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Assessment of the natural jojoba residues as adsorbent for removal of cadmium from aqueous solutions

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ABSTRACT

In this work, Jordanian jojoba was tested as an adsorbent for the removal of cadmium ions from aqueous solutions. Batch adsorption tests were carried out at 25, 35, 45 and 45°C using different initial Cd^{2+} concentrations in the range of 20–80 ppm. The effect of adsorbent concentration on the equilibrium uptake of Cd^{2+} ions was investigated for different jojoba concentrations in the range 5–25 mg/ml. The experimental results showed that the adsorption of Cd^{2+} ions on jojoba residue was dependent on the pH and temperature. The uptake of cadmium ions increased with increasing pH, temperature and initial Cd^{2+} concentration, but decreased with increasing adsorbent concentration. Maximum Cd^{2+} uptake of 9.89 mg/g was achieved at jojoba concentration of 5 mg/ml and Cd^{2+} ion concentration of 25 ppm. The kinetics studies showed that equilibrium uptake attained in the first 120 min. Both Langmuir and Freundlich models were used and fitted the experimental data reasonably well. The presence of salt, in the form of NaCl, in the adsorbent-Cd^{2+} ions suspension resulted in a decreased of cadmium uptake.

Keywords: Jojoba residue; Cadmium; Adsorption

1. Introduction

The removal of toxic heavy metals from water is a matter of great interest in the field of water pollution. It results in a serious cause of environmental degradation. Of one of the main types of wastewater, industrial wastewater streams are polluted with toxic materials such as heavy metals, phenols and dyes. Examples of industries resulted in such streams include paints and dyes, mining, petrochemical, refining ores, fertilizer industries, detergents, batteries, paper industries, pesticides, etc. Removal of toxic heavy metals from wastewater before discharge to the environment is necessary due to the diverse effects of heavy metals to the human being and to the aquatic life. When present at high concentrations, heavy metals can cause many diseases to human being. For example, chronic inhalation and oral exposure of humans to cadmium results in a build-up of cadmium in the kidneys that can cause kidney disease, including proteinuria, a decrease in glomerular filtration rate, and an increased frequency of kidney stone formation. Chronic inhalation or oral exposure of animals to cadmium results in effects on the kidney, liver, lung, bone, immune system, blood, and nervous system [1,2]. The permissible limit for cadmium in drinking water is 0.0005 milligrams per kilogram per day (mg/kg/d), while the dietary exposure to cadmium is 0.001 mg/kg/d; both are based on significant proteinuria in humans [3]. The California Environmental

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Protection Agency California (CalEPA) has established a chronic reference exposure level of 0.00001 milligrams per cubic meter (mg/m^3) for cadmium based on kidney and respiratory effects in humans [3].

Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis [4–7]. Adsorption is a well-known equilibrium separation process that is commonly used to remove pollutants form water because of its simplicity, convenient operation and low cost application. Activated carbon is a well known adsorbent that is often used in such application. It is hydrophobic, has high porous structure and a relatively large surface area between 300 and 2500 m^2/g, which is the largest among all sorbents [8]. However, the relatively high cost of activated carbon largely restricts its use in developing countries. Therefore the availability of substitute adsorbents to maintain treatment cost as low as possible is needed. Agriculture residues such as wood sawdust [9] and olive seeds residue [10] were found to be of acceptable efficiency for removing colors from aqueous solutions and effluents. In the last years, certain raw waste products from industrial or agricultural operations, such as: pine bark [11], grape stalks [12], crop milling waste [13], rice husk [14], and peanut hull [15], have been investigated as adsorbents to remove different heavy metals from water. Relatively recently, Unlu and Eros [16] used bipolymeric material as sorbents for heavy metals. Al-Asheh et al. [17] assessed the ability of naturally occurred clay for copper sorption. Carboxylic modified palm stone was also utilized as sorbent for metal solutions [18]. The potential of cheap cellulose-containing natural materials like groundnut shells and sawdust was assessed for Cu(II), Ni(II) and Zn(II) adsorption from their aqueous solutions [19]. Natural zeolite was used by Motsi et al. for removal of heavy metals from acid mine drainage [20].

Jojoba nuts are grown in Jordan and used for production of oil. The oil is normally obtained by pressing and/or leaching using organic solvent. The by-product of Jojoba nuts is the meal remaining after oil extraction. The by-product constitutes about 50% of the nut; thus, any commercial utilization of Jojoba oil should consider handling of such large amounts of meal and its potential uses [21]. The fact that the nuts contain about 50% oil suggests that it has high porosity once the oil is extracted. The possibility of using this residue is considered in this work. The organic constituents of the meal would suggest it as adsorbent candidate for heavy metals. This is due to the possibility of available legends, i.e. amines, hydroxyl or carboxyl, of the organic matters, which are some times responsible for sorption of heavy metals.

The main objective of this work is to assess the ability of Jojoba nuts residue to adsorb Cd^{2+} ions, as a model of heavy metals, from aqueous solutions. The effects of temperature, adsorbent and adsorbate concentrations and addition of salts on sorption of cadmium by Jojoba residue will be considered. Langmuir and Freundlich isotherm models will be used to represent the equilibrium data collected in this work.

2. Materials and methods

2.1. Materials

Jordanian jojoba nuts were obtained from the Jordan University of Science and Technology (JUST) farm. Jojoba oil was extracted from the seeds using a Soxhlet extractor and hexane as a solvent. Details of the extraction method can be found elsewhere [22]. The jojoba residue solids were collected and then dried at 105°C to guarantee that water and hexane were removed. The dried jojoba seed samples were crushed, and then sieved to the size fractions of 0.0125, 0.212, 0.7, and 1 mm. These were served as adsorbents of Cd^{2+} in this work.

2.2. Adsorption test

The batch adsorption tests were conducted at 25, 35, 45, and 55°C. In this case, water bath shaker was used and each time it was adjusted at specified temperature. Aqueous solution of 25 ppm Cd^{2+} was prepared; then, certain amount of jojoba nuts of residue was placed into tubes containing 10 ml of this solution in order to give a concentration of adsorbent in the final suspension in the range 5 to 25 mg/ml. The pH of the suspensions was adjusted in the range of 1.7–6.65 using either 0.1 M HCl or NaOH. The tubes were then kept in a thermostatic liquid shaker at the desired temperature. At specified periods of time, samples were removed from the shaker for further analysis in order to investigate the kinetics of the process; otherwise they were left until equilibrium. The samples were filtered and the Cd^{2+} ions concentration in the filtrate was measured using atomic absorption spectrophotometer (Spectro AA10, Varian). After that, the amount of Cd^{2+} ions adsorbed, or uptake, was calculated using the balance equation:

$$q = \frac{V(C_0 - C)}{m}, \tag{1}$$

where C_0 is the initial concentration of Cd^{2+} in the solution (mg/l), C is Cd^{2+} ions concentration (mg/l) after adsorption, m is the amount of adsorbent (mg) been added, V is the volume of solution used (l), and q is the uptake (mgCd^{2+}/mg adsorbent). To study the effect of different operating parameters on this process, in each experiment, one parameter was varied while all other parameters were kept constant.

2.3. Adsorption isotherms

Different adsorption models were used to describe the equilibrium relation between the concentration of Cd^{2+} in the liquid phase and that on the solid adsorbent at a given temperature. These include the well known equilibrium isotherms Langmuir and Freundlich models. In its linearized form, the Langmuir model can be expressed as:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QK}\frac{1}{C_e}, \tag{2}$$

where Q and K are the model parameters related to the maximum theoretical adsorption capacity and the energy of adsorption, respectively, C_e and q_e represent concentrations of Cd^{2+} in the solution and in the sorbent, respectively, at equilibrium. Langmuir model assumes monolayer coverage of sorbent by the solute adsorbate. A plot of $1/q_e$ versus $1/C_e$ should be linear if the data follows Langmuir equilibrium isotherm; the slope and intercept of such plot allow calculations of Q and K values.

The equilibrium isotherm Freundlich equation may be applied for heterogeneous surfaces and in linearized form can be expressed as:

$$\ln q_e = \ln k_F + \frac{1}{n}\ln C_e \tag{3}$$

where k_{F} is the Freundlich capacity parameter, $1/n$ is the Freundlich parameter related to sorption intensity. The model parameters k_{F} and $1/n$ can be obtained from the intercept and slope, respectively, of the linear plot of $\ln q_e$ versus $\ln C_e$.

3. Results and discussion

3.1. Effect of agitation time

Study of sorption kinetics is important as it leads to determination of time required to reach equilibrium and possible mechanism for the sorption process. Figure 1 shows the effect of agitation time on the kinetics of Cd^{2+} uptake by Jojoba residue. It can be seen that high adsorption rates occurred at the start of the experiment where the rate of Cd^{2+} ion uptake was rapid during the first 30 min. This indicates that the adsorption process was very fast and led mainly to attachment on the surface of the adsorbent. Although there is no significant change in the metal uptake after the first two hour of the sorption process, all other sorption tests were carried out for 24 hours to ensure equilibrium.

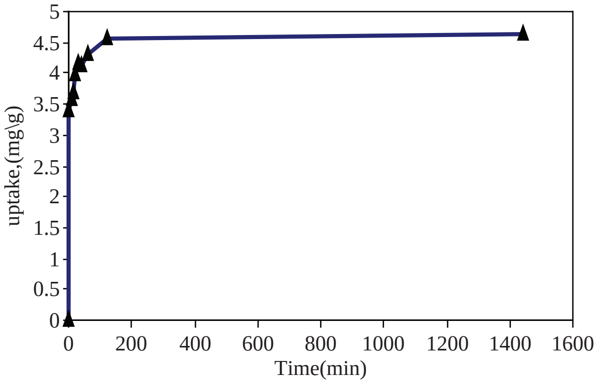

Fig. 1. Kinetics of Cd^{2+} ions uptake by Jojoba residue. Jojoba residue concentration: 5 mg/ml; Cd^{2+} concentration: 25 ppm; initial pH: 6.4; temperature 25°C.

3.2. Effect of adsorbent concentration

The effect of adsorbent concentration on the equilibrium uptake of Cd^{2+} ions was investigated at a fixed temperature, pH, contact time and initial adsorbate concentration. The results are shown in Figure 2 for jojoba concentrations in the range 5 to 25 mg/ml. It is seen that the equilibrium uptake increased as the jojoba concentration increased due to the increase in the available active sites; while, the concentration of Cd^{2+} ions in the solution, or the residual concentration, decreased with the higher amounts of sorbent. This is an expected reasonable trend for such parameter; since as the sorbent particles surrounding the metal ions increased, more metal ions will be attached to these particles.

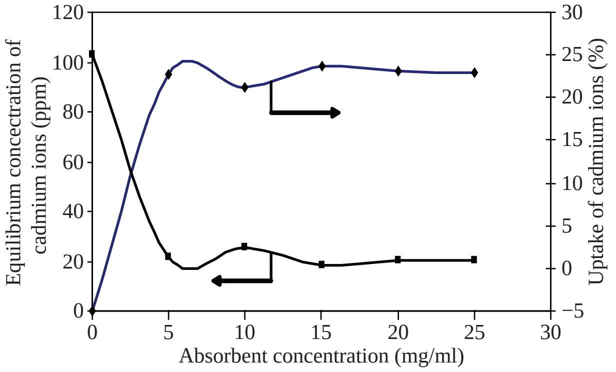

Fig. 2. Effect of adsorbent concentration on the uptake of Cd^{2+} ions. Initial Cd^{2+} concentration: 100 ppm; initial pH: 6.4; temperature 25°C.

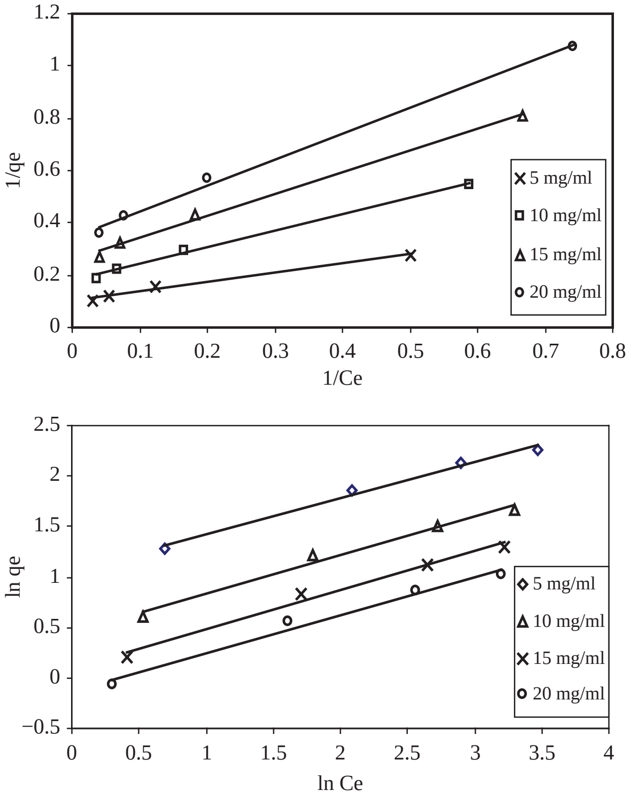

Fig. 3. Representation of equilibrium concentration of Cd^{2+} versus its uptake by Langmuir (A) and Freundlich (B) isotherm models; symbols represent experimental data and lines represent model predictions. Initial Cd^{2+} concentration: 25 ppm; initial pH: 6.4; temperature 25°C.

After sorbent concentration of 10 mg/ml, the residual concentration did not change significantly (Fig. 2). Therefore, economically sorbent concentration of 10 mg/ml was the most convenient for this removal process, at these operating conditions.

Figures 3A and B show the adsorption isotherms onto jojoba residue at different adsorbent concentrations, namely of 5, 10, 15 and 20 mg/l. The experimental data are represented in linearized forms of Linearized Freundlich models. The plots indicate that both models show good representation of the experimental data. Langmuir and Freundlich parameters obtained from such plots are displayed in Table 1 along with the R^2 values for each line, an indication of the goodness-of-fit. The high values of R^2, greater that 0.95, confirm the agreement between the models and the experimental data. It is noticed (Table 1) that the adsorption capacity parameters (Q and k_F) decreased with the increase in the adsorbent concentration. Such variation in the adsorbed amount with concentrations was reported by many workers [23–25].

3.3. *Effect of initial pH*

Adsorption of heavy metal ions is strongly dependant on the pH values of their aqueous solutions [26]. The effect of initial pH value on the adsorption of Cd^{2+} ions onto jojoba residue was investigated over the pH range 1.7–6.6. The results obtained in this work are presented in Table 2. It is seen that cadmium sorption by jojoba residue is favorable over pH range 3.5–6.6. This indicates that the interaction between Cd^{2+} and jojoba residue is enhanced with the increase in the pH. At low pH values, cation exchange between Cd^{2+} ions and H^+ reduces the uptake of Cd^{2+} onto jojoba residue which result in a low adsorption capacity. As the pH values increases, the uptake of Cd^{2+} ions increase since the adsorption occurs at active sites created by the displacement of H^+ ions from the surface [24].

3.4. *Effect of temperature*

The effect of temperature on the adsorption of Cd^{2+} ions onto jojoba residue was investigated. In this case, the adsorption tests were performed at 25, 35 and 45°C using different initial Cd^{2+} concentrations in the range of 20–80 ppm. That way, equilibrium isotherms can be collected at different temperatures, as shown in Figure 4. It is seen that the results follows linearized Langmuir isotherm model and that Cd^{2+} uptake by jojoba residue increased with an increase in the temperature. This conforms to exothermic nature of this sorption process. The Langmuir constants (K) were obtained from the linear plots of Fig. 4 at different temperatures. To determine the thermodynamic characteristics of this

Table 1
Langmuir and Freundlich constants at different adsorbent concentration

Adsorbent concentration (mg/ml)	Langmuir isotherm			Freundlich isotherm		
	K	A	R^2	K_f	$1/n$	R^2
5	9.891	0.168	0.989	2.882	0.3589	0.9915
10	5.621	0.281	0.9959	1.565	0.3838	0.9825
15	3.818	0.315	0.994	1.100	0.3859	0.9862
20	2.897	0.348	0.9951	0.875	0.378	0.9814

Table 2
Effect of initial pH on uptake of Cd^{2+} ions from aqueous solution*

Initial pH	Residual pH	Uptake (mg/g)
6.65	4.60	4.086
5.02	3.80	4.082
4.01	3.20	4.1092
3.53	2.70	4.122
2.19	1.65	0.4
1.71	1.2	0

* Residual pH of adsorbent in distilled water with no Cd^{+2} present: 5.2.

sorption process, the K values at different temperatures were plotted as ln K versus $1/T$, as shown in Figure 5. The slope of this figure should provide the enthalpy of adsorption (ΔH), which was found to be –27.14 kJ/mol. The negative value of the enthalpy of adsorption confirms that adsorption of Cd^{2+} by jojoba residue is an exothermic process. The low value of ΔH, lower that 45 kJ/mol, would indicate that this sorption process is due to physical attachment at the surface of adsorbents [27], i.e. relatively weak interaction between solute and surface.

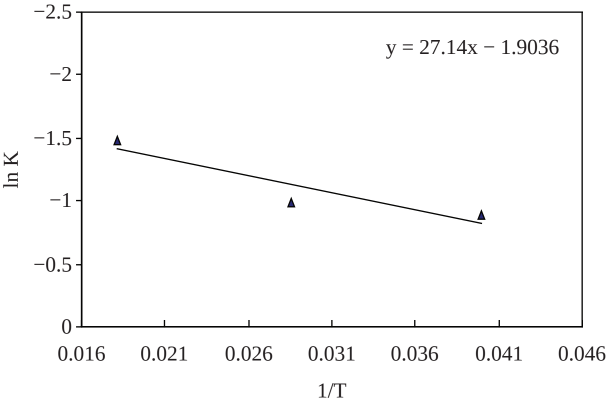

Fig. 5. Relationship between ln K and $1/T$ for adsorption of Cd^{2+} ions by jojoba residue.

3.5. *Effect of salt addition*

It is known that salt ions interfere with the adsorption of heavy metal onto adsorbents. This interference was investigated in this work taking sodium chloride (NaCl) as a model of salt ions. The study considered different concentrations of NaCl which were added to different adsorbent-metal suspensions at given metal and sorbent concentrations. Figure 6 shows that the presence of salt depressed Cd^{2+} uptake and that the increase in salt concentration decreases further cadmium uptake. Since the diffusion coefficient of Na^+ ions in water (1.33×10^{-9} m^2/s) is greater than Cd^{2+} ions in water (0.72×10^{-9} m^2/s) [28], the rate of Na^+ ions adsorption would be higher than that of Cd^{2+} ions on the jojoba residue surface. As a result, an increase in salt concentration results in a decrease in Cd^{2+} ions uptake.

4. Conclusions

Jojoba residue can be considered as a potential adsorbent for the removal of Cd^{2+} ions from industrial wastewater streams. This adsorption process was found to be physical in nature, limited by the surface of the adsorbent. The uptake of Cd^{2+} ions increased with increasing solution temperature or pH. The addition of NaCl to the adsorbent Cd^{2+} ions suspension decreased the uptake of Cd^{2+} ions. Both Langmuir and Fruendlich

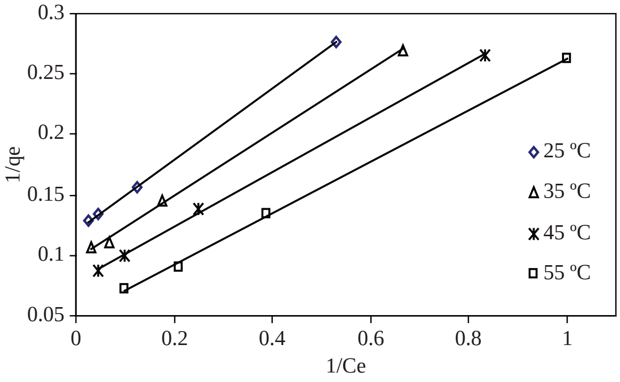

Fig. 4. Relationship between equilibrium concentration and uptake for Cd^{2+} ions at different temperatures; symbols represent experimental data and lines represent Langmuir isotherms. Jojoba residue concentration: 5 mg/ml; initial pH: 6.4.

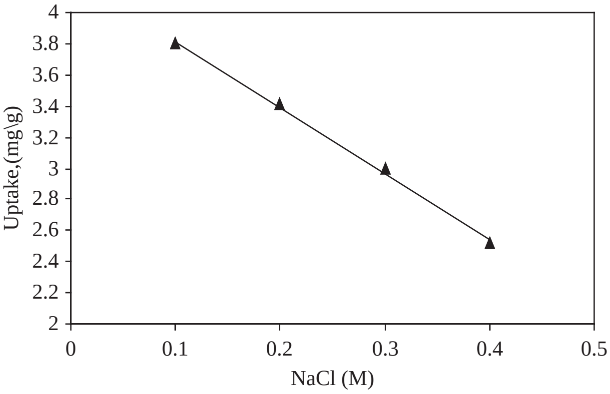

Fig. 6. Effect of NaCl concentration on Cd^{2+} uptake by jojoba residue. Sorbent concentration: 5 mg/ml; Cd^{2+} concentration: 25 ppm; initial pH: 6.4; temperature 25°C.

isotherms were fit reasonably the experimental data of Cd^{2+} uptake by jojoba residue.

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