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Removal of Cadmium Ions from Wastewater by Batch Experiments

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Abstract

Adsorption experiments were carried out using two different low-cost sorbent materials, date seeds and olive seeds. These sorbents used as a single phase (not as mixture) to remove cadmium ions from simulated wastewater by adsorption process. The equilibrium time was found at 2 hr. The experiments include different parameters such sorbent type and weight and contact time. It was found that both of olive seed and date seed have approximately the same adsorption capacity (qm) with 15.644 mg/g and 15.2112 mg/g, respectively. Equilibrium isotherms and kinetic studies have been carried out. Langmuir isotherm model better fits the experimental data compared with the Freundlich isotherm for olive seed, while Freundlich isotherm fits for date seed .A pseudo-second order kinetic model was appropriate to the experimental data for both seeds. It can be concluded that the olive seed and date seed could be a good sorbent for the removal of cadmium ions from wastewater.

Keywords: Cadmium ions, Date and Olive seeds, wastewater.

Introduction

Toxic metal compounds not only contaminate surface water sources (seas, lakes, ponds, and reservoirs), but also contaminate underground water in trace amounts by leaching from the soil after rain and snow [1]. Cadmium takes much attention by environmentalists as one of the most toxic heavy metals. The increasing presence of cadmium in the environment is chiefly due to its use in electroplating, smelting, plastics, pigments, ceramics, battery, and cadmium-rich phosphate fertilizers and mining [2, 3]. Cadmium has negative effects on the environment and is easily accumulated in living systems. The harmful effects of cadmium ions are renal damage, hypertension, proteinuria, kidney stone formation and testicular atrophy [4]. It combines with sulfa hydria group in protein and restrains the activity of enzyme [5]. A lot of methods are investigated to treat the metal contaminated effluent; these methods are either inefficient or expensive especially when the concentration of the containments is low. For this reasons the use of agricultural wastes in removal of heavy metals has been investigated. Agricultural wastes are characterized by ready availability, affordability, eco-friendliness, and high uptake capacity for heavy metals due to the presence of functional groups which can bind metals to increase the removal of heavy metal from effluents [6]. Several low-cost materials such as peanut husk charcoal and fly ash [7], scoria [8], Moringa oleifera bark [9], orange peel [10], watermelon shell [11], sunflower leaves [12], Eichhnornia crassipes [13], soybean meal waste [14], Punica granatum peel waste [15], Acacia leucocephala bark [16], wheat straw [17] and maize cob [18] have been used to remove metal ions from aqueous solutions. Date seed is usually discarded as unwanted material in many date producing countries such as Iraq. Date is cultivated in arid and semi-arid regions and can thrive in long and hot summers, low rainfall and very low relative humidity [19].

Iraq is one of the largest producers of date fruits; while suitable environment for the cultivation of olives is in the areas near the foothills of the mountains and olive trees grow in many types of land. This seed represents a big size of the total weight of fruit (both materials are abundantly available through our country and the world) [20]. Adsorption is the most suitable method used to remove metals ions from the aqueous solutions. Adsorption is a surface phenomenon, in which molecules of adsorbate are attracted and held to the surface of an adsorbent until equilibrium is reached between adsorbed molecules and those still freely distributed in the carrying gas or liquid. The adsorption phenomenon depends on the interaction between the surface of the adsorbent and the adsorbed species. The interaction may be due to: (1) chemical bonding; (2) hydrogen bonding; (3) hydrophobic and (4) van der Waals forces [21]. The adsorption isotherms describe the relationship between the amount adsorbed by a unit weight of solid adsorbent and the amount of solute remaining in the solution at equilibrium. Langmuir and Freundlich isotherms models are used frequently to describe adsorption of metal ions by different materials.

The aim of this work is to explore the possibility of utilizing seeds of date and olive for the adsorptive removal of cadmium (II) from simulated wastewater. Different experimental parameters have been investigated such as sorbents concentration, contact time, and initial cadmium (II) concentration. Adsorption isotherms and kinetics were investigated and different adsorbent models were used to fit the experimental data and to elucidate the possible adsorption mechanism.

Materials and Methods

1. Adsorbate and Adsorbent

Cadmium solutions of requirable concentration (20, 30, 40, and 50 mg/L) have been prepared by dissolving the appropriate amount of cadmium nitrate Cd $(NO_3)_2 \cdot 4H_2O$ in distilled water. The date seeds and olive seeds were prepared for the present study by grinding and sieving to obtain a grain size of range less than 105μm in diameter and then washed with distilled water and dried in an oven at 105^{o}C for 24 hr and stored in a desiccator until use (during the research period approximately 60 days).

2. Batch adsorption experiments

Batch experiments are performed with 100 ml of a sample solution and a requirable adsorbent dose of 0.15, 0.25, 0.35 and 0.45 gm and parameter such as contact time, concentration of solution. The mixture is transferred into a 250 ml conical flask and stirred for 3 hour, filtered and analyzed for its absorbed concentration. All experiments are conducted at room temperature conditions. Absorbed concentrations are determined by Atomic absorption spectrophotometer.

3. Fourier-Transform-Infrared Analysis (FTIR)

It is essential to identify the functional groups present on the biomass involved in this search. The main effective binding sites can be identified by FTIR spectral comparison of the biosorbent, cadmium ions-loaded biosorbent. Biosorbent were examined using (SHIMADZO FTIR, 800 series spectra- photometer). Two flasks of 250 ml were filled with 100 ml of each metal solution 50 mg/L and 1gm of both dried seeds (olive and date). The flasks were then placed on a shaker and agitated continuously for 3hr at 200 rpm. Samples of each flask were dried in oven at 50 C^0 for 48 hr.

Results and Discussion

1. FTIR Analysis

Figure 1 (a and b) show the FTIR spectra of date seeds and olive seeds, respectively. Numerous chemical functional groups have been characterized as potential adsorption sites to be responsible for binding cadmium onto date and olive seeds. The spectrum pattern of loaded Cd (II) showed changes in the peak absorption as compared to unloaded Cd (II) which result from adsorption process. Contribution of each functional group in this process is summarized in Tables 1 and 2.

Table 1: Functional groups responsible for Cadmium adsorption by Date seed

Wave number (cm^{-1})	Assignment Groups	After adsorption of Cd (II)
3387.00	Carboxylic acid, Amides	3402.43
2908.65	Carboxylic acid	2916.37
1373.03	Nitro groups	1373.32
1157.29	Carboxylic acid	1161.15
1111.00	Carboxylic acid	1111.14
817.82	Aromatic	825.53
659.66	Alkyl halides	667.37

Table 2: Functional groups responsible for Cadmium adsorption by Olive seed

Wave number (cm^{-1})	Assignment Groups	After adsorption of Cd (II)
3398.57	Carboxylic acid, Amides	3410.15
1639.49	Carboxylic, Hydroxyle, Alkanes	1654.92
1423.47	Carboxylic acid	1427.32
1327.03	Nitro groups	1334.74
1161.15	Carboxylic acid	1165.00
1122.57	Carboxylic acid	1188.71
1041.56	Carboxylic acid	1045.42
813.96	Aromatic	833.25
601.79	Alkyl halides	605.65

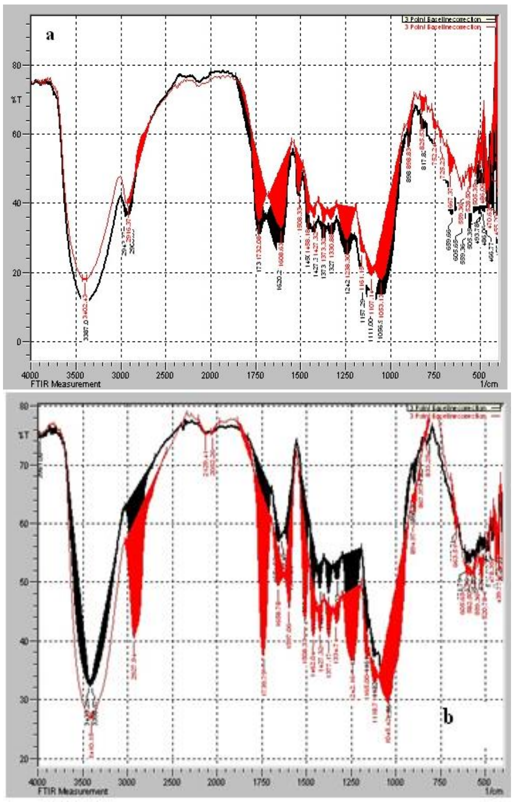

Fig. 1: FTIR spectrums a. Date seed raw, loaded Cd (II); b. Olive seed raw, loaded Cd (II)

2. Effect of Sorbent Type and Amount

Figure 2 shows the effect of sorbent types (date seeds and olive seeds) on the removal percentage (R %) of Cd in simulated wastewater. The obtained data indicated that both of biosorbent showed high removal efficiency towards Cd (II) ions about 98.12% and

96% removal efficiency for date and olive, respectively. Difference in sorption capability of heavy metals by sorbent materials is due to the different affinity of metal ions to active groups on the substrate [22].

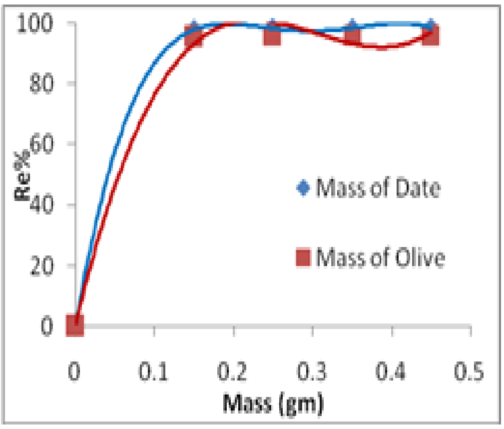

Fig. 2: Type of Adsorbent on Removal Efficiency

3. Effect of Contact Time

The effect of contact time was tested at initial metal ions concentration of 40 ppm/100 ml and pH 5.5 shown in Figure 3. There was a rapid adsorption of Cd (II) in the first 60 min, and, thereafter, the rate of adsorption become slower; this is due to a decrease or lack of number of active sites [23]. It can be concluded that 2 h. contact time is sufficient to reach equilibrium conditions for cadmium ions. The maximum removal efficiency of Cd (II) was (98.2% by date sorbent and 96.15% by olive sorbent, respectively).

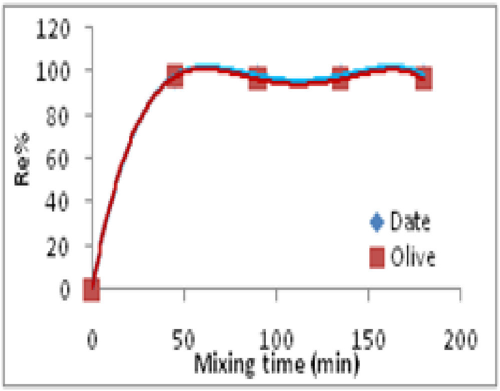

Fig. 3: Effect of Contact Time on Removal Efficiency

4. Effect of Cadmium Initial Concentration

The adsorption experiments were tested at initial concentrations of 20, 30, 40, and 50 mg/L with a constant date and olive amounts of 0.25 g, contact time 60 min and pH 5.5. Figure 4 shows the results. The plot show that increase in the Cd (II) concentration from 20-50 mg/L results in a decrease in percentage Cd (II) removal from 99% to 97.31% for date sorbent, and 97.68% to 94.88% for olive sorbent, respectively. The decrease in the removal efficiency of Cd (II) can be attributed to the saturation of available active sites on the both seeds (date and olive). The increase in adsorption capacity may be due to the higher adsorption rate and the utilization of all available active sites for adsorption at higher Cd (II) concentration [24].

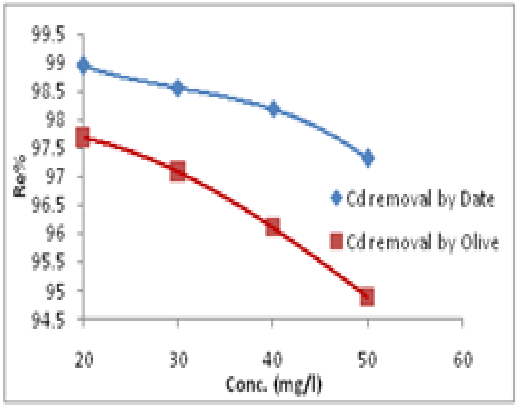

Fig. 4: Effect of Initial Concentration of Cadmium on Removal Efficiency

Adsorption Isotherm Models

Two isotherm models were used to describe how solutes interacted with the sorbents. The Langmuir sorption model is based on the assumption that maximum sorption corresponds to a saturated monolayer of solute on the sorbent surface. This model also supposes that all the sorption sites are assumed to be identical, each site retains one molecule of the given compound and all sites are energetically independent of the sorbed quantity [24]. The linear form of the Langmuir Eq. can be described by:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{bq_m} \qquad \dots(1)$$

Where C_e (mg L^{-1}) is the equilibrium concentration of the sorbate, qe (mg g^{-1}) is the amount of sorbate per unit mass of sorbent, qm (mg g^{-1}) and b (Lmg^{-1}) are Langmuir constants related to sorption capacity and rate of sorption, respectively. The linear plot of specific sorption (C_e/q_e) against the equilibrium concentration (C_e) shown in Figure 5a.

The Freundlich isotherm is the earliest known relationship describing the sorption equation. The fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous surface energy systems [24]. The linear form of the Freundlich model is expressed by the following Eq.:

$$lnq_e = \frac{1}{n} lnC_e + lnK_F \qquad \dots(2)$$

Where K_F ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1}) is roughly an indicator of the sorption capacity and n is the sorption intensity. The equilibrium data were further analyzed using the linear form of Freundlich isotherm, by plotting ln q_e versus ln C_e Figure 5b the calculated Langmuir and Freundlich isotherms constants and the corresponding coefficients of determination are shown in Table 3.

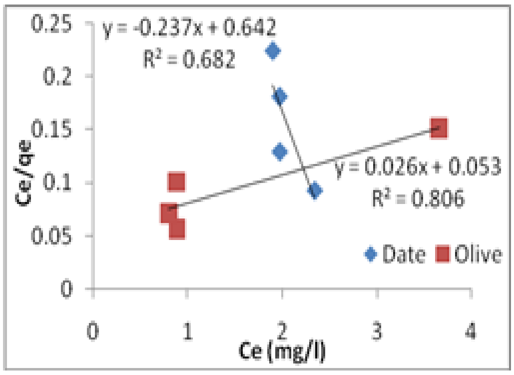

Fig. 5a: Applying Langmuir adsorption isotherm

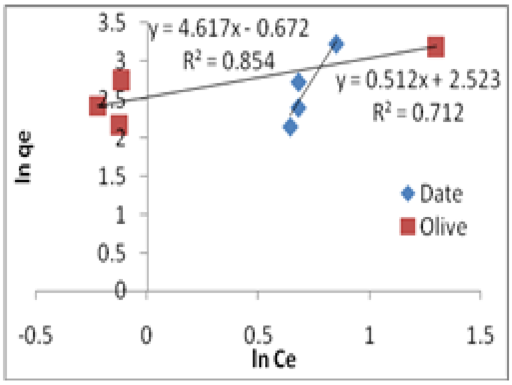

Fig. 5b: Applying Freundlich adsorption isotherm

Table 3: Langmuir and Freundlich isotherms constants and the corresponding coefficients

Adsorbent type	**Isotherm Models**					
	Langmuir			Freundlich		
	R²	a	b	R²	N	K
Date seed	0.682	4.2194	0.3692	0.854	0.217	0.21281
Olive seed	0.806	38.462	0.491	0.712	1.9531	333.423

It can be observed that experimental data fit the isotherm adequately. The applicability of the Freundlich model to the experimental data indicates monolayer coverage on heterogeneous adsorbent surface by each of Cd (II) ion for date seed; while for olive seed Langmuir model is the best model which describes their experimental data.

Adsorption Kinetics

Adsorption kinetics can be described by various kinetics models; pseudo-first-order, pseudo-second order. The linear form of the pseudo-first order rate model is represented in Eq. 3. The pseudo-second-order rate model can be represented by Eq. 4 [25]:

$$\ln(q_e - q) = lnq_e - k_1 t \qquad \dots(3)$$

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad \ldots(4)$$

Where q_e is the amount of metal sorbed at equilibrium (mg/g); q_t is the amount of metal sorbed at time t (mg/g); and k_1, k is the equilibrium rate constant of pseudo first order and pseudo second order sorption, respectively. Figure 6 shows the both kinetics models which were used in this study; constants (k_1, k) and other parameters of both models, compiled in Table 4 along with correlation coefficients (R^2) values.

Table 4: Various kinetics models parameters

Type of adsorbent	q_e experimental mg/g	Pseudo-first-order			Pseudo-second-order		
		k_1 1/min	q_e calculated mg/g	R^2	k_2 g/mg.min	q_e calculated mg/g	R^2
Date seed	15.2112	0.027	4.665	0.845	0.0045	16.667	0.973
Olive seed	15.644	0.022	4.047	0.810	0.0081	16.393	0.995

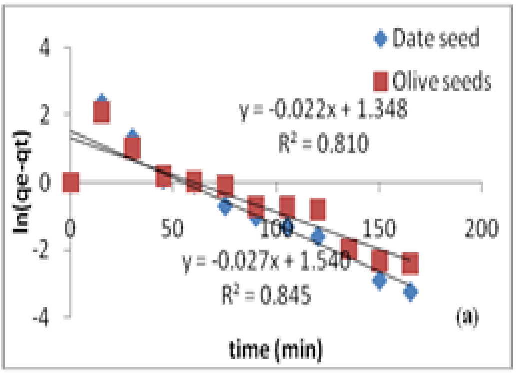

Fig. 6a: Applying Pseudo-first-order for adsorption of Cd^{+2} using Date seed and Olive seed

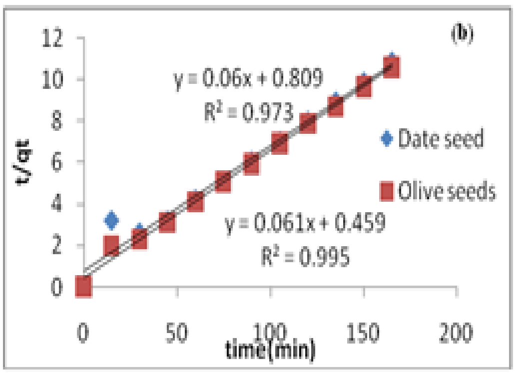

Fig. 6b: Applying Pseudo second- order for adsorption of Cd^{+2} using Date seed and Olive seed

The results indicate that, the adsorption process of Cd (II) at the surface of the both adsorbents (date and olive seeds) followed the second order reaction kinetics.

Conclusions

The removal of Cd (II) in synthetic water by using adsorption technology was studied in the batch experimental systems. Based on the results, the following conclusions can be drawn. The prepared sorbent is an efficient biomaterial for removal of cadmium ion from industrial wastewater. Equilibrium metal adsorption decreased with the increase in the initial concentration of Cd (II) ions suggesting the applicability of the biomaterial at lower concentrations. The sorption of Cd (II) by date seed is a monolayer according to Freundlich adsorption isotherm, while by using olive seed as adsorbent the fit model is Langmuir. The percent removal of Cd (II) by adsorption under the conditions employed in this study is 95.1%, 97.8% by date and olive, respectively, with an effective dose of 0.25 g of bio-adsorbent. Adsorption equilibrium for the metal was reached in about 2 h. The study demonstrated that the adsorption process was coincided second order kinetics. This methodology can be applied to the removal of toxic metals from wastewater efficiently. The method was simple, cost effective and environmental friendly.

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