

Article

Exploring Adsorption Process of Lead (II) and Chromium (VI) Ions from Aqueous Solutions on Acid Activated Carbon Prepared from *Juniperus procera* Leaves

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Received: 1 March 2019; Accepted: 10 April 2019; Published: 16 April 2019



Abstract: The adsorption potential of acid activated carbon prepared from leaves of *Juniperus procera* to remove Pb(II) and Cr(VI) toxic ions from aqueous solutions was investigated. The effects of solution pH, adsorbent mass, contact time, initial ion concentration and temperature on the biosorption process were studied, and the optimum conditions were determined. Moreover, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich adsorption isotherm models were applied to analyze adsorption data. Thermodynamic parameters for the adsorption processes were calculated. Adsorption was found to be a spontaneous and endothermic process. In addition, kinetic studies revealed a pseudo-first order kinetics biosorption process. The obtained results suggest that acid activated *Juniperus procera* leaves powder can be used as a cheap, efficient and environmentally friendly adsorbent material with high removal efficiency up to 98% for Pb(II) and 96% for Cr(VI) at 0.80 and 1.00 g/100 mL, respectively. The duration of the process was 100 min and 120 min for Pb(II) and Cr(VI) ions, respectively. The morphology of the of prepared activated carbon was investigated by scanning electron microscope (SEM).

Keywords: Juniperus procera leaves; acid activation; adsorption; isotherm models

1. Introduction

Recent trends in human growth and their subsequent needs of everyday life have prompted a boom in the development of all industrial sectors from basic food and water processing to luxurious cars and other expensive gadgets production. However, one of the drawbacks of all this is that it puts a huge burden on the available natural resources and increases pollution levels that in turn lead to catastrophic effects on the environment and human health. Chromium and lead are common pollutants in wastewater resulting from numerous industrial activities including electroplating, paint manufacturing plants, textile manufacturing, steel, leather tanning, ceramic and glass industries, petroleum refining, battery manufacture, mining operations and other metal finishing industries. As they are toxic and non-degradable, they have a significant effect on the whole ecosystem with direct effects on human health. Pb(II) can cause damage to the central nervous system, kidneys, liver and reproductive systems. Symptoms related to the presence of Pb(II) include headache, dizziness, irritability, weakness of muscles, etc. [1]. As for the chromium, Cr(VI) is reported to be more toxic than Cr(III) and severely affects human physiology [2].



To overcome these concerns, various strategies have been used to remove heavy metals such as the use of simple desalination, evaporation, reverse osmosis, and ion exchange. However, the recent biosorption technique is environmentally friendly and affordable. Biosorption is a natural biological method and is considered as a good alternative to conventional wastewater treatment methods.

Removal of Pb(II) and Cr(VI) from wastewater has been widely explored. For example, in the case of Cr(VI), the use of materials such as rice straw activated carbon [3], apple pulp [4], activated carbon developed from *Terminalia arjuna* nuts [5], activated carbon from hazelnut [6], sawdust [7], sugarcane baggas [8], activated carbon from mango kernel [9], egg shell and powdered marble [10], rice husk activated carbon [11] and apple peel powder [4] have been explored and reported in the literature. Moreover, numerous studies are available for Pb(II) removal from wastewater. Some recent studies include the use of cocoa shells [12], maize tassel based activated carbon [13], coconut shell [14], activated periwinkle shells [15], bamboo activated carbon [16], caltropis plants roots [17], cashew nut shells [18], activated carbons derived from oil palm and coconut shells [19], mixture of charcoal and peanut shells [20], *Moringa oleifera* bark [21], pumpkin seeds [22], rice husk-based activated carbon [23,24] and untreated orange barks [25].

However, most of the reported adsorbents can only remove a single metal ion. This paper highlights that the adsorbent used in the current investigation could efficiently remove two metal ions from aqueous solutions. Furthermore, the method of generation of the adsorbent is robust and cost effective, as it does not require any high temperature treatment. In addition, to the removal of two metal ions and simple regeneration, the adsorbent can be effectively used at least three times before being discarded. To our knowledge, few biosorbents are capable of removing both Pb(II) and Cr(VI) from aqueous solutions while being efficiently reusable at least three times. *Juniperus procera* is the most abundant plant in Aseer region, Saudi Arabia. The use of leaves of this plant as a low-cost biosorbent material for Pb(II) and Cr(VI) ions is not yet been reported in the literature. Hence, this study focused on the exploitation of this new and environmentally friendly material for Pb(II) and Cr(VI) ion removal from artificial wastewater.

2. Materials and Methods

2.1. Chemicals and Instruments

All chemicals used in this work were purchased from Merck, Germany and BDH, England and used without further purifications. Aqueous stock solutions of Pb(II) and Cr(VI) ions were prepared from lead acetate and potassium dichromate in deionized water. Various concentrations, ranging 50–300 mg/L, were obtained by diluting the stock solutions.

Hydrochloric acid and sodium hydroxide solutions were used for pH adjustment. The pH measurements were carried out by a pH meter (Hanna 211 model). Metal ions concentrations in the treated solutions were determined using an atomic absorption spectrometer (Spectra AA 20).

2.2. Leaves Collection, Preparation and Carbonization

To carry out the experimental work, *Juniperus procera* leaves were collected from Abha City in Saudi Arabia. Theses leaves were thoroughly washed with deionized water to remove any fines, dirt and dust. The leaves were dried at 40 °C for 3 h, crushed and sieved to a particle size with 100 μ m. The obtained leaves powder was then immersed in diethyl ether and left overnight to allow solvent and volatile oil removal by simple evaporation. This step was followed by acid activation in which sulfuric acid was added to the sample in a 1:1.8 ratio, as reported by Singanan [26]. The mixture was continuously stirred for 30 min followed by filtration and rinsing thoroughly with deionized water to remove any residual acid. The activated leaves were then sieved again with 100 μ m mesh and stored in desiccators [27].

2.3. Reliability of Results

Sensitivity of the measurements was estimated by determination of limit of detection (LOD) and limit of quantitation (LOQ). LOD and LOQ, were determined by measuring 10 blank samples and then applying the relationships 3.3SD/b and 10SD/b, respectively. The precision of measurements is usually expressed as relative standard deviation (RSD). Precision was determined by assessing the reproducibility of the results. The same conditions were used to measure 10 blank samples. Typically, recovery studies are performed to determine the accuracy of the measurements. Recovery studies were accomplished by spiking technique.

2.4. Batch Adsorption Studies

Batch experiments for biosorption of Pb(II) and Cr(VI) ions on acid activated *Juniperus procera* leaves (AAJPL) were carried out. The desired amounts of the AAJPL were added to glass flasks containing different concentrations of Pb(II) and Cr(VI) solutions with concentrations ranging from 50 to 300 mg/L. Throughout the experiments, the flask was put on a temperature controlled magnetic stirrer with a stirring speed of 150 rpm for the required period of time. Biosorption quantity was calculated using Equation (1):

$$q_e = \frac{C_o - C_e}{M} \times V \tag{1}$$

where V is the volume of the metal solution in the flask, q_e is the metal uptake capacity (mg/g), M is the dry mass of biosorbent (g), C_o is the initial metal ions concentration, and C_e is the metal ions concentration at the equilibrium. The overall removal efficiency (R%) of metal ions was determined using Equation (2). All experiments were carried out in duplicate and the average value was used for further calculation.

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

2.5. Control Experiments

Control experiments were carried out using the ground *Juniperus procera* leaves without activation. Other experiments were carried out using Pb(II) and Cr(VI) solutions without biosorbent to measure the quantity of ions that may be adsorbed by walls of the glass bottle and magnetic stirrer.

2.6. Reactivation of AAJPL

AAJPL was reactivated by shaking with bi-distilled water for 24 h, and then it was filtered and heated overnight at 105 °C The conditions of these experiments were kept identical to the optimal conditions of the adsorption process.

3. Results and Discussion

3.1. Reliability of the Measurements

Precision of the measurements was found to be 5.6%, whereas the accuracy was determined as 95.3%, which are in the acceptable range.

3.2. Effect of pH

Biosorption efficiency of the system strongly depends on the pH of the solutions. The data presented in Figure 1 highlight the effect of the pH on biosorption of Pb(II) and Cr(VI) ions onto AAJPL. The biosorption increased and attained the maximum values for Pb(II) and Cr(VI) at pH 4.6 and 4, respectively. At pH higher than 6, biosorption activity decreased. This may be attributed to the diminution of free ions due to the formation of hydroxyl complexes at the higher pH range, as reported in [28–30], and the subsequent precipitation of metal ions; thus, removal efficiency dropped sharply.



Figure 1. Effect of pH on biosorption of Pb(II) and Cr(VI) ions on AAJPL (adsorbent mass: 0.80 g/100 mL for Pb(II) and 1.00 g/100 mL for Cr(VI); metal ion concentrations: 50 mg/L for Pb(II) and 70 mg/L for Cr(VI); temperature: 25 °C).

On the other hand, at pH values lower than the optimum, biosorption activity may have been hindered by the H⁺ and metal ions competing for the same active sites on the same active sites on the adsorbent surface [26].

3.3. Effect of Biosorbent Mass

To accomplish this task, series of batch experiments were performed with the adsorbent mass of 0.10, 0.20, 0.40, 0.60, 0.80, 1.00, 1.25, 1.5 and 2.0 g per 100 mL of aqueous solutions of Pb(II) and Cr(VI) ions. Figure 2 clearly shows that, as the mass of biosorbent increased, the removal efficiency of metal ions also increased. A maximum removal efficiency of 98% for Pb(II) and 96% for Cr(VI) was obtained at 0.80 and 1.00 g/100 mL of the AAJPL, respectively. In addition, a further increase of biosorbent mass was found to have no significant effect on the removal of both ions from their aqueous solutions.



Figure 2. Effect of biosorbent mass on the removal efficiency of Pb(II) and Cr(VI) from aqueous solutions (metal ion concentrations: 50 mg/L for Pb(II) at pH 4.6 and 70 mg/L pH 4 for and Cr(VI); temperature: 25 °C).

3.4. Effect of Metal Ion Concentration

The biosorption of Pb(II) and Cr(VI) ions was carried out at various concentrations of Pb(II) and Cr(VI) ranging from 50 to 300 mg/L using 0.80 g and 1.00 g of AAJPL. Results shown in Figure 3 reveal that the maximum achieved adsorption was 50 and 70 mg/L for Pb(II) and Cr(VI) ions, respectively. This could be attributed to the fact that the active sites are covered and saturated as the concentrations increase.



Figure 3. Effect of metal ion concentrations on the adsorption efficiency.

It is well established that the addition of salts to a tested solution may lead to decrease of the maximum adsorption capacity q_{max} . This can be ascribed to the presence of more ions that compete for limited adsorption sites [31].

3.5. Effect of Contact Time

The effect of contact time on biosorption of Pb(II) and Cr(VI) ions onto AAJPL was studied using the optimum biosorbent dosage values of 0.80 and 1.0 g/100 mL obtained earlier. The experiments were carried out at 25 °C with optimum concentration values of metal ions, viz. 50.0 and 70.0 mg/L for Pb(II) and Cr(VI) ions, respectively. As shown in Figure 4, maximum removal efficiencies of 98% and 96% were achieved after 100 and 120 min for the metals under investigation. Moreover, a further increase in contact time had no significant influence on the removal of both metal ions.



Figure 4. Effect of time on removal efficiency of Pb(II) and Cr(VI) ions on AAJPL (adsorbent mass: 0.80 g/100 mL for Pb(II) at pH 4.6 and 1.00 g/100 mL for Cr(VI) at pH 4; metal ion concentrations: 50 mg/L for Pb(II) and 70 mg/L for Cr(VI); temperature: 25 °C).

(3)

3.6. Biosorption Isotherms

Adsorption isotherms describe the interaction between adsorbate and adsorbents and express the relationship between the sorption capacity and equilibrium concentration. Biosorption of Pb(II) and Cr(VI) ions onto AAJPL was analyzed by means of four adsorption isotherms: Langmuir, Freundlich, Temkin and D-R isotherms.

3.6.1. Langmuir Isotherm

Adsorption in the Langmuir isotherm model is assumed to occur as a monolayer on a uniform surface with a fixed number of adsorption sites [18]. When a site is filled, no further adsorption can occur at that site. Thus, the adsorbent surface will reach its saturation point where the maximum adsorption is attained. When applying the linear equation of Langmuir isotherm model given by Equation (3), a linear plot was obtained, as shown in Figure 5.



Figure 5. Linear fit of experimental data obtained using Langmuir isotherm model (adsorbent mass: 0.80 g/100 mL for Pb(II) at pH 4.6 and 1.00 g/100 mL for Cr(VI) at pH 4.0; temperature: 25 °C).

Here, K_L is the Langmuir constant related to the adsorption energy and q_{max} is the maximum uptake capacity (mg/g). Values of q_{max} and K_L were determined from the slope and intercept of the graph presented in Figure 5.

In addition, values of the parameters derived from Langmuir isotherm model are tabulated in Table 1. Furthermore, significant evidence related to sorption nature can be deduced from the separation factor (R_L) values, which is an important characteristic of Langmuir isotherm. It can be used to understand the attraction/interactions between the sorbent and sorbate. Values of R_L were calculated from Equation (4):

$$R_L = \frac{1}{1 + K_L C_o} \tag{4}$$

where C_o is the maximum preliminary concentration of the metal ions. The R_L values indicate the type of adsorption as unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L > 1$) or irreversible ($R_L = 0$). In this study, the R_L values indicated that the biosorption of Pb(II) and Cr(VI) ions onto AAJPL was a favorable process with values of 0.05 and 0.25, respectively.

Langmuir Isotherm							
	q _{max} , mg/g K _L , L/g						
Pb(II)	30.3	0.08	0.997				
Cr(VI)	23.0	0.01					
Freundlich Isotherm							
	n	K _f ,	R ²				
	11	(mg/g)/(mg/L) ⁿ					
Pb(II)	0.50	21.23	0.965				
Cr(VI)	0.20	24.45	0.920				
Temkin isotherm							
A, L/g B R ²							
Pb(II)	0.89	6.45	0.992				
Cr(VI)	0.23	3.29	0.935				
D-R isotherm							
	β	q _{max} , mg/g	R ²				
Pb(II)	2.0×10^{-6}	20.1	0.851				
Cr(VI)	8.0×10^{-5}	13.5	0.712				

Table 1. Adsorption isotherm constants obtained from the four adsorption models.

3.6.2. Freundlich Isotherm

The Freundlich isotherm was also applied to the biosorption data. This model is an empirical expression and applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules. Application of Freundlich isotherm model proposes an exponential decrease in adsorption energy upon completion of the sorption centers of sorbent. The linear form of Freundlich isotherm model can be described by Equation (5):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{5}$$

where K_f is the relative adsorption capacity of the sorbent that is associated with the bonding energy and n is the heterogeneity factor expressing the deviation from linearity of biosorption. A plot of ln q_e against ln C_e was used to validate Freundlich adsorption isotherm. Values of K_f and n were determined from the intercept and slope of Figure 6 and the values obtained are listed in Table 1. In this model, the n values determine the degree of nonlinearity between solution concentration and adsorption in the following manner: if n = 1, then adsorption is linear; if n > 1, then adsorption is a chemical process; and if n < 1, adsorption is considered as a physical process. The obtained numerical values of n for Pb(II) and Cr(VI) ions removal were found to be 0.50 and 0.20, indicating physical adsorption processes.



Figure 6. Linear fit of experimental data obtained using Freundlich isotherm model (adsorbent mass: 0.80 g/100 mL for Pb(II) at pH 4.6 and 1.00 g/100 mL for Cr(VI) at pH 4.0; temperature: 25 °C).

3.6.3. Temkin Isotherm

In Temkin isotherm model, the sorption heat of all molecules in the layer is assumed to decrease linearly with coverage of the sorbent surface because of a decrease in the adsorbent–adsorbate interactions. Temkin isotherm model can be described by Equation (6):

$$q_e = B \ln A + B \ln C_e \tag{6}$$

where $B = (RT)/b_t$, T is the absolute temperature and R is the universal gas constant. The constant b_t is related to the heat of adsorption (J/mol). A is the equilibrium binding constant corresponding to the maximum binding energy. Values of A and B were calculated from slope and intercept of Equation (6), as displayed in Table 1. Values of b_t for Pb(II) and Cr(VI) sorption were determined as 387 and 753 J/mol, respectively, indicating physical adsorption processes.

3.6.4. Dubinin-Radushkevich (D-R) Isotherm

Dubinin–Radushkevich (D-R) isotherm model was also used to describe the sorption data. It explains the adsorption nature and is usually used to determine the mean free energy of the sorption process [32]. The linear form of the D-R isotherm is given by Equation (7):

$$\ln q_e = \ln q_{max} - \beta \varepsilon^2 \tag{7}$$

where ε is:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{8}$$

In Equations (7) and (8), T refers to the absolute temperature, R is the universal gas constant, and q_{max} and β are the D-R isotherm constants. The D-R isotherm constants q_{max} and β were calculated from the intercept and slope of Equation (7), as shown in Table 1. The mean free energy of adsorption process, E_f , is defined as the free energy change when one mole of ions is moved to the solid surface from infinity in solution and can be determined from Equation (9).

$$E_f = \frac{1}{\sqrt{2\beta}} \tag{9}$$

It is known that the magnitude of E_f is useful for estimating the type of adsorption. For $8 < E_f < 16 \text{ kJ/mol}$, the adsorption is classified as chemisorption process, and, when $E_f < 8 \text{ kJ/mol}$, the adsorption is a physical process. In this study, lower values of E_f were found, viz. 2.42 kJ/mol and 1.84 kJ/mol for Pb (II) and Cr (IV), respectively, indicating that the adsorption processes were of physical type.

3.7. Effect of Temperature

To investigate the effect of temperature on the biosorption of Pb(II) and Cr(VI) ions onto AAJPL, experiments were conducted in temperatures ranging from 25.0 to 40.0 °C, under the optimal conditions determined previously. Results presented in Figure 7 reveal that the removal efficiency increased with increasing temperature. The maximum removal of metal ions from aqueous solutions was achieved at 40.0 °C for both metal ions under investigation. This may be ascribed to: (i) activation of more sites on the sorbent surface as the temperature increased; and (ii) cations speed increased at elevated temperatures.



Figure 7. Effect of temperature on the adsorption efficiency of Pb(II) and Cr(VI) on AAJPL.

Thermodynamic Parameters

Some thermodynamic activation parameters, viz., entropy change of activation ΔS° , enthalpy change of activation ΔH° and free energy change of activation ΔG° , were calculated using Equations (10)–(12)

$$\Delta G^{"} = RT \ln K_D \tag{10}$$

In Equation (10), the parameter K_D is the distribution coefficient and equal to the initial concentration (C_o) divided by the final concentration (C_e). The free energy change with respect to the entropy change of activation is given in Equation (11):

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{11}$$

Substituting Equation (10) into Equation (11) and rearranging leads to:

$$\ln K_D = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{12}$$

Enthalpy and entropy change were calculated from the slope and intercept of Equation (12), respectively, while values of free energy change of activation ΔG° were determined from Equation (10).

Numerical values of the free energy change (ΔG°) are shown in Table 2. The obtained negative values indicate that the biosorption process was spontaneous. In addition, it can be noticed that, as the temperature increased, the negative values of free energy change increased. This may be attributed to the fact that more sites on the surface of AAJPL were activated with the rise in temperature. Values of

free energy change ΔG° for Pb(II) and Cr(VI) biosorption onto AAJPL were found in the ranges of -2.5 to -11.7 kJ/mol for Pb(II) ions and -4.2 to -11.0 kJ/mol for Cr(VI) ions. As it is known that physical adsorption free energy change (ΔG°) ranges between -20 and 0 kJ/mol and chemical adsorption between -80 to -400 kJ/mol, the adsorption process was predominantly a physical biosorption process. This is in good agreement with results derived from n, E_f and b_t values of Freundlich, (D-R) and Temkin isotherms.

Т, К	KD	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
Pb(II)				
298	22.83	-2.5	107.58	369.3
303	5.36	-4.3		
313	2.50	-8.0		
323	1.41	-11.7		
Cr(VI)				
298	22.86	-4.2	78.59	274.4
303	9.78	-5.5		
313	5.60	-8.3		
323	2.94	-11.0		

Table 2. Thermodynamic parameters of the biosorption of Pb (II) and Cr (VI) ions onto AAJPL.

Furthermore, values of entropy, ΔS° , for Pb(II) and Cr(VI) adsorption onto AAJPL were 369.3 and 274.4 J/mol K, respectively. Positive values indicate increased randomness in interactions at the solid–liquid interface during the adsorption process. Results in Table 2 suggest that the biosorption is an endothermic process, i.e., increase in removal efficiency with increasing temperature.

3.8. Biosorption Kinetics

To investigate the kinetics of the adsorption process, two kinetic models were examined: pseudo-first order and pseudo-second order kinetics. The pseudo-first order model can be expressed as follows [29]:

$$\ln\left(q_{e}-q_{t}\right) = \ln q_{e} - k_{1}t \tag{13}$$

where q_e and q_t are amounts of ions (mg/g) adsorbed at equilibrium and time (t), respectively, and k_1 is the adsorption rate constant. Pseudo-second order kinetics model (Equation (14)) was also fitted to the experimental data. Figure 8 shows that biosorption of both Pb(II) and Cr(VI) obeyed Equation (13), indicating pseudo-first order kinetics. The R² values for the pseudo-first order kinetics were 0.997 and 0.991 for Pb(II) and Cr(VI), respectively, indicating that the adsorption system was most likely best described by the pseudo-first order kinetic model. This is in good agreement with reported conclusions [29]. It is clear from the literature that the adsorption kinetics depend on the adsorbent nature.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{14}$$

3.9. Control Experiments

The control experiments revealed that only a negligible amount (<0.1%) of Pb(II) and Cr(VI) ions were adsorbed by walls of the glass bottles and magnetic stirrer. Results also reveal that the removal efficiency of the inactivated *Juniperus procera* leaves was much lower than those obtained using the AAJPL. Removal efficiencies measured for the inactivated leaves were 25% and 21% for Pb(II) and Cr(VI) ions and for activated leaves were 98% and 96%, respectively. These results indicate that acid activation of *Juniperus procera* leaves was the determinant factor in removal of Pb(II) and Cr(VI) ions.



Figure 8. Linear fit of experimental data obtained using pseudo-first order kinetics model (adsorbent mass: 0.80 g/100 mL for Pb(II) at pH 4.6 and 1.00 g/100 mL for Cr(VI) at pH 4.0; metal ion concentrations: 50 mg/L for Pb(II) and 70 mg/L for Cr(VI); temperature: 25.0 °C).

3.10. Reactivation and Reusability of AAJPL

Results of reusing of AAJPL are presented in Figure 9. It clear that the efficiency of AAJPL decreased gradually with reuse. Results prove that AAJPL could be used 2–3 times efficiently to remove Pb(II) and Cr(VI) ions from aqueous solutions.



Figure 9. AAJPL reactivation and reuse.

3.11. Comparison of AAJPL with other Sorbents

Comparisons of maximum adsorption capacity, q_m , isotherm model, adsorption type and kinetics of AAJPL with those of various biosorbents reported previously are shown in Table 3. The difference in q_m values could be attributed to the properties and nature of each biosorbent. The comparison with other adsorbents proves that AAJPL can be classified an excellent biosorbent for Pb(II) and Cr(VI) ions.

Adsorbent	q_{m}	Kinetics	Isotherm model	Adsorption Type	References
Pb(II)					
Juniperus procera	30.3	2nd order	Langmuir	physical	This study
Tridax procumbens	4.5	1st order	Langmuir	physical	[28]
Pumpkin seed shell	14.3	2nd order	Langmuir	**	[22]
Water Hyacinth	33.4	2nd order	Langmuir	physical	[33]
Cr(VI)			-		
Juniperus procera	23.0	2nd order	Langmuir	physical	This study
Ficus nitida	21.0	2nd order	Langmuir	physical	[34]
Annona squamosal	7.9	2nd order	Freundlich	chemical	[4]
Olive stones	25.6	1st order	Langmuir	**	[35]
Rosmarinus officinalis	1.0	**	Langmuir	**	[36]
Walnut hull	98.1	2nd order	Langmuir	**	[31]

Table 3	Comparison	between AA	IPL and	other	activated	carbon	biosorbent
Table 5.	Companison	Detweening	JI L and	ould	activated	carbon	Diosofficiati.

** Not Reported.

3.12. Morphology of AAJPL Surface

The morphology of AAJPL was investigated using scanning electron microscope (SEM). Results are displayed in Figure 10. Figure 6a clearly shows that there were many vacant pores and cavities, which facilitated the adsorption process, while Figure 6b shows that these cavities were full of Pb(II) and Cr(VI) ions, indicating good adsorption efficiency of AAJPL.



Figure 10. (a) SEM for AAJPL surface before adsorption; and (b) SEM for AAJPL surface after adsorption.

4. Conclusions

From the above discussion, it is concluded that AAJPL can be used as a cheap, efficient and eco-friendly biosorbent material for the removal of Pb(II) and Cr(VI) ions from aqueous solutions. The maximum removal efficiency for Pb(II) and Cr(VI) ions were 98% and 96% and obtained within 100 and 120 min, respectively. Adsorption efficiency increased gradually when the adsorbent mass was increased up to an optimum dosage of 0.8 mg/L for Pb(II) and 1.0 mg/L for Cr(VI). The best temperature for the maximum adsorption was found to be 40.0 °C. The maximum removal of Pb(II) and Cr(VI) ions was achieved at pH of 4.6 and 4.0, respectively. Moreover, the obtained experimental data were well explained using Langmuir, Freundlich, Temkin and D-R isotherm models. In addition, for both metal ions, adsorption processes were found to be endothermic, spontaneous and following pseudo-first order kinetics. AAJPL could be reused efficiently three times.

Author Contributions: Data curation, M.D.; Formal analysis, I.H.A. and M.I.K.; Funding acquisition, M.K.A.M.; Methodology, I.H.A.; Supervision, M.K.A.M.; Validation, I.H.A.; Writing—original draft, M.I.K.; and Writing—review and editing, M.M.A.

Funding: The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University for funding this work through research groups program under grant number R.G.P.1/97/40.

Conflicts of Interest: The authors declare no conflict of interest.

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