Contamination by heavy metals, including lead, is an increasing threat to global environmental, ecological, and nutritional balances. The main source of lead in water bodies is, not only industrial effluent but also, the natural erosion and corrosion of lead pipes in water systems[1, 2]; there are numerous health hazards associated with lead; it is known to be absorbed by red blood cells and aggregate in the bones, brain, muscles, and kidneys, causing cancer and acute conditions including neurological and nervous disorders, and Alzheimer's disease [3]. The effects of lead exposure in children are much greater and long-term exposure may impact IQ levels[4]. Lead poisoning is considered irreversible, therefore, it becomes essential to remove such species from the water systems. According to the Environmental Protection Agency, the concentration of lead, Pb(II), ions in industrial wastewaters approaches 200–500 mg L⁻¹ whereas, the acceptable limit is 0.05 mg L⁻¹[5].

A number of methods have been suggested for the amelioration of lead pollution, however, adsorption processes offer many advantages over other routes, including precipitation, ion exchange, reverse osmosis, cementation, electrodialysis and coagulation[6]. These latter processes are expensive and inadequate for small scale industries due to constraints such as low selectivity, low percentage retention, energy consumption and generation of sludge. By contrast, water treatment utilising natural materials as sorbents for the removal of pollutants is a simple, cost effective and accessible method. Based on surface phenomena, pollutants may bind to the surface of the sorbent via physisorption or chemisorption. Several studies have shown that natural materials [7, 8], or agriculture waste[9], offer potential as sorbents for the elimination of heavy metal ion pollutants from aqueous media. A previous study [10] reports the adsorption efficiency of tea, maize cobs, and sawdust for the removal of Pb(II) ions from water bodies, and, in this context, abundant desert plants are potential sorbents for the removal of heavy metal ions from water [11-13].

The work presented here focuses on the utilization of a desert plant, calligonum crinitum, as an adsorbent for the enhanced sorption of Pb(II) ions from aqueous media, by studying the impact of pH, contact time, sorbent dosage on sorptive capacity. The working behaviour of a sorbent can be predicted by establishing a correlation between key system parameters and the sorption equilibrium, as described by isotherms[14]. Here, Langmuir, Freundlich and Temkin models were used to analyse the experimental data obtained, using non-linear regression analysis to determine the most appropriate model. Additional analysis on kinetic and thermodynamic results provides insight into the mechanism of adsorption for Pb(II) ions onto calligonum crinitum, and its suitability for use in water treatment systems.

2. Materials and Methods

2.1. Materials and Reagents

Calligonum crinitum, lead acetate, nitric acid, sodium hydroxide, sodium carbonate, Ethylenediaminetetraacetic acid (EDTA), hydrochloric acid, ethyl alcohol, and acetone were procured from Merck, Germany and were used without any further processing.

2.2. Sorbent Preparation

Calligonum crinitum, is a desert plant widespread in Saudi Arabia and was acquired from Shaqra Desert (Saudi Arabia). The roots and stems were separated and rinsed with distilled water. The washing procedure was repeated until the filtrate was colourless to ensure the removal of unwanted particles adhered to the surface. Only the roots were processed as they contain the highest cellulose content. Hence, stem separated roots were dried using an electric oven for 3 h at 105°C, followed by grinding and then filtering through a 120 µm sieve.

2.3. Sorbent Characterization

The functional moieties on the surface of calligonum crinitum and resulting chemical linkages for Pb(II) loaded calligonum crinitum were determined using Fourier Transform Infrared

1 Spectroscopy (FTIR) spectroscopy. A Perkin–Elmer Spectrum 1000 spectrophotometer was used to
2 record spectra for KBr discs (2–10 mg sample in 300 mg KBr) with scan interval 1 cm^{-1} over 4000–
3 400 cm^{-1} . Resultant vibrational frequencies were assigned to functional groups present on the
4 surface of the adsorbent and to verify subsequent binding of Pb(II) ions.

5 Morphological analyses of sorbent samples were undertaken using Scanning Electron Microscopy
6 (SEM) (Model JEOL-JSM-5600; accelerating voltage 25 kV); images of sample morphology were
7 recorded at 2000x magnification to identify the surface characteristics and morphology of
8 calligonum crinitum before and after Pb(II) adsorption. Prior to analysis, samples were sputter
9 coated with a thin layer of gold (Polaron Diode Sputter unit). Energy-dispersive X-ray (EDX)
10 spectrometry (Oxford Instruments attached to an SEM Model JEOL-JSM-5600) was used to examine
11 the presence or absence of Pb(II) ions, on Pb(II)-loaded calligonum crinitum, through the
12 characteristic band.

13 Textural analysis of calligonum crinitum was performed at 77 K using nitrogen adsorption measured
14 on an Autosorb I system (Quantachrome); surface area was determined using Brunauer-Emmett-
15 Teller theory (BET) and pore size was evaluated using Barrett-Joyner-Halenda (BJH) theory.

16 The pH at point of zero charge (pH_{PZC}) of calligonum crinitum was evaluated via a solid addition
17 method [15]. Analysis followed the addition of 100 ml of 0.01 N NaCl into a series of Erlenmeyer
18 flasks, with pH adjustment (2 to 6) through addition of 0.01 N HCl solution and 0.01 N NaOH, and
19 subsequent addition of a weighed mass of adsorbent material. Initial pH was measured and
20 recorded prior to solid addition, while final pH was recorded after a 24 h incubation period. The
21 initial and final pH were plotted with the intersection indicating the value of pH_{PZC} for the adsorbent.

22 *2.4. Experimental*

23 Adsorption experiments were conducted by adding 0.03 g of the adsorbent to 100 ml of Pb(II) ion
24 solution in sealed conical flasks, and the pH adjusted via addition of 0.1 M HNO_3 or 0.1 M NaOH.

After the predefined contact time, direct titration of the filtered solution was performed against EDTA solution to determine the Pb(II) ion concentration before and after adsorption. The equilibrium adsorption capacity, q_e (mg g⁻¹), was calculated using:

$$q_e = \frac{(C_o - C_e) \cdot V(l)}{W} \quad (1)$$

While the respective percentage removal of Pb(II) ions was calculated via:

$$\text{Removal\%} = \frac{C_o - C_e}{C_o} \times 100\% \quad (2)$$

where C_o and C_e are the initial Pb(II) ion concentration and Pb(II) concentration at equilibrium, respectively. W is the weight (g) of the calligonum crinitum and V is the volume (L) of Pb(II) ion solution.

2.5. Error analysis

In order to determine the most appropriate model for adsorption equilibrium and kinetic interpretation, an error function is used to evaluate the nonlinear models used. Minimum R^2 and ARE (Absolute Relative Error) values approaching unity were used as criteria to determine the fit of kinetic and isotherm models, to determine those that best describe the experimental data. The coefficient of determination (R^2) was determined via [16]:

$$R^2 = \frac{\sum (q_{ecal} - q_{mexp})^2}{\sum (q_{ecal} - q_{mexp})^2 + (q_{ecal} - q_{mexp})^2} \quad (3)$$

and absolute relative error (ARE) was evaluated via [17]:

$$ARE = \frac{100}{n} \sum_{i=1}^n \left[\frac{q_{e,i,cal} - q_{e,i,exp}}{q_{e,i,exp}} \right] \quad (4)$$

where n is the range of input data, q_{exp} , is experimental uptake, and q_{cal} , is the calculated uptake of Pb(II) ions.

3. Results and Discussion

3.1. Sorbent characterization

3.1.1. FTIR analysis

Figures 1a and b represent FTIR spectra of calligonum crinitum and Pb(II) loaded calligonum crinitum, respectively. The peaks observed signify the presence of several functional groups including carboxylate, hydroxyl, and methoxy groups that are potentially active in binding of metal ions, as expected for cellulose based adsorbents. The bending vibrations observed in the range of 1500 to 1200 cm^{-1} are assigned to C-H bonding, again expected for organic samples. It is notable that the peaks appear to be shifted in the Pb(II) ion loaded sample with weak-to-medium intensity peaks observed for this sample, possibly due to interactions between the metal ions and the sorbent, e.g. via chelation. The band at 3310 cm^{-1} , which is characteristic of O-H stretching on calligonum crinitum, is observed to have broadened and shifted to a lower wave number (3289 cm^{-1}), as shown by spectrum in Figure 1b, while the peak at 2930 cm^{-1} , ascribed to backbone C-H stretching vibration, is shifted to 2918 cm^{-1} , and the peak ascribed to carboxylate groups (1607 cm^{-1}) shifts to 1604 cm^{-1} . This latter shift, to a lower wave number, suggests that oxygen containing functional groups within the cellulosic structure of the adsorbent are active sites for attachment of metal ions. This is supported by the shift in the stretching vibrations of C-OH and C-O-C bonds, from 1027 cm^{-1} to 1042 cm^{-1} , after the adsorption of Pb(II) ions [9].

3.1.2. Morphological analysis

Surface morphologies of calligonum crinitum and Pb(II) loaded calligonum crinitum samples are represented in Figure 2. This technique reveals a disordered material with varied pore type, which is heterogeneous with a large void space. There is no significant difference in the morphology of the adsorbent after the adsorption of Pb(II) ions (Figure 2b), suggesting that the sorbent can be potentially be commercialised for sorption processes. The presence of sharp peaks, corresponding to elemental Pb in the Pb(II) loaded calligonum crinitum sample affirms the adsorption of Pb(II) onto

1 the surface of the adsorbent. Adsorption of Pb(II) ions is validated through elemental analysis,
2 indicating a significant uptake of 71% Pb within the surface composition of Pb(II) loaded calligonum
3 crinitum.

4 The textural analysis of calligonum crinitum was determined via N₂sorption isotherms. The values for
5 BET surface area (8 m² g⁻¹) and total pore volume (0.02 cm³ g⁻¹) were observed to be low. The
6 average pore width (11 nm) is within the mesoporous range[18], therefore, the material can
7 potentially be used for aqueous phase applications by enabling adsorption and mass transport of
8 Pb(II) ions. Previous studies have reported that low surface area does not necessarily negatively
9 impact the adsorption capacity, with other adsorbents of low surface area showing high metal
10 adsorption [19]. This is attributed to efficient binding between the metal species and the relevant
11 chemical moieties on the surface of the adsorbent.

12 *3.2. Factors affecting sorption of Pb(II) ions*

13 *3.2.1 Point of zero charges (pH_{PZC}) and the effect of pH*

14 The data obtained for pH_{PZC} is presented in Figure 3, and the pH_{PZC} value of calligonum crinitum was
15 determined to be 6.0, at which the surface of adsorbent is neutral in nature. When the pH value is
16 higher than the pH_{PZC}, that is, in the basic range, the surface charge of the adsorbent, being negative
17 will favour the binding of cations whereas, lower pH values lower than the pH_{PZC}(i.e. more acidic)
18 indicate positive surface charge, hence the binding of cations will be unfavourable[17]. While it is
19 expected that basic conditions would be beneficial to cation adsorption, pH values higher than 6.0
20 can lead to formation and precipitation of Pb ion complexes and therefore, adsorption cannot be
21 studied at pH values above 6.0[20]. Figure 4 shows the effect of pH on the sorption of Pb(II) ions by
22 calligonum crinitum in the range pH 2–6, and an initial Pb(II) ion concentration of 400 mg L⁻¹. As
23 expected, the results obtained show the adsorption of Pb(II) ions increase from 0 to 177.3 mg g⁻¹
24 with an increase in pH, however, maximum adsorption (322.9 mg g⁻¹) is obtained at a pH just below
25 the pH_{PZC}, at 5.5. At low pH, the surface of the adsorbent is positive, and adsorbate has to compete

with positive ions for the adsorption sites. As the pH increases, the competing effect diminishes and Pb(II) ions can adsorb easily onto available binding sites of the adsorbate [21].

3.2.2 Effect of sorbent dosage

Previous reports have suggested that the dosage of adsorbent in the solution affects the adsorption capacity. Therefore, the influence of calligonum crinitum dosage was studied in the range of 0.3-10 g L⁻¹ at pH 5.5, with an initial Pb(II) ion concentration of 400 mg L⁻¹. Figure 5 presents data obtained, in terms of the adsorption capacity for Pb(II) ions. It can be observed that adsorption capacity decreases from 322.9 to 37.4 mg g⁻¹, as adsorbent dosage increases to 10 g L⁻¹. This decrease is ascribed to a significant quantity of unsaturated sorption sites causing a relative decrease per unit mass, as well as overlapping of sorption sites, and overcrowding of the adsorbent particles, as has been previously reported [14].

3.2.3 Effect of contact time

The sorption capacity of calligonum crinitum for Pb(II) ions was determined with respect to the contact time of the adsorbent and metal species, as shown in Figure 6. The contact time ranged from 0 to 300 min, with an initial concentration in the range of 200 to 600 mg L⁻¹, and an adsorbent dosage of 0.3 g L⁻¹. As can be seen from Figure 6 the degree of adsorption increases with agitation time; and it is notable that, for the adsorptive concentration of 200 mg L⁻¹, equilibrium was achieved within 60 min, while for concentrations higher than 200 mg L⁻¹, equilibrium is achieved after ~180 min. The attainment of equilibrium is attributed to the occupation of vacant sites as adsorption progresses, resulting in no further increase in the adsorption of Pb(II) ions once all available sites are occupied, offering no further interaction points. Overall, the observed duration of equilibration time is relatively short [22], hence, this material is viable for water treatment from this aspect.

3.2.4. Isothermal analysis of Pb(II) ion sorption on calligonum crinitum

To study the interactions occurring between the adsorbent and metal ions, the adsorption isotherms were analysed to allow interpretation of the adsorption systems and the bound species. All isothermal data analysed was obtained for sorption of Pb(II) ions onto 0.3 g L⁻¹ of calligonum crinitum, at pH 5.5, allowing an equilibration time of 60 min and plotted as mass (q_e , mg g⁻¹) against equilibrium concentration (C_e mg L⁻¹). Langmuir, Freundlich and Temkin models[23-25] were used to model the adsorption isotherm data, and, hence, determine the maximum uptake capacity for adsorption of Pb(II) ions onto calligonum crinitum at 30 °C. Table 1 presents ARE and R² values for each model, and selection of the most appropriate model was based on a combination of highest R² value and lowest ARE values; using these criteria (Table 1), the isothermal models can be ordered Langmuir > Temkin > Freundlich. Langmuir model in providing the best overall fit for adsorption of Pb(II) onto calligonum crinitum (Figure 7). Consequently, Langmuir analysis provides the best level of fit, and the value of maximum adsorption capacity was evaluated as 336.9 mg L⁻¹ for Pb(II) ions onto the surface of calligonum crinitum. In addition, the Langmuir model is based on the assumption that the ions form a complete monolayer on the surface of the adsorbent, which suggests that the adsorption behaviour is influenced by homogenous character of the sorbent. The value of the Langmuir equilibrium constant K_L (10.3 L g⁻¹) shows a good affinity between the metal ions and the adsorbent. Meanwhile, the Freundlich model provides a reasonable level of fit (Table 1), therefore, the values determined from this fit can be additionally used to understand this system. The value of n (5.5) falls within the range 0-10, which indicates that the adsorption of Pb(II) ions onto calligonum crinitum is favourable, which is supported by the isotherms obtained. Calligonum crinitum adsorbent offers a high level of affinity for the removal of Pb(II) ions, as compared to other natural adsorbents previously reported[22].

3.4. Sorption kinetics

Further to studying the equilibrium adsorption behaviour for this system, it is essential to understand the sorption kinetics of the processes occurring, which gives an indication of the charging characteristics of the material, as well as providing insight into the mechanism of sorption.

In the present work, the kinetics of Pb(II) ion sorption was examined via three models: pseudo-first-order, pseudo-second-order, and intra-particle diffusion.

The pseudo-first-order model is based on diffusion control and is classed as physical adsorption. The nonlinear pseudo-first-order represented by the following equation[24]

$$q_t = q_e[1 - \exp(-k_1 t)] \quad (5)$$

where q_t is the quantity of Pb(II) ions sorbed in mg g^{-1} at time t (min), q_e is the quantity of Pb(II) ions sorbed(mg g^{-1}) at equilibrium, and the rate constant of sorption is given by k_1 (min^{-1}). Plots using the pseudo first-order equation to model adsorption of Pb(II) ions onto calligonum crinitum, in the range of initial concentrations of 200-600 mg L^{-1} , are shown in Figure 8. The values of k_1 , and q_e along with the R^2 and ARE determined for the fits are shown in Table 2.

The pseudo-second-order kinetic model [25] is represented by:

$$q_t = \frac{k_2 q_e^2 t}{(1 + k_2 k_e t)} \quad (6)$$

where q_t , q_e and t are as previously defined, and the rate constant, in this case, is defined by k_2 ($\text{g mg}^{-1} \text{min}^{-1}$). The pseudo-second-order model presumes that the rate of sorption is controlled by the sharing of electrons between the sorbent and sorbate, meaning that the interaction is defined as a chemical process. Plots of non-linear fits of the pseudo-second-order model for the adsorption of Pb(II) ions onto calligonum crinitum, at concentrations 200- 600 mg L^{-1} , are shown in Figure 9. The rate constant (k_2) and q_e values calculated for this study, along with the R^2 and ARE values determined for the fits are summarised in Table 1; it is evident that the pseudo-second-order model correlates well with the experimental data and ARE and R^2 values are optimised in comparison with the pseudo-first-order model for all concentrations studied. This suggests that the adsorption of Pb(II) onto calligonum crinitum occurs via a chemical interaction [26].

The overall kinetics of sorption process by intra-particle diffusion [27], is represented by:

$$q_t = k_{id}t^{0.5} + C \quad (7)$$

where q_t , and t are as previously defined, and the rate constant for intra-particle diffusion is k_{id} ($\text{mg g}^{-1}\text{min}^{1/2}$). Previous reports have stated that a plot of q_t vs. $t^{1/2}$ shows multi-linear steps correlating with different modes of control within the sorption process [26]. Due to bulk diffusion effects, the initial segment is curved, followed by a linear segment, which is ascribed to intra-particle diffusion, before the system ultimately reaches equilibrium. The thickness of the boundary layer can be interpreted by the intercept values of these lines, where a larger intercept denotes a greater boundary effect [16]. The rate limiting step for the adsorption process occurring for this system, was determined from the rate of diffusion, which includes the transport of Pb(II) ions to the interior surface of the pores in calligonum crinitum from bulk solution. It has been reported that, for batch experiments, the rate is controlled by the transfer of Pb(II) ions from solution into the pores of the adsorbent [27]. Intra-particle diffusion rate parameters (k_p) were determined for four initial concentrations of Pb(II) ions and the data is presented in Figure 10 and listed in Table 2. The graphical results show a two-segment linear plot, which indicates that the mechanism of sorption of Pb(II) on calligonum crinitum could be controlled by more than two steps. Initially, rapid diffusion occurs, which is followed by intra particle diffusion until the system approaches equilibrium. k_p is defined by the slope of the plot where intra particle diffusion rate is the controlling factor (Table 2) and, due to the difference in mass transfer rate between the initial and final adsorption stages, the second segment deviates from the origin. Overall, the three kinetic models, evaluated using non-linear regression, show that the sorption kinetics for the sorption of Pb(II) ions onto calligonum crinitum are most appropriately modelled by a pseudo-second-order model, followed by intra-particle, and finally pseudo-first-order.

3.5 Adsorption Thermodynamics

Process temperatures can be crucial in determining the efficacy of adsorbent materials, altering the effective working capacity as a consequence of thermodynamic effects, hence the adsorption capacity of Pb(II) ions onto calligonum crinitum was studied at pH 5.5 and an adsorbent dose of 0.3 g L⁻¹, at 30, 40, and 50°C (Figure 11). Thermodynamic parameters, including the standard free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated through the application of Equations 8-10 [28]. The standard free energy (ΔG°) was calculated from the relationship:

$$\Delta G^\circ = -RT \ln a_L \quad (8)$$

where a_L is the Langmuir constant, R is the universal gas constant (8.31441 J/mol·K) and T is the absolute temperature (K). The Langmuir constant, a_L , can be used in the van't Hoff equation to determine the enthalpy change, ΔH° , of the adsorption process as a function of temperature as follows:

$$\ln\left(\frac{a_{L2}}{a_{L1}}\right) = \frac{\Delta H^\circ}{R} \cdot \frac{(T_2 - T_1)}{T_1 T_2} \quad (9)$$

where a_{L1} , a_{L2} and a_{L3} are the Langmuir constants at 30, 50 and 60 °C, respectively. The data presented in Table 3 shows that a negative value was obtained for ΔH° in the range of 30–50 °C, which suggests that the adsorption process of Pb(II) ions onto calligonum crinitum is exothermic over this temperature range, indicative of a physisorption process. Finally, the entropy change (ΔS°) was calculated from Equation 10:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

and the negative value of ΔS° in the range of 30–50 °C, is related to a decrease in randomness at the solid/solution interface during the adsorption of Pb(II) ions onto calligonum crinitum, as expected for adsorption of solute from an aqueous media.

3.6. Adsorption mechanism

Previous studies have reported a number of different adsorption phenomenon in the systems studied, including ion-exchange, surface adsorption, chemisorption, complexation, and adsorption–complexation, with ion exchange being the most prevalent[6]. Here, it has been determined that the equilibrium adsorption data is most appropriately described by the Langmuir isotherm model, while a pseudo-second-order kinetic model provides the best fit to the experimental kinetic data obtained for adsorption of Pb(II) ions onto calligonum crinitum. While applied to different data, both of these models assume that the adsorbent surface contains reactive functional groups to bind Pb(II) ions. The Langmuir model indicates that the surface is homogenous, and the pseudo-second-order model suggests that the mechanism involves chemisorptions, with the sharing or exchange of ions between Pb(II) ions and the adsorbent. Cation exchange occurs where Pb(II) ions attach themselves to the adjacent carboxyl or hydroxyl group to form chelated compounds; as indicated above, this chemical reaction involves electron donation from the functional groups, present on the surface of calligonum crinitum, via ion exchange, to bind the Pb(II) ions onto the surface of the adsorbent, resulting in the release of hydrogen ions into the bulk solution [29, 30]. Surface characterisation of calligonum crinitum pre- and post-adsorption supports these findings, which is influenced by intramolecular dispersion, involving movement of Pb(II) ions from the bulk solution to the boundary of the adsorbent particles, diffusion of Pb(II) ions to the external surface of the sorbent, sorption at the adsorbent surface sites and, finally, intra-particle diffusion of the Pb(II) ions to the internal pores of the sorbent.

4. Conclusions

Calligonum crinitum was prepared as an adsorbent for the removal of Pb(II) ions from aqueous media. It was demonstrated that the sorption capacity of calligonum crinitum was influenced by sorbent dosage, pH, contact time and Pb(II) ion initial concentration, and the results used to determine optimal adsorption conditions. Using these ideal conditions, isothermal equilibrium data

obtained for sorption of Pb(II) ion on calligonum crinitum were collected and analysed using two-parameter isotherm models, with the best fit determined using non-linear regression analysis. The results obtained showed that the maximum adsorption capacity, according to the Langmuir equation, was 336.9 mg g⁻¹ at 30 °C. Thermodynamically, the system shows exothermic character and a decrease in disorder of the system, indicative of physical processes within the mechanism and an ordering of the solute on the adsorbent surface. The kinetics of adsorption of Pb(II) ions onto calligonum crinitum were analysed using a series of models, evaluated by non-linear regression, and the results confirming that pseudo-second-order kinetic and intra-particle diffusion models are the most appropriate, which suggests that adsorption occurs via a chemical interaction, between the surface functional groups and the cations in solution. The overall process is also influenced by bulk diffusion effects and intra-particle diffusion; however, it is notable that equilibrium can be achieved in less than 60 minutes for optimal conditions. Consequently, calligonum crinitum has been shown to be a potential sorbent for the removal of Pb(II) ions from aqueous solutions, such as water treatment processes.

References

1. Barakat, M., *New trends in removing heavy metals from industrial wastewater*. Arabian journal of chemistry, 2011. **4**(4): p. 361-377.
2. Dong, L., et al., *Removal of lead from aqueous solution by hydroxyapatite/magnetite composite adsorbent*. Chemical Engineering Journal, 2010. **165**(3): p. 827-834.
3. Needleman, H., *Lead poisoning*. Annu. Rev. Med., 2004. **55**: p. 209-222.
4. Organization, W.H., *Childhood lead poisoning*. 2010.
5. Brooks, R.M., et al., *Removal of lead from contaminated water*. International journal of soil, sediment and water, 2010. **3**(2): p. 14.
6. Arbabi, M., S. Hemati, and M. Amiri, *Removal of lead ions from industrial wastewater: A review of Removal methods*. International Journal of Epidemiologic Research, 2015. **2**(2): p. 105-109.
7. Abdel-Ghani, N., M. Hefny, and G.A. El-Chaghaby, *Removal of lead from aqueous solution using low cost abundantly available adsorbents*. International Journal of Environmental Science & Technology, 2007. **4**(1): p. 67-73.
8. Abdel-Halim, S., A. Shehata, and M. El-Shahat, *Removal of lead ions from industrial waste water by different types of natural materials*. Water Research, 2003. **37**(7): p. 1678-1683.
9. Singha, B., et al., *Cr (VI) ions removal from aqueous solutions using natural adsorbents-FTIR studies*. Journal of Environmental Protection, 2011. **2**(06): p. 729.

10. Salem, A. and R.A. Sene, *Removal of lead from solution by combination of natural zeolite–kaolin–bentonite as a new low-cost adsorbent*. Chemical engineering journal, 2011. **174**(2-3): p. 619-628.
11. Hashem, A., H.A. Hammad, and A. Al-Anwar, *Modified Camelorum tree particles as a new adsorbent for adsorption of Hg (II) from aqueous solutions: kinetics, thermodynamics and non-linear isotherms*. Desalination and Water Treatment, 2016. **57**(50): p. 23827-23843.
12. Hashem, A. and S.M. Badawy, *Sesbania sesban L. biomass as a novel adsorbent for removal of Pb (II) ions from aqueous solution: non-linear and error analysis*. Green Processing and Synthesis, 2015. **4**(3): p. 179-190.
13. Baig, T., et al. *Adsorption of heavy metal ions by the biomass of Solanum elaeagnifolium (Silverleaf night-shade)*. in *Proceedings of the 1999 conference on Hazardous Waste Research*. 1999.
14. Hashem, A., et al., *Isotherms and kinetic studies on adsorption of Hg (II) ions onto Ziziphus spina-christi L. from aqueous solutions*. Green Processing and Synthesis, 2016. **5**(2): p. 213-224.
15. Malandrino, M., et al., *Adsorption of heavy metals on vermiculite: influence of pH and organic ligands*. Journal of Colloid and Interface Science, 2006. **299**(2): p. 537-546.
16. Kannan, N. and M.M. Sundaram, *Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study*. Dyes and pigments, 2001. **51**(1): p. 25-40.
17. Kapoor, A. and R. Yang, *Correlation of equilibrium adsorption data of condensable vapours on porous adsorbents*. Gas Separation & Purification, 1989. **3**(4): p. 187-192.
18. Thommes, M., et al., *Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)*. Pure and Applied Chemistry, 2015. **87**(9-10): p. 1051-1069.
19. Hu, M., H. Tian, and J. He, *Unprecedented Selectivity and Rapid Uptake of CuS Nanostructures toward Hg (II) Ions*. ACS applied materials & interfaces, 2019. **11**(21): p. 19200-19206.
20. Akpomie, K.G., F.A. Dawodu, and K.O. Adebowale, *Mechanism on the sorption of heavy metals from binary-solution by a low cost montmorillonite and its desorption potential*. Alexandria Engineering Journal, 2015. **54**(3): p. 757-767.
21. Hashem, A., H.A. Hammad, and A. Al-Anwar, *Chemically modified Retama raetam biomass as a new adsorbent for Pb (II) ions from aqueous solution: non-linear regression, kinetics and thermodynamics*. Green Processing and Synthesis, 2015. **4**(6): p. 463-478.
22. Hashem, A., et al., *Aminated Hydroximoyl Camelthorn Residues as a Novel Adsorbent for Extracting Hg (II) From Contaminated Water: Studies of Isotherm, Kinetics, and Mechanism*. Journal of Polymers and the Environment, 2020: p. 1-13.
23. Freundlich, H., *Über die adsorption in lösungen*. Zeitschrift für physikalische Chemie, 1907. **57**(1): p. 385-470.
24. Temkin, M., *Kinetics of ammonia synthesis on promoted iron catalysts*. Acta physiochim. URSS, 1940. **12**: p. 327-356.
25. Langmuir, I., *The constitution and fundamental properties of solids and liquids. Part I. Solids*. Journal of the American chemical society, 1916. **38**(11): p. 2221-2295.
26. Tütem, E., R. Apak, and Ç.F. Ünal, *Adsorptive removal of chlorophenols from water by bituminous shale*. Water Research, 1998. **32**(8): p. 2315-2324.
27. Poots, V., G. McKay, and J. Healy, *Removal of basic dye from effluent using wood as an adsorbent*. Journal (Water Pollution Control Federation), 1978: p. 926-935.
28. Gupta, V.K., *Equilibrium uptake, sorption dynamics, process development, and column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag, a low-cost adsorbent*. Industrial & Engineering Chemistry Research, 1998. **37**(1): p. 192-202.

- 1 29. Vazquez, G., et al., *Removal of cadmium and mercury ions from aqueous solution by sorption*
2 *on treated Pinus pinaster bark: kinetics and isotherms*. Bioresource technology, 2002. **82**(3):
3 p. 247-251.
- 4 30. Yu, L.J., et al., *Adsorption of chromium from aqueous solutions by maple sawdust*. Journal of
5 hazardous materials, 2003. **100**(1-3): p. 53-63.

Fig. 1: FT-IR of Calligonum crinitum (a) and calligonum crinitum-loaded Pb(II) ions(b).

Fig. 2: SEM of *Calligonum crinitum*(a, b and c) at different magnification, calligonum crinitum-loaded Pb(II) ions(d) and EDX of calligonum crinitum loaded –Pb(II) ions (e).

Fig. 3 Point of zero charge (PZC) of Calligonum crinitum surface

Fig. 4 Effect of pH on adsorption capacity of Pb(II) ions onto Calligonum crinitum at 30 °C. Reaction Conditions: adsorbent conc., 0.3 g/l; contact time, 2h; reaction temperature, 30 °C; Pb(II), 400 mg/l; particle size range, 50-120 μ m.

Fig. 5 Effect of adsorbent concentration onto both adsorption capacity and % removal of Pb(II) ions onto Calligonum crinitum at 30 °C. Reaction Conditions: pH, 5.5; contact time, 2h; reaction temperature, 30 °C; Pb(II), 400 mg/l; particle size range, 50-120 μ m.

Fig.6 Effect of contact time and adsorbate concentrations on adsorption capacity of Pb(II) ions onto Calligonum crinitum at 30°C.

Reaction Conditions: Adsorbent conc., 0.3 g/l; pH, 5.5; reaction temperature, 30 °C; particle size range, 50-120 μ m.

Fig. 7: Comparison between the two parameter models and experimental data.

List of Tables

Table 1: Isotherm constants of two-parameter models for Pb(II) ions adsorption onto calligonum crinitum at 30 °C.

Isotherm Model	Parameter	Value	Error Analysis	Value
Langmuir	a_L	0.0305 L/mg	R^2	0.9993
	q_{max}	336.9 mg/g	ARE	0.1209
	k_L	10.29 L/g		
Freundlich	n	5.54	R^2	0.9971
	K_F	100mg/g	ARE	0.2708
Temkin	A_T	1.510 L/g	R^2	0.9987
	b_T	53.33 mg/L	ARE	0.1956

Table 2: Kinetic parameters for the adsorption of Pb(II) ions onto calligonum crinitum at different initial concentrations.

Parameters	$C_o(\text{mg L}^{-1})$			
	100	200	300	600
$q_e \text{ exp (mg/g)}$	202.3	284.5	322.4	366.7
Pseudo-first-order				
$q_e(\text{mg/g})$	366.7	366.7	366.7	366.7
$K_1(1/\text{min})$	0.1663	0.1663	0.1663	0.1663
R^2	0.9933	0.9933	0.9933	0.9933
ARE	0.6485	0.6485	0.6485	0.6485
Pseudo-second-order				
$q_e(\text{mg/g})$	376.6	376.6	376.6	376.6
$K_2(\text{g/mg.min})$	0.0001	0.0001	0.0001	0.0001
R^2	0.9986	0.9986	0.9986	0.9986
ARE	0.2675	0.2675	0.2675	0.2675
Intra-Particle				
k_{id}	5.7325	5.7325	5.7325	5.7325
C	297.34	297.34	297.34	297.34
R^2	0.9976	0.9976	0.9976	0.9976
ARE	0.4117	0.4117	0.4117	0.4117

Table 3: Thermodynamic parameters of Pb(II) ions onto calligonum crinitum

Temp. (°C)	$\Delta G^\circ(\text{kJ mol}^{-1})$	$\Delta H^\circ(\text{kJ mol}^{-1})$	$\Delta S^\circ(\text{J K}^{-1} \text{mol}^{-1})$
30	8.7884	-50.8101	-50.8445
40	10.7554		
50	8.6347		

Table 1: Isotherm constants of two-parameter models for Pb(II) ions adsorption onto Calligonum crinitum at 30 °C.

Isotherm Model	Parameter	Value	Error Analysis	Value
Langmuir	a_L	0.030547018 (l/mg)	R^2	0.999331647
	k_L	10.29047176 (l/g)	ARE	0.120850905
Freundlich	n	5.539956357	R^2	0.997172748
	K_F	100 (mg/g)	ARE	0.270836797
Tempkin	A_T	1.509738376 (l/g)	R^2	0.998727268
	b_T	53.33369883 (mg/l)	ARE	0.195645322

Table 2: Kinetic parameters for the adsorption of Pb(II) ions onto Calligonumcrinitum at different initial concentrations.

Parameters	$C_e(\text{mg/l})$			
	200	300	400	600
$q_e \text{ exp}(\text{mg/g})$	202.3109	284.4998	322.4331	366.6886
Pseudo-first-order				
$q_e(\text{mg/g})$	366.6881716	366.6881716	366.6881716	366.6881716
$K_1(1/\text{min})$	0.166255252	0.166255252	0.166255252	0.166255252
R^2	0.993268222	0.993268222	0.993268222	0.993268222
ARE	0.648546843	0.648546843	0.648546843	0.648546843
Pseudo-second-order				
$q_e(\text{mg/g})$	376.6378119	376.6378119	376.6378119	376.6378119
$K_2(\text{g/mg.min})$	0.000992455	0.000992455	0.000992455	0.000992455
R^2	0.998616129	0.998616129	0.998616129	0.998616129
ARE	0.267464452	0.267464452	0.267464452	0.267464452
Intra-Particle				
k_{id}	5.732470778	5.732470778	5.732470778	5.732470778
C	297.3355227	297.3355227	297.3355227	297.3355227
R^2	0.997575708	0.997575708	0.997575708	0.997575708
ARE	0.41173233	0.41173233	0.41173233	0.41173233

Table 3: Thermodynamic parameters of Pb(II) ions onto Calligonumcrinitum at 30 °C

Temp. (K)	$\Delta G^\circ(\text{KJ.mol}^{-1})$	$\Delta H^\circ(\text{KJ.mol}^{-1})$	$\Delta S^\circ(\text{JK}^{-1}.\text{mol}^{-1})$
303	8.78842	-50.8101	-50.8445
313	10.75537		
323	8.634674		