



## Green Process for Lead Ions Uptake from Polluted Aqueous Medium

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### Abstract

The removal of lead cations from aqueous solutions was studied under different experimental conditions using dried cactus cladodes powder (DCCP) as a biosorbent. It was found that Pb(II) biosorption is sensitive to the solution pH, biosorbent dosage, lead ions initial concentration, contact time and temperature. The increase in these parameters enhanced Pb<sup>2+</sup> retention. Among the pseudo-first and second-order kinetic models, the biosorption kinetics was well described by the pseudo-second-order model. The equilibrium experimental data fitted very well to the Langmuir model, assuming a monolayer and uniform Pb<sup>2+</sup> biosorption. Moreover, the thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ) determined from the temperature-dependent isotherms, showed that lead ions' retention by DCCP was spontaneous, endothermic and feasible in the temperature range 20-60°C. Regarding the mechanism, EDS and FTIR analyses revealed the retention of Pb<sup>2+</sup> by DCCP through exchange of magnesium and potassium cations and complexation involving primarily carboxyl and hydroxyl functional groups. Conclusively, the findings of the present study highlighted that Dried Cactus Cladodes Powder could be a cost-effective and ecological alternative for the restoration of pb(II) contaminated aqueous sources.

### 1. Introduction

Recently, environment pollution with heavy metal ions has worldwide attracted more attention due to its drastic rise over the last decades. One of the main sources of such environment contamination is the growing industrialization associated with an excessive generation of wastewaters. The huge volumes of liquid wastes released from industry are often loaded with one or more heavy metal ions (Cd, Pb, Zn, Cr, Mn...). These ions are extremely harmful to humans, aquatic organisms, and other life forms because of their toxicity, carcinogenicity, accumulation, and non-biodegradable nature. Accordingly, there is a considerable need to remove heavy metal ions from industrial effluents before discharge to protect the environment and public health.

The common methods actually available for wastewaters treatment are sorption [1] chemical precipitation [2], solvent extraction [3], reverse osmosis [4], ion exchange [5], filtration [6], and electrochemical treatment [7]. Among these techniques, sorption is often considered as the most suitable for metal ions removal due to its high efficiency, easy handling and availability of different sorbents. However, the expensive cost of conventional sorbents remains the main limit of this process. With the intention to avoid this drawback, the use of local cheap materials has recently emerged as a promising

alternative for heavy metals removal. In spite of several works dealing with the retention of metal ions from aqueous wastes using various biomaterials [8-15], the search for suitable, natural and low-cost sorbents is still needed.

The present work is therefore a contribution to the topic of natural materials valorization for environmental purposes. The objective is to investigate the retention of lead ions by dried cactus cladodes powder (DCCP). The reasons behind selecting cactus cladodes are numerous. For instance, but not limited to, these natural materials are cheap, abundant, available, sustainable, renewable and environmentally safe. Another point that supports our choice is its ability to bind metallic ions by the donation of electron pair and form complexes or exchange ions for metallic ones in solution. Moreover, cactus cladodes can be easily used as biosorbent in many cases without chemical addition or treatment at high temperature. In our case, as already mentioned, a cactus cladode powder was checked for lead ions uptake from polluted aqueous media. Particularly, we studied the influence of pH, Pb(II) initial concentration, biosorbent dosage, contact time and temperature on the biosorption efficiency. The Kinetics of Pb<sup>2+</sup> retention by DCCP was fitted by kinetic models. The experimental equilibrium biosorption data were analyzed by different isotherm models to determine the best fit isotherm equation. DCCP was characterized before and after biosorption using FTIR and EDS analyses to investigate the mechanisms involved in Pb<sup>2+</sup> retention.

## **2. Materials and methods**

### ***2.1 Biosorbent preparation and characterization***

Cactus cladodes were collected from El kef (North West of Tunisia). After manual separation of the spikes, the cladodes were washed with distilled water to remove the surface-adhered particles, then dried for 48 hours in an oven at 60°C until reaching a constant weight. After drying, the cladodes were ground and sieved to less than 212 µm. Finally, the obtained powder was stored in a glass bottle for further use without any pre-treatment. To identify the functional groups responsible for metal binding, a sample of the dried cactus cladodes powder (DCCP) was subjected to FTIR analysis using a NICOLET 560 spectrophotometer, Canada. The biosorbent surface morphology was examined by scanning electron microscopy (SEM) using a Quanta FEG 650 apparatus. Energy dispersive spectroscopy (EDS) was also carried out to highlight the change in the chemical composition of DCCP before and after Pb(II) biosorption.

### ***2.2 Lead solution preparation***

Analytical grade lead nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>] and distilled water were used for the preparation of a stock Pb<sup>2+</sup> solution of 1000 mg/L. Lead solutions of different concentrations were prepared by diluting the lead nitrate stock solution with distilled water. The initial pH was adjusted to the desired value using dilute solutions of HCl (0.1M) or NaOH (0.1M).

### ***2.3 Biosorption experiments***

All biosorption experiments were carried out in 50 ml capped flasks under constant mechanical stirring (250 rpm) at fixed initial pH and constant temperature using a thermostatic shaking water bath. At the end of each experiment, the suspension was centrifuged at 3600 rpm for five minutes to separate the liquid phase from the solid one. The concentration of Pb<sup>2+</sup> in the filtrate was determined using an analytical flame atomic absorption spectrometer (AAS VARIO 6). The biosorbent phase concentrations  $q_t$  of Pb<sup>2+</sup> were calculated based on the following equation:

$$q_t = \frac{(C_0 - C_t) * V}{w} \quad \text{Eqn. 1}$$

where  $C_0$  and  $C_t$  are the initial and at time  $t$  Pb(II) concentrations (ppm), respectively,  $V$  (ml) is the volume of the solution and  $w$  (g) is the biosorbent mass.

The respective effects of the solution's initial pH, biosorbent dosage,  $Pb^{2+}$  initial concentration and temperature on lead cations retention by DCCP were examined.

The study of solution's initial pH was held at 20°C using 100 ppm  $Pb^{2+}$  concentration and 10g/L of DCCP. The pH value was varied between 1.5 and 6 using 0.1 M HCl and NaOH solutions. Each experiment was conducted for 120 minutes which is sufficient time to achieve equilibrium. Concerning the effect of biosorbent dosage, it was determined for a  $Pb^{2+}$  initial concentration of 100 mg/L, an initial pH of 3, a temperature of 20°C and a contact time of 120 minutes. The biosorbent doses were varied from 0.4 to 20 g/L.

To study the impact of  $Pb^{2+}$  initial concentration and temperature, the biosorbent dosage was fixed at 4 g/L and pH at 3. Six  $Pb^{2+}$  initial concentrations (40, 50, 60, 70, 80, 90 and 100 ppm) were selected and a set of experiments was carried out. For each experiment 0.2 g of biosorbent and 50 ml of the considered  $Pb^{2+}$  solution were kept under stirring for different contact times ranging between 2.5 and 120 min at various temperatures (20, 30, 40, 50, 60°C). The results of these experiments were also used for the study of the kinetics, thermodynamics and biosorption isotherms.

## 2.4 Biosorption isotherms

A sorption equilibrium isotherm describes the relationship between the amount of solute sorbed onto a solid phase  $q_e$  (mg/g) and its concentration in the equilibrium solution  $C_e$  (mg/L) at a given constant temperature. This isotherm is of great importance as it determines the maximum biosorption capacity and the nature of sorption.

In the present work, Langmuir [16], Freundlich [17], Dubinin-Radushkevich [18] and Temkin [19] isotherm models were used to fit the equilibrium experimental data of Pb(II) retention by DCCP at five constant temperatures (20, 30, 40, 50, 60°C). These isotherms are briefly described in the next paragraph. The Langmuir isotherm theory [16] presumes monolayer solute adsorption on a homogeneous surface containing a finite number of energetically equivalent binding sites without interactions between sorbed species. It is based on the empirical model given by Eqn. 2, where  $C_e$  (mg/L) represents the equilibrium solute concentration,  $q_e$  (mg/g) the amount of solute sorbed at equilibrium,  $Q_m$  (mg/g) the adsorption capacity to form a complete monolayer coverage on the sorbent surface and  $K_L$  (L/mg) the Langmuir constant related to the sorption energy. The linearized form of Langmuir isotherm model is represented by Eqn. 3. The characteristic parameters of Langmuir isotherm  $K_L$  and  $Q_m$  were estimated from the intercept and the slope of the plot  $C_e/q_e$  versus  $C_e$ .

The essential features of Langmuir isotherm can also be expressed by a dimensionless constant separation factor ( $R_L$ ) defined in Eqn. 4, where  $C_0$  stands for the initial solute concentration (mg/L). The value of  $R_L$  indicates the type of isotherm to be either favorable ( $0 < R_L < 1$ ), irreversible ( $R_L = 0$ ), linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ) [20].

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad \text{Eqn. 2}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad \text{Eqn. 3}$$

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{Eqn. 4}$$

The Freundlich isotherm [17] is rather valid for a multilayer sorption onto a heterogeneous surface presenting different sites with several adsorption energies. The model of this isotherm is represented by Eqn. 5 and its linear form by Eqn. 6, where  $K_F$  ( $\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$ ) and  $n$  are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively, and can be estimated from the intercept and the slope of the linear plot  $\text{Ln}(q_e)$  versus  $\text{Ln}(C_e)$ . Depending on  $n$  value, the adsorption is considered poor ( $n < 1$ ), moderately difficult ( $1 < n < 2$ ) or good ( $2 < n < 10$ ) [21].

$$q_e = K_F C_e^{1/n} \quad \text{Eqn. 5}$$

$$\text{Ln } q_e = \text{Ln } k_F + \frac{1}{n} \text{Ln } C_e \quad \text{Eqn. 6}$$

Concerning the Dubinin-Radushkevich (D-R) model [18], expressed by Eqn. 7, it does not assume homogeneous surface or constant biosorption energy as the Langmuir model.

$$q_e = Q_m \exp\left(-K \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2\right) = Q_m \exp(-K \varepsilon^2) \quad \text{Eqn. 7}$$

Where  $Q_m$  ( $\text{mg}/\text{g}$ ) is the maximum amount of the metal ion that can sorb onto unit weight of sorbent,  $\varepsilon$  is the Polanyi potential which is equal to  $RT \ln(1 + 1/C_e)$ , where  $R$  and  $T$  are the universal gas constant ( $\text{kJ}/\text{mol K}$ ) and the absolute temperature ( $\text{K}$ ), respectively.

Finally, the Temkin isotherm [19] supposes that the adsorption heat of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions [22], and that adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. It is represented by the following equation:

$$q_e = \frac{RT}{b} \ln(K_T C_e) = B_1 \ln(K_T C_e) \quad \text{Eqn. 8}$$

Where  $B_1 = RT/b$ , is a constant related to the adsorption heat,  $R$  the universal gas constant ( $\text{J}/\text{molK}$ ),  $T$  the temperature ( $\text{K}$ ),  $b$  ( $\text{J}/\text{mol}$ ) the variation of adsorption energy and  $K_T$  ( $\text{L}/\text{mg}$ ) is the equilibrium binding constant corresponding to the maximum binding energy.

## 2.5 Biosorption kinetic modelling

The study of kinetics allows understanding the mechanisms of  $\text{Pb}^{2+}$  biosorption on DCCP. Two kinetic models (pseudo-first-order [23], pseudo-second-order [24]) were selected in our case to fit  $\text{Pb}^{2+}$  biosorption experimental data obtained for different initial concentrations (40-100ppm) and temperatures (20-60°C).

The original and linearized forms of these models are illustrated in Table1, where  $Q_e$  and  $Q_t$  (both in  $\text{mg}/\text{g}$ ) are respectively the amounts of  $\text{Pb}^{2+}$  adsorbed at equilibrium and at a given time  $t$  (min).  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g}/\text{min mg}$ ) are the rate constants of pseudo-first-order and pseudo-second-order models, respectively.  $Q_{eI}$  and  $Q_{eII}$  are the theoretical  $\text{Pb}^{2+}$  equilibrium concentrations on DCCP for the pseudo-first-order and the pseudo-second-order models, respectively. The best kinetic model was determined considering both linear regression correlation coefficient ( $R^2$ ) and the coherence between the calculated and experimental  $Q_e$ .

### 3. Results and Discussion

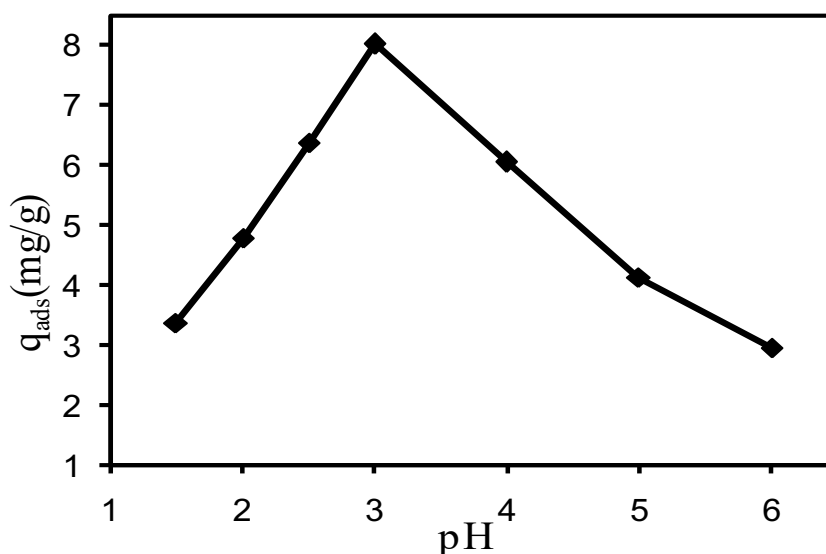
#### 3.1 Influence of the solution pH

The pH of the aqueous solution is a key experimental parameter controlling the metallic cation species and the adsorbent surface charge which are in turn responsible for the biosorption process. In our case, the pH effect was examined for values ranging between 1.5 and 6. The choice of this pH range is supported by the lead speciation diagram indicating the presence of lead cations mainly in  $Pb^{2+}$  form up to pH 6. Beyond this pH occurs the precipitation of lead hydroxide. **Figure 1** summarizes the removal of Pb(II) by dried cactus cladodes powder (DCCP) as a function of pH. It shows a rise of biosorption with pH increase, reaching an optimum value at pH 3. Thereafter it dropped.

The weak retention of  $Pb^{2+}$  at low pH can be attributed to the high concentration of proton ( $H^+$  or  $H_3O^+$ ) in the solution which compete with Pb(II) ions for the biosorbent surface. However, such competition decreased with increasing pH, thus favoring  $Pb^{2+}$  retention. In fact, the biosorption capacity of DCCP nearly tripled upon increasing the solution pH from 1.5 to 3.

**Table 1.** Original and linear forms of the used kinetic models and their characteristic parameters

| Kinetic model             | Original form                        | Linearized form   | Plots               | Deduced parameters                     |
|---------------------------|--------------------------------------|---|---------------------|--|
| Pseudo-first-order model  | $\frac{dQ_t}{dt} = k_1(Q_e - Q_t)$   | $Ln(Q_e - Q_t) = LnQ_{e1} - k_1t$                           | $Ln(Q_e - Q_t)vst$  | Slope : $k_1$<br>intercept : $Q_{e1}$  |
| Pseudo-second-order model | $\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2$ | $\frac{t}{Q_t} = \frac{1}{k_2Q_{e1}^2} - \frac{1}{Q_{e1}}t$ | $\frac{t}{Q_t} vst$ | Slope : $Q_{e11}$<br>Intercept : $k_2$ |

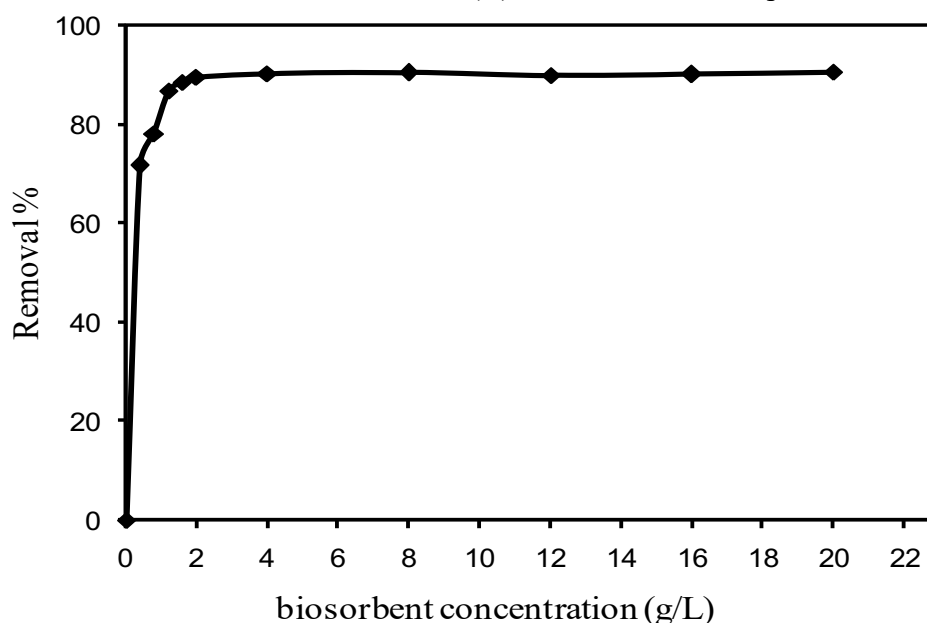


**Figure 1.** Effect of pH on the biosorption capacity of Lead on DCCP (biosorbent concentration = 10 g/L,  $[Pb^{2+}] = 100$  mg/L, temperature =  $20 \pm 1$  °C)

The improvement of lead removal with increasing pH values could also be attributed to the fact that more negatively charged sites became available at the biosorbent surface. This change in surface charges resulted in lower repulsion of Pb cations and more affinity through electrostatic forces of attraction, which enhances the biosorption of positively charged lead cations. Finally, the decreased biosorption at pH higher than 3 might be linked to the formation of soluble hydroxylated complexes of the lead ions which would prevent the Pb(II) retention.

### 3.2 Influence of the biosorbent dose

The removal rate of Pb(II) with varying DCCP doses is represented in **Figure 2**. Note that the initial concentration of lead was kept at 100 ppm, pH at 3, temperature at 20°C, contact time at 2h and stirring speed at 250 rpm. As expected, lead removal yield was sharply affected by the biosorbent dose. It reached 90% with 4 g/L of DCCP. The observed improvement could be explained by the existence of greater biosorbent surface area and more binding sites [25]. Over the dose of 4 g/L, the removal efficiency remained almost constant as a consequence of a partial aggregation of DCCP particles, causing a decrease in the biosorbent surface area [26]. This dose (4 g/L) was, therefore, taken as the appropriate DCCP concentration for maximum Pb(II) retention for subsequent batch experiments.



**Figure 2.** Effect of biosorbent dose on the removal % of lead by DCCP (pH = 3, [Pb<sup>2+</sup>] = 100 mg/L, temperature = 20 ± 1 °C)

### 3.3 Influence of lead ions initial concentration and contact time

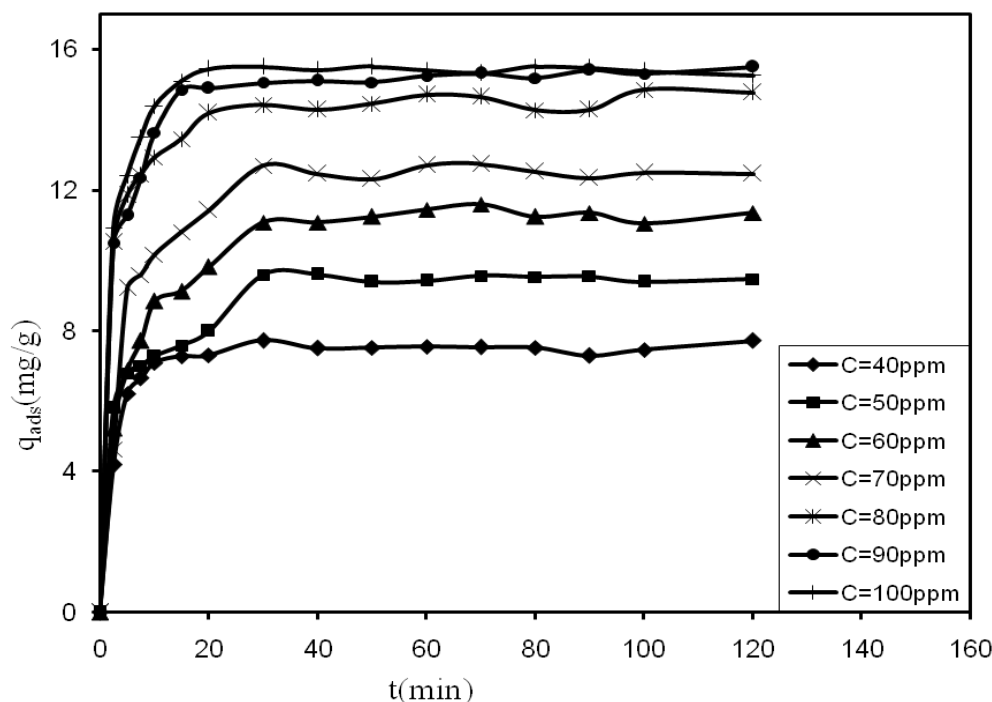
**Figure 3** shows the effect of contact time on lead removal. Experiments were carried out at pH 3, 20°C using 4g/L of biosorbent and Pb(II) initial concentrations ranging from 40 to 100 mg/L. It is noted that the biosorption increased sharply with contact time in the first 10 minutes and equilibrium states were reached at almost 30 minutes within the considered concentration range. The fast increase in Pb(II) retention at an early stage of the biosorption process could be related to the fact that, initially, all the biosorbent active sites were vacant and the solute concentration was high. After that, the biosorption rate became slower and then stagnated, denoting the progressive filling of surface active sites and the achievement of equilibrium. Furthermore, it can be clearly seen from **Figure 3** that raising Pb<sup>2+</sup> initial concentration from 40 to 100 ppm resulted in increasing DCCP biosorption capacity. This may essentially be explained by the great driving forces of lead concentration gradient between the aqueous solutions and the biosorbent, expected to overcome all mass transfer resistance of Pb ions between the aqueous and solid phases.

### 3.4 Effect of Pb<sup>2+</sup> initial concentration on temperature dependence

The results of Pb(II) retention by DCCP at various initial concentrations and different temperatures, summarized in **Table 2**, showed an improvement of the equilibrium uptake capacity between 20 and 60°C. This indicates a temperature-dependent lead biosorption equilibrium. The



biosorption capacity enhancement with temperature can be attributed to a number of eventual explanations which include (i) the rise in the kinetic energy of sorbent particles resulting in a higher collision frequency between the sorbent and the sorbate; (ii) the increase in the diffusion rate of Pb cations through the external boundary-layer and the internal pores of the biosorbent particles, owing to the decrease in the solution's viscosity and the widening of biosorbent particle pores; and (iii) the bond rupture of functional groups of biosorbent surface which may increase the number of active biosorption sites.



**Figure 3.** Effect of  $Pb^{2+}$  initial concentration on the biosorption capacity of Lead on DCCP (pH=3, biosorbent concentration = 4 g/L, temperature =  $20 \pm 1$  °C)

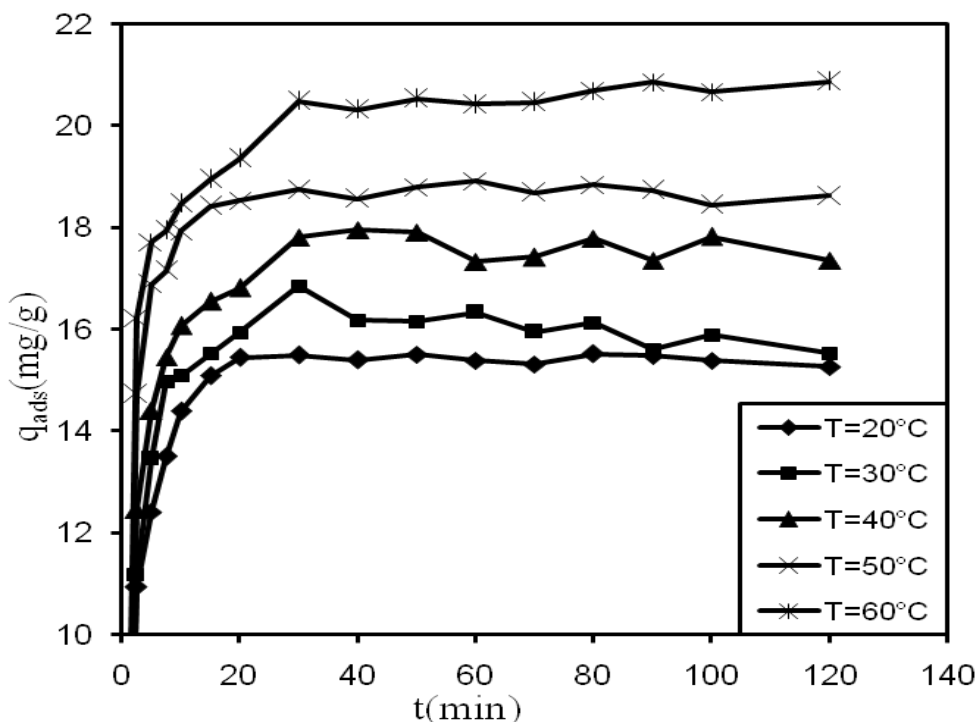
**Table 2.** Equilibrium uptake capacities at various  $Pb^{2+}$  initial concentrations and temperatures

| [ $Pb^{2+}$ ] (ppm) | Equilibrium uptake capacities ( $mg\ g^{-1}$ ) |        |        |        |        |
|---------------------|--|--------|--------|--------|--------|
|                     | 20°C   | 30°C   | 40°C   | 50°C   | 60°C   |
| 40                  | 7.727  | 7.947  | 8.75   | 8.940  | 9.157  |
| 50                  | 9.592  | 9.797  | 10.567 | 10.95  | 11.273 |
| 60                  | 11.075   | 11.732 | 12.5   | 12.9   | 13.472 |
| 70                  | 12.692   | 12.837 | 13.945 | 15.095 | 15.52  |
| 80                  | 14.42  | 15.157 | 15.977 | 16.335 | 17.206 |
| 90                  | 15.05  | 16.467 | 17.177 | 17.712 | 19.082 |
| 100                 | 15.492   | 16.842 | 17.805 | 18.737 | 20.487 |

### 3.5 Effect of contact time on temperature dependence

The variation of the biosorption capacity with time at different temperatures, depicted in **Figure 4**, revealed a three-stage retention process of Pb ions on DCCP for all studied temperatures (20 - 60 °C). This retention mostly occurred quickly during the first 10 minutes, and then slowed to saturation.

With increasing temperature, the rate of lead biosorbed in the first 10 minutes was improved, more time was needed to reach equilibrium and greater equilibrium uptake capacity was reached. The most likely explanation for this behavior may be the decrease in the solution's viscosity and the widened pores on the biosorbent particles surfaces resulting in increased boundary-layer and intraparticle diffusions of solute molecules, allowing a contact with large surface area. Moreover, changing the temperature is generally known to modify the equilibrium capacity of the adsorbent for a given solute.



**Figure 4.** Effect of contact time on biosorption capacity of Lead on DCCP at different temperatures (pH = 3, biosorbent concentration = 4 g/L, [pb<sup>2+</sup>] = 100 mg/L)

### 3.6 Biosorption kinetic modelling

**Table 1** reports the original and linear forms of the used pseudo-first and second-order models. As shown, their characteristic parameters ( $k_1$ ,  $Q_{eI}$ ,  $k_2$ ,  $Q_{eII}$ ) are determined from the slope and intercept of the linearized form plots. The values of these parameters are given in **Tables 3 and 4**.

**Table 3.** Kinetic rate constants related to Pb(II) biosorption on dried cactus cladodes at various initial concentrations

| Kinetic models                                | Initial lead concentration (mgL <sup>-1</sup> ) at constant temperature 20°C |       |        |        |        |        |        |
|---|--|-------|--------|--------|--------|--------|--------|
|   | 40   | 50    | 60     | 70     | 80     | 90     | 100    |
| Experimental $Q_e$                            | 7.727  | 9.592 | 11.075 | 12.692 | 14.42  | 15.05  | 15.492 |
| Pseudo-first-order                            |  |       |        |        |        |        |        |
| $k_1$ (min <sup>-1</sup> )                    | 0.142  | 0.069 | 0.098  | 0.105  | 0.170  | 0.23   | 0.255  |
| Calculated $Q_{eI}$ (mg g <sup>-1</sup> )     | 1.881  | 2.081 | 2.454  | 2.572  | 2.519  | 2.935  | 3.013  |
| $R^2$   | 0.843  | 0.726 | 0.921  | 0.882  | 0.922  | 0.958  | 0.974  |
| Pseudo-second-order                           |  |       |        |        |        |        |        |
| $k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> ) | 0.065  | 0.032 | 0.019  | 0.017  | 0.046  | 0.035  | 0.044  |
| Calculated $Q_{eII}$ (mg g <sup>-1</sup> )    | 8.196  | 10    | 12.345 | 14.285 | 15.151 | 16.129 | 16.393 |
| $R^2$   | 0.998  | 0.978 | 0.993  | 0.991  | 0.999  | 0.998  | 0.999  |



The low correlation coefficients ( $R^2$ ) for the pseudo-first-order model obtained at all the studied  $Pb^{2+}$  initial concentrations and temperatures, and the high discrepancy between the theoretical and the experimental  $Q_e$  values suggest the bad fitting of the pseudo-first-order model to the experimental data. Concerning the pseudo-second-order kinetic model, it showed correlation coefficients close to 1 ( $R^2 \geq 0.99$ ) and comparable values of the predicted and the measured  $Q_e$ . This indicates that the pseudo-second-order model best fits the biosorption of lead cations on DCCP for the various concentrations and temperatures. Therefore, this biosorption is presumably a chemisorption process involving cations exchange and/or sharing of electrons between lead ions present in the solution and the functional groups of the biosorbent.

**Table 4.** Kinetic rate constants related to the lead ions biosorption on dried cactus cladodes at various temperatures

| Kinetic models                                | Temperatures ( $^{\circ}C$ ) at constant concentration 100 mg L <sup>-1</sup> |        |        |        |        |
|---|---|--------|--------|--------|--------|
|   | 20  | 30     | 40     | 50     | 60     |
| Experimental $Q_e$                            | 15.492  | 16.842 | 17.805 | 18.737 | 20.487 |
| Pseudo-first-order                            |   |        |        |        |        |
| $k_1$ (min <sup>-1</sup> )                    | 0.255   | 0.126  | 0.126  | 0.204  | 0.112  |
| Calculated $Q_{eI}$ (mg g <sup>-1</sup> )     | 3.013   | 2.518  | 2.542  | 2.516  | 2.464  |
| $R^2$   | 0.974   | 0.824  | 0.825  | 0.909  | 0.723  |
| Pseudo-second-order                           |   |        |        |        |        |
| $k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> ) | 0.044   | 0.036  | 0.037  | 0.069  | 0.040  |
| Calculated $Q_{eII}$ (mg g <sup>-1</sup> )    | 16.393  | 17.543 | 18.518 | 19.230 | 21.276 |
| $R^2$   | 0.999   | 0.999  | 0.999  | 0.999  | 0.998  |

### 3.7 Biosorption isotherms

The biosorption isotherms of lead retention were investigated for different Pb(II) concentrations ranging from 40 to 100 ppm at 20, 30, 40, 50 and 60 $^{\circ}C$  while maintaining the other conditions constant. The characteristic parameters of the four studied isotherms as well as the linear regression coefficients  $R^2$  are listed in **Table 5**. Considering the  $R^2$  values, the Langmuir isotherm model ( $R^2 = 0.933 - 0.996$ ) was the most suitable for describing the equilibrium of Pb(II) biosorption on DCCP.

The Langmuir type biosorption isotherm indicates a monolayer coverage of the biosorbent surface containing a finite number of homogeneous binding sites, equivalent biosorption energies and finally no interaction between sorbed lead cations.

All the calculated  $R_L$  values (0.06 - 0.29) were between 0 and 1, suggesting the favorable biosorption of lead ions on DCCP for the different Pb(II) concentrations between 293-333K.

Furthermore, It was shown that the maximum monolayer biosorption capacity ( $Q_m$ ) and the Langmuir constant ( $K_L$ ) increased with raising temperature. This behavior suggests a greater affinity of lead ions for the binding sites [27] at high temperature and supports the fact that their retention by DCCP is endothermic. The maximum biosorption capacity of Pb(II) was estimated to be 23.25 and 29.41 mg/g at 293 and 333K, respectively. These  $Q_m$  values are higher than the biosorption capacities of some other low-cost biosorbents [28-31].

### 3.8 Thermodynamic analysis

Besides the kinetics, the thermodynamic aspect is also important to understand whether the adsorption process is spontaneous and exothermic or endothermic.

The thermodynamic parameters ( $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ ) that describe Pb(II) biosorption on DCCP were determined using the following equations.

$$\Delta G^\circ = -RT \ln K$$

Eqn. 9

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Eqn. 10

$$\ln K = (\Delta S^\circ/R) - (\Delta H^\circ/RT)$$

Eqn. 11

where  $R(8.314 \times 10^{-3} \text{ kJ/mol K})$  is the universal gas constant,  $T(\text{K})$  the absolute temperature and  $K (\text{L/g})$  an equilibrium constant obtained by multiplying the Langmuir constants  $Q_{\max}$  and  $K_L$  [32].

**Table 5.** Isotherm parameters for lead biosorption on dried cactus cladodes at various temperatures

| Isotherm   |   | Temperature ( $^\circ\text{C}$ ) |        |        |        |        |
|------------|---|----------------------------------|--------|--------|--------|--------|
|            |   | 20                               | 30     | 40     | 50     | 60     |
| Langmuir   | $Q_{\max}(\text{mgg}^{-1})$                         | 23.255                           | 27.777 | 23.809 | 24.390 | 29.411 |
|            | $K_L(\text{Lmg}^{-1})$                              | 0.061                            | 0.052  | 0.111  | 0.141  | 0.136  |
|            | $R^2$   | 0.973                            | 0.933  | 0.99   | 0.994  | 0.996  |
| Freundlich | $K_F(\text{mg}^{1-1/n}\text{g}^{-1}\text{L}^{1/n})$ | 2.792                            | 2.564  | 4.477  | 5.211  | 5.345  |
|            | $n$   | 2.016                            | 1.766  | 2.320  | 2.403  | 2.070  |
|            | $R^2$   | 0.932                            | 0.933  | 0.968  | 0.968  | 0.975  |
| Temkin     | $B_1$   | 5.709                            | 6.888  | 5.591  | 5.638  | 6.916  |
|            | $K_T$   | 0.459                            | 0.398  | 0.929  | 1.210  | 1.174  |
|            | $R^2$   | 0.956                            | 0.944  | 0.974  | 0.972  | 0.993  |
| D-R        | $Q_{\max}(\text{mgg}^{-1})$                         | 15.721                           | 17.013 | 16.609 | 17.672 | 19.163 |
|            | $K_{DR}$  | 0.011                            | 0.009  | 0.003  | 0.002  | 0.001  |
|            | $R^2$   | 0.961                            | 0.935  | 0.871  | 0.918  | 0.92   |

The Gibbs free energy change of biosorption  $\Delta G^\circ$  (kJ/mol) was calculated using Eqn. 9. The standard enthalpy change ( $\Delta H^\circ$ ) and the standard entropy ( $\Delta S^\circ$ ) were evaluated from the slope and the intercept of the linear plot ( $\ln K$ ) versus ( $1/T$ ). The values of the different thermodynamic parameters are summarized in Table 6.

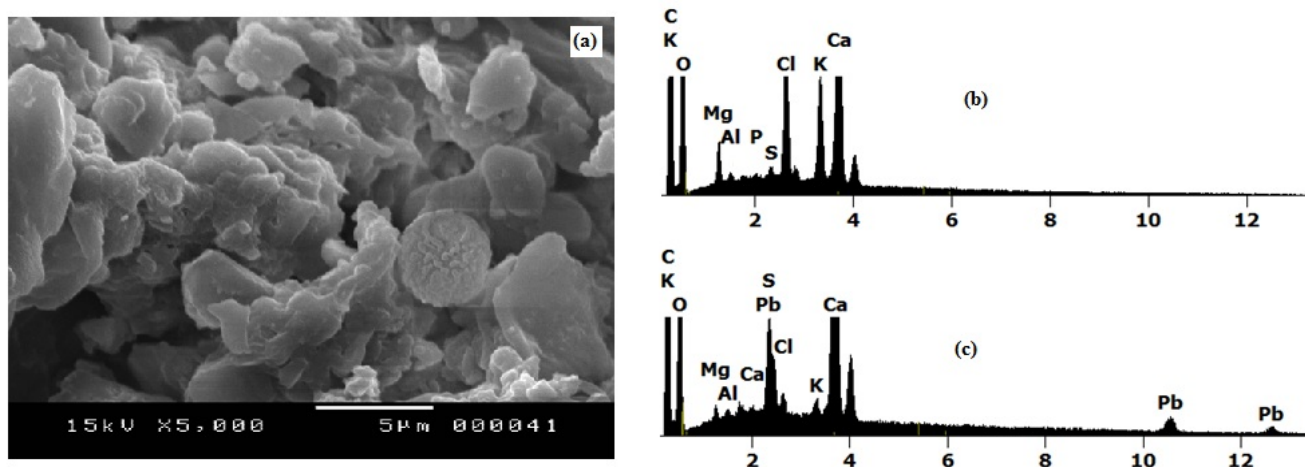
**Table 6.** Thermodynamic parameters for Pb(II) biosorption on dried cactus cladodes powder at different temperatures

| Temperatures (K) | $\Delta G^\circ$ (kJ mol $^{-1}$ ) | $\Delta H^\circ$ (kJ mol $^{-1}$ ) | $\Delta S^\circ$ (J mol $^{-1}$ K $^{-1}$ ) |
|------------------|------------------------------------|------------------------------------|---|
| 293              | -0.86                              |                                    |   |
| 303              | -0.94                              |                                    |   |
| 313              | -2.54                              | 23.71                              | 83.1  |
| 323              | -3.33                              |                                    |   |
| 333              | -3.83                              |                                    |   |

The  $\Delta G^\circ$  value was negative, indicating a spontaneous retention of Pb(II) ions by DCCP. This value increased with temperature increase, implying a more favorable biosorption at higher temperatures. The positive  $\Delta H^\circ$  value suggests that Pb(II) biosorption on DCCP is endothermic in the temperature range 20-60 $^\circ\text{C}$ . This endothermicity may be due to the fact that lead cations are well solvated in water. To adsorb, these ions must be relatively stripped of their hydration sheath. The energy required for this desolvation (endothermic process) considerably exceeds the enthalpy of cations biosorption. The implicit assumption is that after adsorption, the environment of the metal ions becomes less aqueous than in the solution [33]. Concerning  $\Delta S^\circ$ , its positive value indicates an increase in randomness at the solid/liquid interface during the retention process of lead cations by DCCP [34].

### 3.9 SEM and EDS analyses

SEM micrograph of DCCP given in **Figure 5** clearly shows a rough surface with cracks and cavities which most likely have a main role in the biosorption of lead ions.

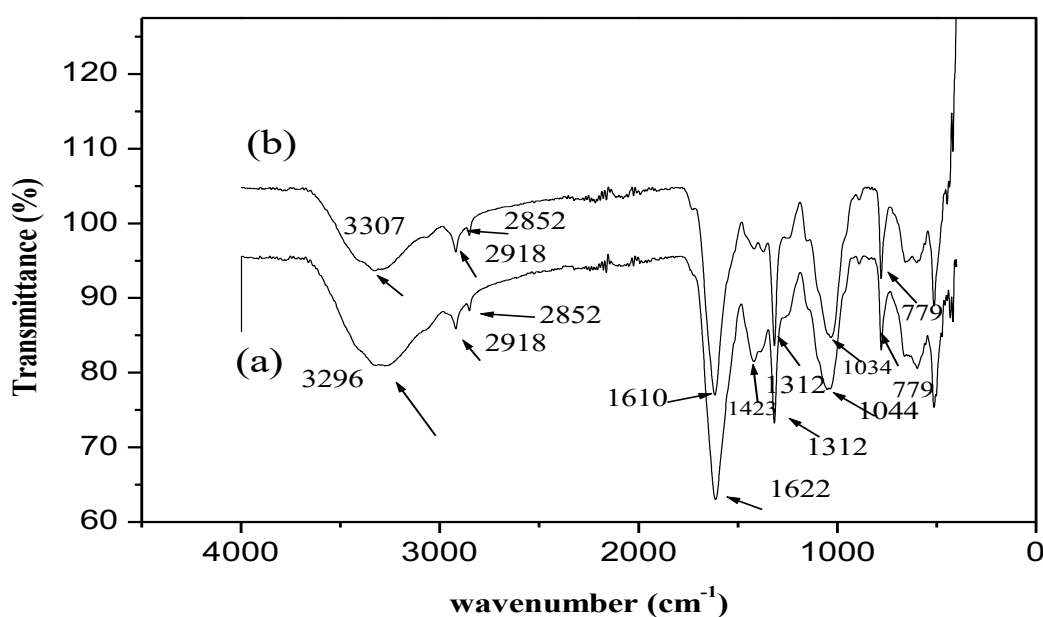


**Figure 5.** SEM micrograph (a) and EDS spectra of dried cactus cladodes powder (b) before and (c) after lead ions retention

Concerning the EDS spectra (**Figure 5**), they reveal the presence of some exchangeable ions ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $K^{+}$ ) before lead cations biosorption. After  $Pb(II)$  retention, a new lead (Pb) peak appeared and the peaks of  $K^{+}$  and  $Mg^{2+}$  decreased significantly, which probably indicates the exchange of these cations with the lead ones present in the solution. It is important to mention here that ion-exchange has already been highlighted for the biosorption of heavy metals such as cadmium [35, 36] and mercury [37].

### 3.10 FTIR analysis

FTIR spectra of DCCP before and after lead ions retention are shown in **Figure 6**. The different absorption bands and their assignments are summarized in **Table 7**. Some of these infrared bands slightly shifted after lead cations biosorption. They correspond to carboxyl (COOH), carbonyl (C=O), hydroxyl (O-H) and amino (N-H) groups. These functional groups could thus be involved in lead cations biosorption through complexation mechanism.



**Figure 6.** FTIR spectra of dried cactus cladodes powder (a) before and (b) after lead cations biosorption

**Table 7.** FTIR absorption bands of dried cactus cladodes powder and their possible responsible groups before and after Pb<sup>2+</sup> retention

| Wavelength range (cm <sup>-1</sup> ) | Dried cactus cladodes powder |                 |            | Assignment   |
|--------------------------------------|------------------------------|-----------------|------------|--|
|                                      | Before retention             | After retention | Difference |  |
| 3500–3200                            | 3296                         | 3307            | +11        | Carboxylic acid and amino groups                           |
| 3000–2850                            | 2918                         | 2918            | 0          | C- H methyl and methylene groups                           |
| 3000–2850                            | 2852                         | 2852            | 0          | C- H stretching  |
| 1640–1500                            | 1622                         | 1610            | -12        | Asymmetric stretching Carboxylic groups C=O                |
| 1450–1375                            | 1423                         | Absent          | -          | C -H bending   |
| 1375–1300                            | 1312                         | 1312            | 0          | C- O stretching of COOH                                    |
| 1350–1000                            | 1044                         | 1034            | -10        | O- H alcohols (primary and secondary) and aliphatic ethers |
| 990–690                              | 779                          | 779             | 0          | N containing bioligands                                    |

## Conclusion

In this study, we have investigated and proposed the use of cactus cladode based powder as a biosorbent for the retention of Pb ions from aqueous medium. In fact, it was found that the retention process depends on contact time, solution pH, biosorbent dose, temperature and Pb<sup>2+</sup> initial concentration. The amount of Pb(II) removed increased with increase in these operating parameters and the equilibrium was reached in 30 minutes. From kinetic, isotherm and thermodynamic studies, it was concluded that the retention of lead ions occurs with monolayer formation on the biosorbent surface and follows the pseudo-second-order kinetic model. The maximum Pb<sup>2+</sup> biosorption capacity according to the Langmuir isotherm model at 60°C was 29.41 mg/g. Moreover, the retention process is endothermic, favorable, spontaneous and disordered at the solid-solution interface. According to the FTIR and EDS analyses, this retention process takes place mainly through surface ion-exchange involving magnesium and potassium cations as well as electron-sharing between Pb<sup>2+</sup> and the functional groups of the biosorbent. Given the findings of the current investigation, the studied cactus cladodes powder seems to be a potential low-cost biosorbent for effective remediation of lead ions contaminated water.

**Disclosure statement:** *Conflict of Interest:* The authors declare that there are no conflicts of interest.

*Compliance with Ethical Standards:* This article does not contain any studies involving human or animal subjects.

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