

Adsorption of Cadmium onto Activated and Non-Activated Date Pits

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Abstract—In this project cadmium ions were adsorbed from aqueous solutions onto either date pits; a cheap agricultural and non-toxic material, or chemically activated carbon prepared from date pits using phosphoric acid. A series of experiments were conducted in a batch adsorption technique to assess the feasibility of using the prepared adsorbents. The effects of the process variables such as initial cadmium ions concentration, contact time, solution pH and adsorbent dose on the adsorption capacity of both adsorbents were studied. The experimental data were tested using different isotherm models such as Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich. The results showed that although the equilibrium data could be described by all models used, Langmuir model gave slightly better results when using activated carbon while Freundlich model, gave better results with date pits.

Keywords—Adsorption, Cadmium, Chemical Activation, Date Pits.

I. INTRODUCTION

IN many developing countries surface water, ground water or those reused for irrigation purposes are polluted with toxic anions, heavy metals such as: arsenic, cadmium, chromium, copper, lead, mercury, zinc, organic compounds and dyes due to effluents from industries. These unwanted chemicals generate health problems such as accumulative poisoning, cancer, brain damage, etc., when they exceed the tolerance limits in water. Cadmium is accumulated in the human body, causing erythrocyte destruction, nausea, salivation, diarrhea and muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity. The drinking water guideline value recommended by World Health Organization (WHO) is 0.005 mg Cd/l [1].

Various treatment techniques are available for anions, heavy metals, organics and dyes removal. These methods include ion exchange, evaporation, reverse osmosis and chemical precipitation. Most of these methods suffer from drawbacks such as high capital, operational cost and several problems in the disposal of the residual metal sludge. The use of activated carbons to remove organic and inorganic pollutants from waters is very common, because of their high surface area, microporous character and the chemical nature of

their surface. Commercially available activated carbons from coconut shell, lignite, peat etc, are effective for the removal of various pollutants. However, they are expensive and their regeneration cost is also high. Thus, there is a need for low-cost and readily available materials for the removal of toxic pollutants from water. Some of the low-cost adsorbents already reported for the removal of heavy metals are waste tea leaves for the removal of Pb^{2+} , Cd^{2+} , and Zn^{2+} [2], agricultural by products such as almond shells, olive stones and peach stones for the removal of Zn^{2+} , Cd^{2+} and Cu^{2+} [3], sediments of rivers for the removal of Cd^{2+} , Zn^{2+} , Cu^{2+} , and Pb^{2+} [4], peanut hull for the removal of Hg^{2+} [5], rice husk [6], bentonite [7] and zeolite [8]. Essa et al. [9] studied the potential of chemical activated date pits as an adsorbent. The date pits were impregnated with 70% phosphoric acid followed by thermal treatment between 300 to 700°C. The effects of activation temperature and acid concentration on pore surface area development were studied. Samples prepared at 500°C showed a specific area of 1319 m²/g and total pore volume of 0.785 cm³/g. Aqueous phenol adsorption trends using the local activated carbon sample were compared to a commercial sample (Filtrisorb-400). Adsorption of zinc and cadmium from aqueous solutions on raw date pits and activated carbon was investigated by Al-Sheryani [10]. Results showed that activated carbons gave higher adsorption capacity than raw date pits. Affinity of zinc to raw date pits was found to be greater than that of cadmium on date pits, while cadmium affinity was greater for activated carbon than that of zinc on activated carbon.

This work aims to produce activated carbon prepared from date pits to remove cadmium from water. The effects of initial cadmium ions concentration, contact time, solution pH, adsorbent mass and concentration will be investigated.

II. ADSORPTION THEORY

The successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases. Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent equals to the amount being desorbed. At this point, the equilibrium solution concentration remains constant. By plotting solid phase concentration against liquid phase concentration graphically, it is possible to depict the equilibrium adsorption

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isotherm. There are many theories relating to adsorption equilibrium. *Langmuir isotherm model* assumes monolayer coverage of adsorbate over a homogenous adsorbent surface where sorption is assumed to take place at specific homogeneous sites within the adsorbent; *Freundlich isotherm model* describes heterogeneous systems and assumes that as the adsorbate concentration increases the concentration of adsorbate on the adsorbent surface increases; *Temkin isotherm* suggests that the heat of adsorption of all the molecules in the layer will decrease linearly with coverage and is only valid over an intermediate range of concentrations and Dubinin-Radushkevich model which assumes monolayer adsorption but does not assume a homogeneous surface or constant sorption potential. It was applied to distinguish between the physical and chemical adsorption.

III. METHODOLOGY

Stock solutions of 1000 ppm of Cd ions were prepared by diluting predetermined amounts of cadmium metal with distilled water. The adsorbate stock solution containing Cd ions was prepared from cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$). Date Pits were collected and washed with hot tap water then by distilled water and allowed to dry in an oven at 80 °C for 2 hours. The dried samples were crushed and ground by using an electric agitated mortar; for more powder sample a coffee blender was used. The powdered sample was sieved in a sieve series 60-mesh size ($D < 125 \text{ nm}$). The sieved date pits was used for batch experiments as raw material (DP) and as activated carbon (AC).

Date pits powder was mixed with 85% phosphoric acid (PA) in weight ratio 1:3 then diluted 5 times with deionized water in a 1000 ml beaker. The mixture was gently boiled with stirring for few hours until the mixture turns to a black paste. The temperature of the paste at this stage was kept at 160 °C. Primary air activation was carried out during continuous heating while the material stirred for 15 minutes under air injection at a flow-rate of 3.0 l/min. During this period of carbonization and activation, the temperature was increased from 160 to 215 °C. This is followed by secondary air activation in which the black paste was poured in a test tube, mesh and fleece placed vertically in a tubular furnace heated electrically for 30 min. The matrix was activated for 1.5-2.0 bar at a temperature of about 600 °C and 800 °C. After activation, the tube from the furnace was removed and cooled for 10 min with the tap water. The synthesized carbon was washed with boiling deionized water, the slurry was filtered, the pH of the wash water was measured to assure neutrality, the carbon was dried in an oven at 100 °C for 12 hour, then cooled in desiccators, weighed, grounded, transferred to a container, and stored in the desiccators.

All adsorption experiments were carried out using reagent bottles of 100 mL capacity containing different amounts of each adsorbent in 50 mL solutions of different concentrations. The initial pH adjustment were carried out either by phosphoric acid or sodium hydroxide solutions before adding

the adsorbent. The bottles were shaken for a predetermined periods at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$) in a reciprocating shaker. The solution reaction mixture was separated using a centrifuge, and the concentrations of cadmium ions were determined in the filtrate by a Varian (Spectra AA-10/20) atomic absorption spectrophotometer. Metal solutions without adsorbent were analyzed before and after filtration. Neither precipitate nor metal ions adsorbed to the wall of the flasks were observed with the tested metals under the experimental conditions. All the experiments were duplicated to confirm the reproducibility of the experimental effects. The characterization of date pits was presented in Table I.

TABLE I
APPROXIMATE COMPOSITION OF DATE PITS

Test	mg/kg
Moisture	6.10
Ash	1.17
Crude fiber	9.18
Protein	5.27
Ether extract (crude fat)	1.73
Ca	507
Mg	641
Fe	135
Cu	5.44
Zn	40.7
Al	6.88

Prepared activated carbon in ratio (1:3) mainly exhibits lactones and phenol functional groups, showed in Table II.

TABLE II
SURFACE FUNCTIONAL GROUPS FOR DATE PITS AND ACTIVATED CARBON

Group	AC	DP
Lactones & Phenol (Meq H^+ /g)	0.017	0.015
Lactones (Meq H^+ /g)	0.008	0.016

IV. RESULTS AND DISCUSSION

A. Effect of Adsorbent Doses on Cadmium Adsorption

One of the important factors that influence the adsorption capacity is the mass of the adsorbent. The engineering oriented methodology is always targeting the economics of any process. Minimum costs for the system can be obtained by optimizing the size of the adsorption and regeneration units using the basic design equations. The influence of the adsorbent dose on the metal uptake and percent removal was studied for the heavy metal investigated in this study. The

experiments were carried out at pH 5.5 and fixed cadmium initial concentration of 100 ppm solution on date pits and activated carbon, the results are shown in Figs. 1 and 2. As can be depicted from these figures, when the adsorbent mass increased, the uptake of cadmium decreased and the percentage removal increased for both the date pits and activated carbon. In case of date pits, increasing weight from 0.1 to 3.0 g, increasing the percentage removal of Cd^{2+} from 11.3 to 74.6% and decreasing cadmium ions uptake from 5.1 to 1.1 mg Cd^{2+} /g adsorbent. The optimum mass of adsorbents was found to be 0.49 g for the date pits and 0.05 g for the activated carbon as shown in Figs. 1 and 2, respectively.

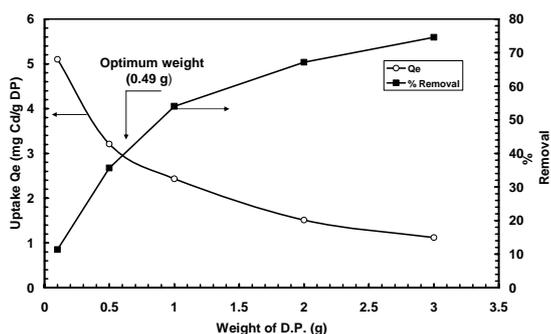


Fig. 1 Effect of date pits weight on the uptake and percentage removal of cadmium ions at initial Cd ions = 100 ppm, temperature = 18 °C and pH= 5.5

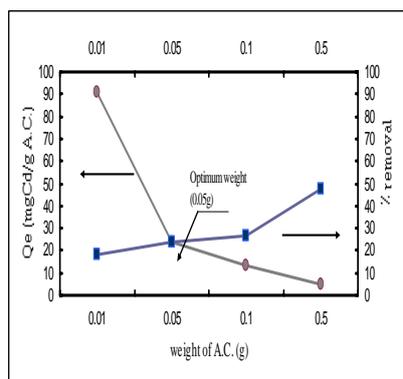


Fig. 2 Effect of activated carbon weight on the uptake and percentage removal of cadmium ions at initial Cd ions = 100 ppm, temperature = 18 °C and pH= 5.5

B. Effect of Solution pH

There are many factors that affect the wastewater treatment process such as adsorbent surface charge, solution pH, the degree of ionization, and the nature of the adsorbates. The effect of solution pH on cadmium adsorption onto date pits (DP) and activated carbon (AC) is shown in Fig. 3. This figure shows that metal uptake increases by increasing pH. This is due to the fact that at lower pH values, excess concentration of hydrogen ions (positive charge) competes with the cadmium ions on the active sites of the adsorbent. The optimum

solution pH was found to be 5.5 for both adsorbents. At higher pH values, precipitation of the heavy metal may occur.

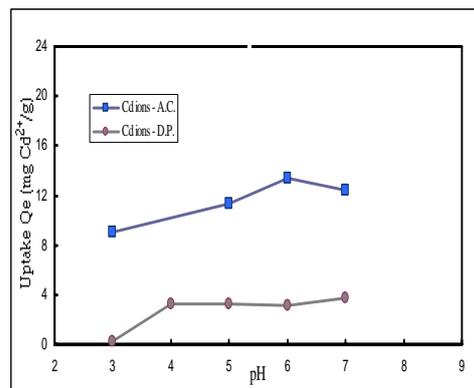


Fig. 3 Effect of initial solution pH on the activated carbon and date pits uptake of cadmium ions at initial Cd ions = 100 ppm, mass of D.P. = 0.5 g, mass of A.C. = 0.1 g and temperature = 18 °C

C. Effect of Agitation Time

Experiments with each adsorbent (DP and AC) were performed to determine the adsorption equilibrium time for cadmium ions. The adsorption rate of cadmium on either the raw date pits or activated carbon was found to be rapid in the initial period of contact time and then become slower until the rate approaches zero, where equilibrium is reached. It is clearly seen from Fig. 4 that ultimate adsorption for cadmium ions occurs within the first 45 min in the case of date pits and within the first 60 min in the case of activated carbon.

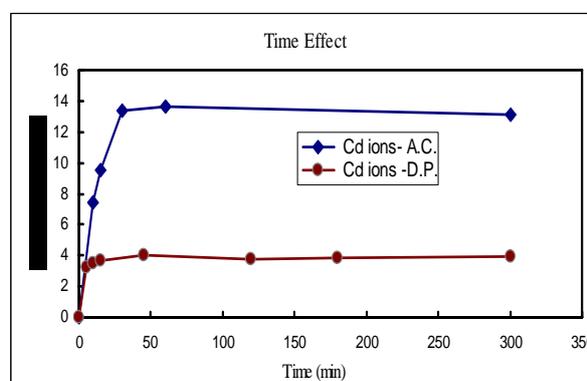


Fig. 4 Effect of agitation time on the activated carbon and date pits uptake of cadmium ions at initial concentration = 100 ppm, mass of DP = 0.5 g, mass of AC = 0.1 g, temperature = 18°C and pH = 5.5

The difference in the time needed to reach the equilibrium uptake between raw date pits and activated carbon in Cd^{2+} adsorption was due to the increase in total pore volume and specific surface area which resulted from the treatment with phosphoric acid. The first rapid predominant stage which is probably due to the abundant availability of active sites on the adsorbent and the second slower insignificant stage, in which

the sorption becomes less significant due to the gradual occupancy of these sites. The advantage of such rapid sorption in practical applications is that smaller reactor volumes can be used.

D. Effect of Initial Cadmium Ions Concentration

Fig. 5 showed the adsorption dependency on the initial concentration of cadmium ions, as the initial Cd^{2+} concentration increases the equilibrium concentration and the uptake of Cd^{2+} increases. The results for activated carbon used as adsorbent showed higher favorable adsorption rather than date pits, due to functional group existing, larger surface area and high porosity of A.C. For closely approach, at 110 ppm Cd^{2+} concentration equilibrium uptake values for both activated carbon and date pits are 26.5 and 6.2 (mg Cd^{2+} / g adsorbent), respectively.

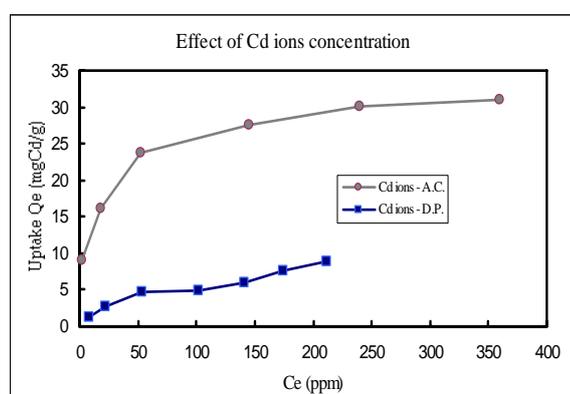


Fig. 5 Adsorption isotherm for cadmium ions. Experimental conditions: mass of DP = 0.5 g, mass of AC = 0.1 g, temperature = 18 °C, pH = 5.5

E. Equilibrium Isotherm Study

Out of several isotherms equations, four have been applied for this study: Langmuir, Freundlich, Tempkin and Redlich-Peterson isotherms. The parameters in the models were estimated by fitting experimental data to the linearized forms of the models for cadmium ions adsorption on date pits and activated carbon. Adsorption model constants, the values of which express the surface properties and affinity of sorbet, with correlation coefficients were determined and tabulated in Table III.

Based on the correlation coefficients (R^2), the equilibrium data of cadmium ions adsorption on date pits was better fitted to Freundlich model since the correlation coefficient (R^2) was 0.949. Freundlich isotherm model is based on the assumption that sorption occurs on heterogeneous surfaces and the k_f parameter is useful in the evaluation of the adsorption capacity of metal ions in dilute solutions. The k_f parameter for cadmium ions adsorption is equal to 0.378 (l/g). On the other hand, Langmuir model was fitted very well to cadmium ions adsorption on activated carbon since the correlation coefficient (R^2) was 0.998. The Langmuir isotherm parameter Q_o which is numerically equal to (K_L/a_L) indicates the

maximum adsorption capacity of the material. The adsorption capacity was correlated with the variation of surface area and porosity of the adsorbent, the results showed Q_o for cadmium ions 31.98 (mg/g). Higher surface area and pore volume showed higher adsorption capacity of cadmium for activated carbon than date pits. Smaller a_L value leads to stronger binding of metal ions to adsorbents surface, the data implied that cadmium bonded strongly to activated carbon, this finding could be attributed to the fact that both the pore sizes and surface functional groups were favoring Cd^{2+} .

TABLE III
CADMIUM ADSORPTION MODEL CONSTANTS FOR DATE PIT (DP) AND ACTIVATED CARBON (AC)

	<i>Langmuir</i>		
	k_L (l/g)	a_L (l/mg)	R^2
DP	0.106	0.0065	0.6732
AC	2.146	0.0671	0.998
	<i>Freundlich</i>		
	k_f (l/g)	b_f	R^2
DP	0.375	0.596	0.9496
AC	8.100	0.242	0.9798
	<i>Tempkin</i>		
	A (ml/mol)	B (mol/g)	R^2
DP	0.121	2.838	0.7748
AC	3.498	4.390	0.9853
	<i>Dubinin- Radushkevich</i>		
	q_o (mmol/g)	B ($1/J^2 \cdot \text{mol}^2$)	R^2
DP	0.075	$4.8 \cdot 10^{-8}$	0.8428
AC	0.205	$9.0 \cdot 10^{-7}$	0.7522

V. CONCLUSION

This study proved that activated carbons with high adsorption capacities can be produced from date pits. The date pits were converted into activated carbons by air and phosphoric acid activation. The prepared activated carbons showed very large surface areas and micropore volumes, which makes them suitable adsorbents.

Adsorption of cadmium from aqueous solutions on raw date pits and activated carbons was investigated. Results showed that activated carbons gave higher adsorption capacity than raw date pits. The adsorption of cadmium was found to fit the Langmuir, Freundlich, Tempkin, and D-R adsorption isotherm models.

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