



Dates Pits Activated Carbon as Cheap Sorbent for the Decontamination of the Cadmium Ions in Battery Mills Wastewater

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Abstract

In the current study, a novel date pit activated carbon, an environmentally friendly adsorbent, was, chemically activated by phosphoric acid, and employed as a bio-sorbent for Cd²⁺ adsorption from a simulated polluted solution. Utilizing a variety of characterization techniques, the surface morphology and functional groups of manufactured activated carbon and raw date pits are identified. The prepared activated carbon had an adsorption surface area and pore diameter values of 1700 m²/g and 3.78 nm, and this indicated the greatest increase in surface area. The effect of pH, initial Cd²⁺ concentration, contact time, and operating temperature on Cd²⁺ removal by date pit activated carbon was studied. A higher Cd²⁺ adsorption capacity of 48.34 mg/g was attained for a contact time of 240 min, initial concentration of 100 mg/L, and pH of 6 at 30 °C. The efficacy of Cd²⁺ adsorption on date pit activated carbon improved as the initial pH of the adsorbate increased to 6 and Cd²⁺ concentration decreased. At a given temperature of 30 °C, the Freundlich isotherm demonstrated to be the most adaptable one, indicating multilayer coverage with a 41.15 mg/g maximum adsorption capacity. For sorption favorability, the separation factor has been within the range of 0.001 to 0.003. Subsequently, the results demonstrated that the removal efficiency was adversely impacted by the rise in treatment temperature from 30 to 40 °C.

Keywords: Date pits; Heavy metals; wastewater; Cadmium; adsorption.

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1- Introduction

On the surface of the earth, more than 100 million date palm trees occupy 1.3 million ha. Due to date culture's long history, as well as the widespread exchange between cultures of date cultivars, it is unknown where the date originated, but it most likely came from ancient Mesopotamia (southern Iraq) or western India. With more than 21 million date palm trees and a production of about 400,000 tons annually, Iraq is the world's largest producer of dates. Date pits (DP) are abundant when pitted dates are manufactured in packing plants or commercial date processing facilities based on juice extraction [1]. Waste from date pits has been a significant problem for the dating sector. Repurposing it is a promising first step as a result. On the other hand, DP fibers are lignocellulosic materials made of three crucial components: cellulose (40–50%), hemicellulose (20–35%), and lignin (15–35%) [2]. Date pit-based agricultural wastes are attracting considerable interest as efficient adsorbents due to the availability of date pits, low cost, bio-cellulose content, and their great adsorption capability for the removal of various contaminants.

Water is an important resource for life on Earth. However, it can be a dangerous item for everyday use if it is contaminated and not treated properly. Water pollution is primarily caused by wastewater discharged from

residential areas, sewage outlets, solid waste dump sites, livestock rearing facilities (such as dairy and poultry), and fertilizers and pesticides applied to farmer fields [3]. Due to the rapidly expanding agriculture and metal industries, inappropriate waste management, fertilizers, and pesticides, these inorganic pollutants are being discharged into the rivers, soils, and environment [4]. One of the main environmental contaminants, heavy metals can harm human physiology and other biological systems when exposure levels are exceeded. Industry is considered to be one of the primary contributors to contamination with heavy metals [5]. Through the food chain or drinking water, heavy metals from plants can enter bodies of people bodies. Due to its toxic and accumulative nature, heavy metal pollution affects life and puts the environment at risk. Limits are set for these metals in food products and drinking water to prevent high exposures to metal contamination in the human body [3]. Particulate matter released from heavy metals-based battery production is associated with Cd, Pb, Ni, Cu, and other metals that may deposit in neighboring locations and may contaminate local ponds, lakes, or soil [6].

Cadmium (Cd²⁺) is one of the toxic metals that are important for public health because of its high level of toxicity. It could cause widespread soil pollution, and it is difficult to degrade due to strong persistence.



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Furthermore, Cd^{2+} accumulation in humans is considered a systemic toxicant that is known to induce multiple organ damage as liver or kidneys to cause organ failure or induce carcinoma, bringing serious harm to human health, even at minimal exposure levels [7]. It is classified as a human carcinogen according to the U.S. Environmental Protection Agency, and the International Agency for Research on Cancer [8]. Therefore, this pollutant must be completely detoxified before it is discharged into the environment. One of the most significant environmental problems in the world is groundwater pollution, in which cadmium is in certain groundwater at a maximum value of 0.006 mg/L [9]. In twenty-one villages in Western Uttar Pradesh (India), a study investigated the presence of heavy metals in the pond sludge, pond soil, and groundwater. The mean concentration of Cd^{2+} in pond sludge with a mass of 0.010 mg per 1 kg sludge and in pond soil the concentration of Cd^{2+} was 0.06 mg per 1 kg soil [3]. Also, at eight locations in open drainage channels in the Nairobi manufacturing industry of Kenya, heavy metals were found in wastewater and soil samples with the average metal concentrations in wastewater ranging from 0.0001 to 0.015 mg/L [10].

Many methods were used for treating contaminated water with heavy metals such as chemical precipitation [11], electrochemical treatment [12], membrane [13], solvent extraction [14], reverse osmosis [15], ion exchange [16], bioremediation [17] and adsorption [18]. Adsorption is one of the most used technologies because it is inexpensive, effective, and simple to use [19] and activated carbon is unquestionably regarded as a universal adsorbent for the removal of various types of contaminants from water [1]. There are a wide variety of adsorbents that are used to get rid of heavy metal pollutants such as activated carbon [20], graphene oxide [21], zeolite [22], carbohydrate biopolymers [23], carbon nanotubes [24], raw date pits [25] and clay minerals [26]. The aim of this study was focused on the preparation and characterization of an efficient and eco-friendly adsorbent from date pits for the removal of Cd^{2+} as an inorganic pollutant using an adsorption technique. Analyzing isotherm models, adsorption kinetics, and thermodynamic variables to analyze the batch adsorption process of Cd^{2+} elimination.

2- Materials and Methods

2.1. Adsorbent Preparation

A variety of date pits were gathered, and properly washed using ionized distilled water. The pits were dried for eight hours at 110°C in an air oven. The date pits were ground into powder using a mixer grinder after drying. As the precursor, 50 g of 1 mm-sized crumpled date pits were blended with 60% H_3PO_4 at a desired impregnation ratio (IR) (3), which was 1:3 [27]. Where the IR ratio is the gram ratio of dry date pits powder to phosphoric acid. The mixture was left for a whole day to ensure that the date pits were completely saturated, and then it was dried at 110°C for 24 hr. The powdered dried date pits were

carbonized at a temperature of 650°C in an activation time of 120 min [28], in a tubular furnace which is purged with nitrogen atmosphere. After carbonization, the powder is left to be cooled at ambient temperature. The samples were washed multiple times with deionized distilled water to achieve a neutral pH and verify that phosphoric acid was eliminated. The product was then dehydrated in an air oven at 110°C for five hours.

2.2. Adsorption Experiments

Each adsorption experiment was conducted using a reagent container with a 100 mL capacity that contained trace amounts of adsorbent in 50 mL of the simulated wastewater with various initial concentrations of (20–100 ppm), different initial pH solutions (3–10), temperature (30, 35, 40 °C), and different adsorption duration (0–240) min. Batch sorption tests were carried out by adding a suitable dose of DPAC sorbent (0.1 g/ 50 mL) to a container containing 50 ml of an aqueous solution of cadmium ions with the desired initial concentration [28]. Before the experiment began, the pH of the solution was adjusted to the desired value using HNO_3 or KOH solutions. The sample container was put in a water bath shaker with a uniform speed of 200 rpm at desired temperature control and agitation. The solution reaction mixture was separated using a centrifuge at 2000 rpm for 20 minutes, before and after filtering, metal ions solutions without adsorbent were tested. Under the experimental conditions, neither precipitate nor metal ions adsorbed to the container walls were seen with the tested metals.

2.3. Equilibrium Isotherms

After cadmium ions have been adsorbed by DPAC, equilibrium concentrations in the aqueous solution and the equilibrium adsorption capacity of the adsorbent can be used to estimate adsorption isotherm. With the use of DPAC dose is 2 g/L in the contaminated solution. The suspension was put in the shaker and shaken for 24 h at room temperature with a uniform speed of 200 rpm to reach an equilibrium state and then filtered the samples and centrifuged at 2000 rpm for 20 minutes. Using an atomic absorption spectrophotometer analysis, the centrifuged product is used to determine the amount of Cd^{2+} in the contaminated solution.

3- Methods

3.1. Adsorption Equilibrium

One significant parameter is the isothermal equilibrium. Equilibrium data are used to calculate how much adsorbent is needed in the absorber, which in turn establishes the process's primary dimension and duration. Depending on the adsorbent, the adsorbate, and how the adsorbent and adsorbate interact, the adsorption isotherm can take on several forms [29]. When equilibrium has been attained, the aqueous-phase concentration of the

adsorbate is determined, and the following expression is used to calculate the adsorption equilibrium capacity [28]:

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

Where q_e is the equilibrium concentration of adsorbate in the adsorbent phase (mg adsorbate/g adsorbent), V is the volume of fluid phase (L), and m is the mass of adsorbent (g), C_e is the equilibrium concentration of Cd^{2+} in fluid-phase (mg/L) and C_o is the initial Cd^{2+} concentration in the fluid phase (mg/L). Cd^{2+} removal percentage (%R) was estimated by the formula [30]:

$$R \% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

3.2. Isotherm Models

Adsorption isotherms are a relationship that can be used in many models to explain how the adsorbate molecules bind on solid adsorbent surfaces when the adsorption process reaches an equilibrium state [31]. The concept of the adsorption isotherm describes the relationship between the mass of heavy metals adsorbed per gram of adsorbent (q_e) and the adsorbate concentration that remains in the solution once the equilibrium state (C_e) is attained at a constant temperature (30 °C) and contact time (24 h). To characterize the adsorption behavior of several pollutants that are frequently found in wastewater streams, Freundlich and Langmuir's isotherms have been widely used.

Langmuir proposed the theory of adsorption on solid surfaces to explain adsorption in solid-gas systems [32]. Later, it was simply developed with liquid systems by replacing the partial pressure of adsorbate with its equivalent value in concentration [33]. Langmuir adsorption isotherm has characterized the relationship between the amounts of adsorbate held on adsorbents at which the equilibrium concentration is achieved in an aqueous solution when neglecting the attractive interactions between adsorbate molecules [34]. The Langmuir isotherm model has the following formula [35]:

$$q = \frac{q_m b C}{1 + b C} \quad (3)$$

Where q_m is the maximum adsorption capacity of the adsorbent, mg adsorbate/g adsorbent, and b is the Langmuir adsorption equilibrium constant of the adsorbate. The (R_L) explains the adsorption favor if $0 < R_L < 1$ and is given by the expression [28]:

$$R_L = \frac{1}{1 + b C_o} \quad (4)$$

Another isotherm model of adsorption was proposed by Freundlich and was used to describe adsorption processes (Freundlich, 1906). According to the Freundlich model, when the concentration of a certain species in the liquid phase is raised, the concentration of the ionic species adsorbed on the surface of the solid would also rise. According to the model, the adsorption energy of an

adsorbent decreases exponentially as it approaches the end point of its adsorption centers [36]. It has the general formula [37, 38]:

$$q_e = K_f C_e^{1/n} \quad (5)$$

where K_f is Freundlich constant, related to adsorption capacity, (mg/g) (L/mg)^{1/n}, and n is the adsorption intensity and is usually greater than 1, which is a dimensionless parameter.

The following linearized equation can be used to explain the Freundlich model:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

The plots of $\log q_e$ versus $\log C_e$ result in a linear graph with a slope of $1/n$ and an intercept of $\log K_f$, allowing for the calculation of n and K_f , respectively.

4- Results and Discussion

Date pits from different sources were collected and activated, characterized, and used to remove cadmium ions (Cd^{2+}) from a simulated solution similar in concentration to contaminated water discarded from battery mills wastewater.

4.1. Characterization Techniques

The structures of the date pit DP and date pits activated carbon DPAC were characterized by several analysis techniques. The FT-IR spectra of DP and DPAC are shown in Fig. 1 a. Date pits contain lignocellulose, which is made up of protein, lignin, hemicellulose, and cellulose, as one of their adsorbent components. The main factor influencing Cd^{2+} binding with date pit adsorbents is the presence of carbonyl types and hydroxyl ether in greater abundance in both hemicellulose and cellulosic materials [39]. The FTIR curve of DPAC was compared to that of DP at 3650 to 3000 cm^{-1} , and a wide absorption peak appeared at this spectrum as a result of the introduction of $-OH$ in the modification process, enhancing the adsorption capacity. The presence of various lignocellulose peaks of $-OH$, $-NH$, or both $-OH$ and $-NH_2$ is believed to be responsible for the wide adsorbent peak seen in the FTIR spectra that stretches 3238–3570 cm^{-1} [40]. The DP and DPAC peaks at 2927 and 2850 cm^{-1} are caused by the stretching vibrations of C–H functionalities, respectively. Vibrations at 1639, 1535, and 1008 cm^{-1} , respectively, denote the unconjugated carbonyl (C=O), imine (C=C), and C–O functionalities. The band at 514708 cm^{-1} showed that OH polysaccharide groups were present. Additionally, the DPAC contained the C–O–C vibration bands and $-COOH$ acid bands, which were found at regions of 1008 to 1126 cm^{-1} and 1234 cm^{-1} , respectively. Asymmetric and symmetric stretching vibrations of the $-CH$ bond of the CH_2 group were attributed to two nearby bands at 2763 and 2908 cm^{-1} [41]. These observations point to

Cd^{2+} adsorption on DPAC. The $-\text{OH}$, $-\text{NH}$, $-\text{CO}$, and $\text{C}=\text{O}$ peaks of DPAC exhibit slight adjustments and increases in peak intensities after adsorption as depicted in Fig. 1 b, showing their involvement in the adsorption of Cd^{2+} as well. These findings show that Cd^{2+} adsorption is predominantly caused by the coordination binding and electrostatic interactions of the heteroatoms of the $\text{C}-\text{O}$, $\text{C}=\text{O}$, and $-\text{OH}$ or $-\text{NH}$ functional groups. [42].

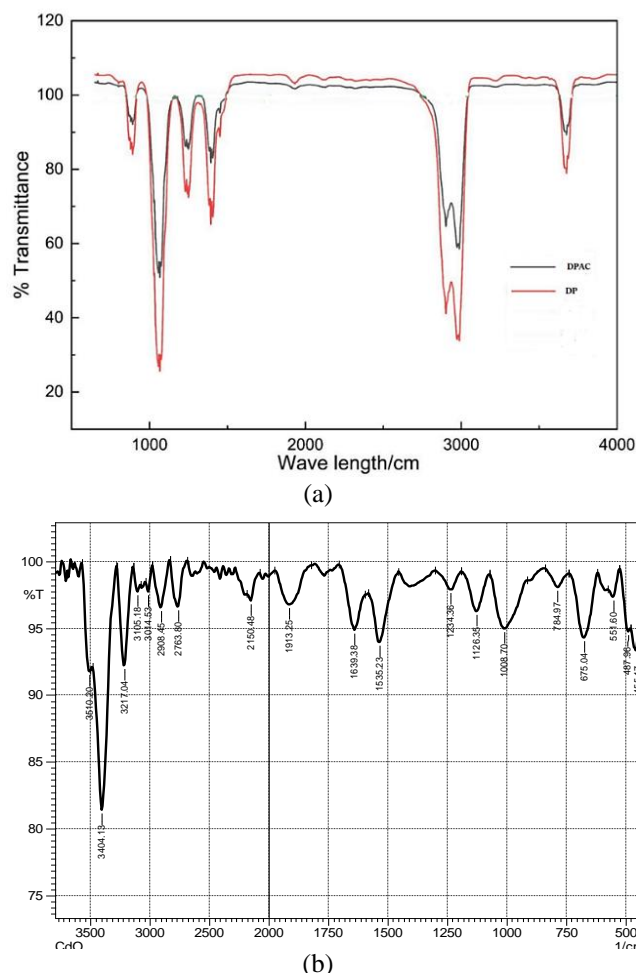


Fig. 1. FTIR, (a) DP and (b) after Cd^{2+} Adsorption

The surface morphology of the DPAC prepared using an adsorbent was examined using SEM. The SEM image in Fig. 2 a and Fig. 2 b shows the rough, very porous, and defined surface morphologies of the adsorbents, which are suitable for metal adsorption. Furthermore, SEM micrographs demonstrated that the treated date pits DPAC had larger porosity than the raw material date pits DP as shown in Fig. 2 a. Therefore, the surface of the adsorbent porous and irregular and is excellent for attracting heavy metal ions for adsorption [43].

The BET surface areas of DP and DPAC powder were estimated. The treated surface area for DP was estimated from 735.408 to 1700 m^2/g . These variations in certain areas revealed that porosity development causes date pits to be activated, improving their adsorption capacity [42]. The International Union of Pure and Applied Chemistry (IUPAC) classifies pores into three main groups based on

their size: micropores (pore diameter < 2 nm), mesopores ($2 \text{ nm} < \text{pore diameter} < 50$ nm) and macropores (pore diameter > 50 nm). The average pore diameter of DPAC was found to be 3.78 nm, which is within the range of the size of the mesopores. A value of 0.694 cm^3/g representing the quantity of nitrogen adsorbed at P/P_0 of 0.99459 was used to calculate the total pore volume of DPAC. It becomes more challenging to measure the pore diameter precisely at higher P/P_0 values [44]. Fig. 3 depicts the mesopore size distribution of DPAC and shows that the region of low pore diameter values has the highest mesopore volume values [45].

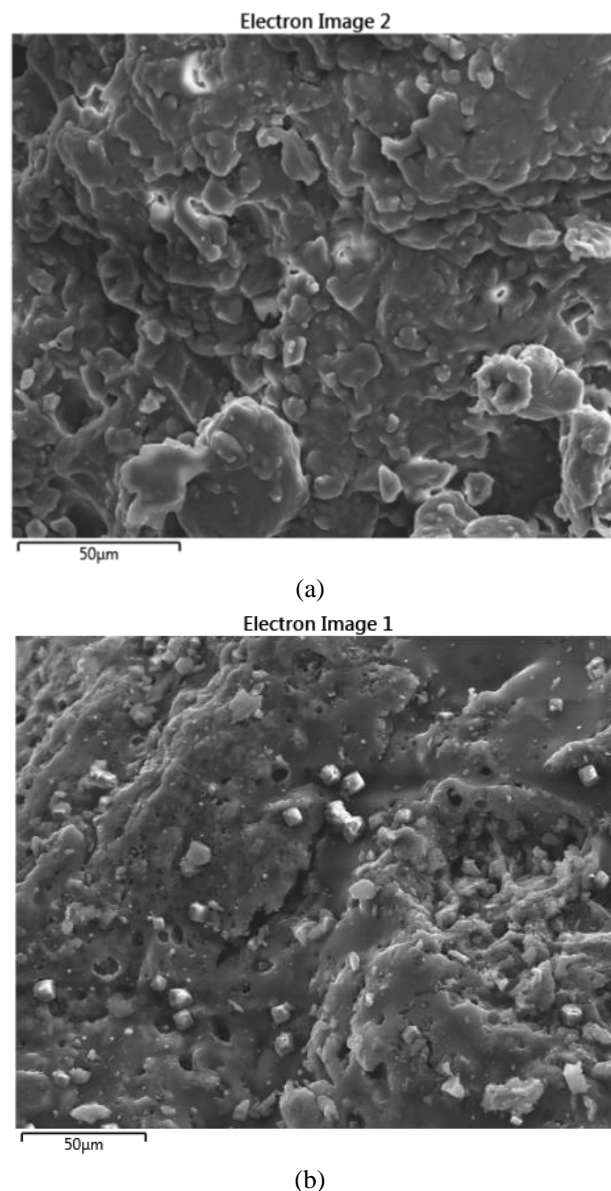


Fig. 2. Scanning Electron Microscopy of (a) DP and (b) DPAC

4.2. Effect of pH on the Adsorption Process

Due to the direct impact that pH has on metal solubility, the pH of the solution is a crucial factor in the adsorption process. Many variables, including adsorbent surface

charge, solution pH, degree of ionization, and adsorbate type, have an impact on the wastewater treatment process. Fig. 4 a and Fig. 4 b depict how the pH of the solution affects the adsorption of cadmium onto activated carbon (DPAC). As shown in Fig. 4 a when the pH solution rose from 2 to 6, it was observed that Cd^{2+} adsorption capacity increased, and an increase in pH enhanced metal adsorbed to reach maximum removal of 96.68 % at pH 6. This is because the extra (H^+) prevented Cd^{2+} ions from sticking to DPAC functional groups [46]. The optimal solution pH was discovered to be 6 with q_e 48.34 mg/g as shown in Fig. 4 b. As the possibility of heavy metal precipitation grows due to Cd^{2+} metal hydroxide starting to precipitate from the solutions, the adsorption capacity will start to drop after pH 6, and effective sorption tests will become challenging when the pH rises to 7–10. These results were in agreement with [27, 28, 46]. Adsorption of cadmium ions is minimal at lower pH because H^+ has saturated the adsorption sites; however, when pH rises, more adsorption sites become accessible and cadmium ion adsorption increases as shown in Fig. 5. The cadmium precipitated at higher pH levels when using KOH for pH adjustment, and K^+ now competes with the residual Cd^{2+} [47].

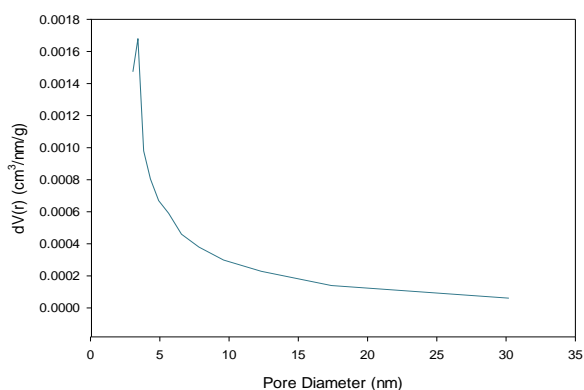
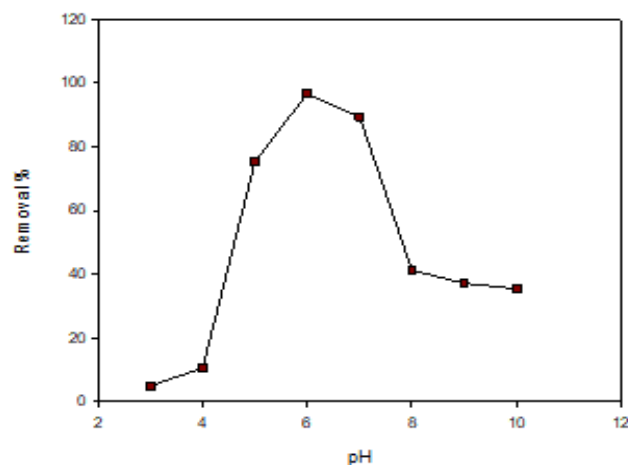


Fig. 3. Mesopore Size Distribution by the Barrett-Joyner-Halenda (BJH) Method for DPAC

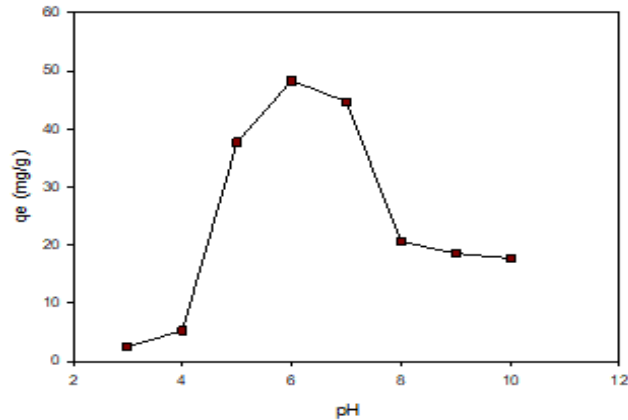
4.3. Effect of Initial Cd^{2+} Concentration on Adsorption Process

Fig. 6 shows the effect of initial Cd^{2+} concentration on the percent removal and Cd^{2+} adsorption capacity. The study results from the investigation of the adsorption process at various initial Cd^{2+} concentrations of 40–100 mg/L at pH 6 and contact times of 24 hours with 0.1 g DPAC for 50 mL Cd^{2+} solution. When the initial Cd^{2+} concentration decreased, the removal efficiency of Cd^{2+} on DPAC was increased. As Cd^{2+} concentrations increase from 40 to 100 mg/L, the removal efficiency decreases while the adsorption rate increases. A higher removal efficiency of 99.73% with a low adsorption rate of 19.95 mg/g was achieved with an initial Cd^{2+} concentration of 40 mg/L. The ratio between the adsorption sites and the initial Cd^{2+} concentration is significant at lower concentrations where Cd^{2+} is absorbed by specific sites in

the adsorption medium. However, as the initial heavy metal concentration rises, this ratio falls, and the specific sites become saturated [47]. On the other hand, it was known that an increase in feed concentration leads to higher Cd^{2+} adsorbed on the surface of DPAC (q_e) as shown in Fig. 6. As to the adsorption capacity growth curves, the amount of Cd^{2+} that was adsorbed rose noticeably from (19.95 to 48.34 mg/g) as the initial concentration was increased from (40 to 100 gm/mL). This occurred because the high initial feed Cd^{2+} concentration led to more prominent concentration gradients, which increased the driving force of the adsorption process. This result was consistent with [28].



(a)



(b)

Fig. 4. Effect of pH on (a) the Removal Efficiency of Cd^{2+} and (b) Adsorption Capacity on DPAC (Conditions: DPAC dose 0.1 g/50 mL, Initial Concentration 100 mg/L; Adsorption Time, 24 h; Temperature, 30 °C)

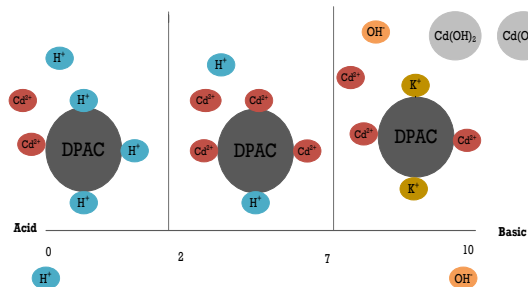


Fig. 5. Effect of pH on Cadmium Adsorption onto DPAC

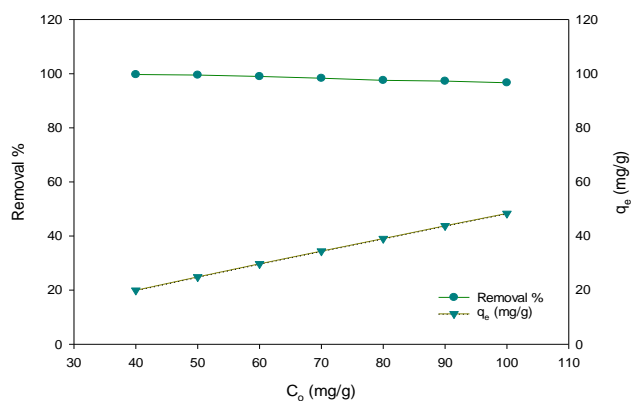


Fig. 6. Effect of the Initial Cd²⁺ Concentration on the Capacity for Equilibrium Adsorption and Cd²⁺ Removal (pH: 6, dosage: 0.1 gm / 50 mL, T: 30 °C)

4.4. Temperature Effect on Adsorption Process

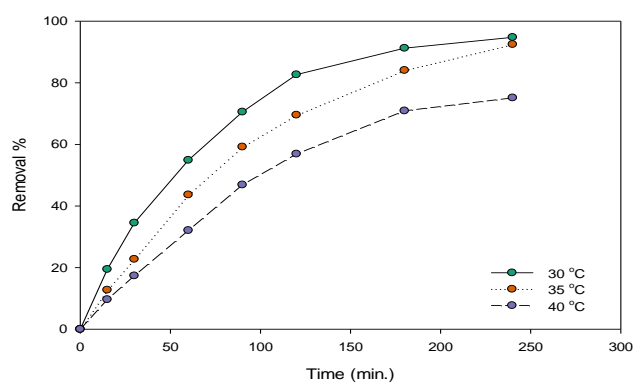
As it is well known, temperature plays a significant role in the adsorption process. The effect of temperature on the Cd²⁺ adsorbed on DPAC was examined in a series of batch experiments conducted at 30°C, 35°C, and 40°C with adsorption duration time (0–240) min. With fixed variable conditions, such as pH 6, initial cadmium ion concentration of 100 mg/L, and adsorbent dosage of 0.1g/50mL, the effect of solution temperature was examined. At a temperature range of 30 °C, high removal efficiency > 97% was attained C in time 250 min as demonstrated in Fig. 7 a. Increasing the temperature over the study range resulted in a decrease in the adsorption of Cd²⁺ as shown in Fig. 7 b. So, the raising temperature is unfavorable to the adsorption of Cd²⁺ on DPAC, consequently showing that the sorption process is exothermic. This is consistent with the results of [48] who demonstrated the exothermic sorption of Cd²⁺ onto activated carbons made from surplus agricultural solid waste. When the temperature was raised above 40 °C, the amount of Cd²⁺ adsorption decreased or almost disappeared. The reason was due to the deformation of some Cd²⁺ absorption sites on the surface of the adsorbent was to fault for the reduced Cd²⁺ adsorption. Additionally, for each study, the removal percentage increased throughout time until it stabilized at around 200 min.

4.5. Adsorption Isotherms

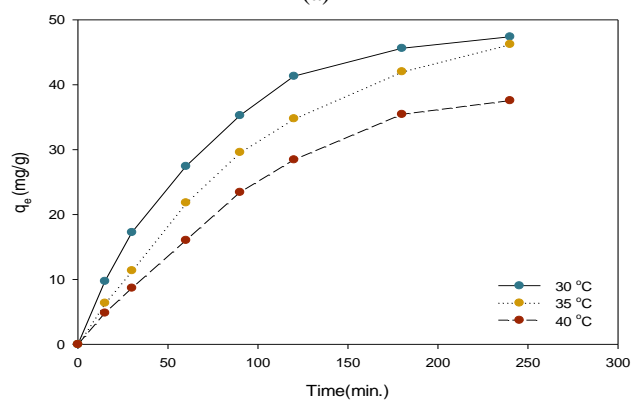
Variable initial feed Cd²⁺ concentrations of 40–100 mg/L were used with DPAC adsorbent loading of 10 g/50 mL were carried out at 30°C as shown in Fig. 8. The Langmuir model and the Freundlich model were the two most popular and significant adsorption isotherm models.

Table 1 displays the matching estimated parameters of models. The results showed that the Freundlich isotherm model ($R^2 = 0.9903$), as shown in Fig. 9 b, fit Cd²⁺ better than the Langmuir isotherm model ($R^2 = 0.8971$), which is more appropriate for characterizing the adsorption process Fig. 9 a. Because of this, it may be assumed that multilayer adsorption is the primary mechanism by which Cd²⁺ is adsorbed. It was determined that the highest

adsorption capacity (q_{max}) was 41.15 mg/g at 30 °C, indicating that DPAC is an effective adsorbent for the removal of Cd²⁺ from polluted aqueous solutions. For Cd²⁺ adsorption on the DPAC surface, the separation factor (R_L) was calculated from Eq. 4 to range from 0.001 to 0.003, indicating favorable adsorption occurs for the removal of Cd²⁺ [43]. Table 2 summarizes the q_{max} of many other researchers. As a result, the highest adsorption capacity was found for our study as compared with other literature.



(a)



(b)

Fig. 7. The Effect of Temperature on Cd²⁺ Adsorption, (a) Cd²⁺ Removal Percentage and (b) Adsorption Capacity. Adsorption Conditions: 10 g/50 mL Adsorbent, 100 mg/L Cd²⁺ Solution and pH 6

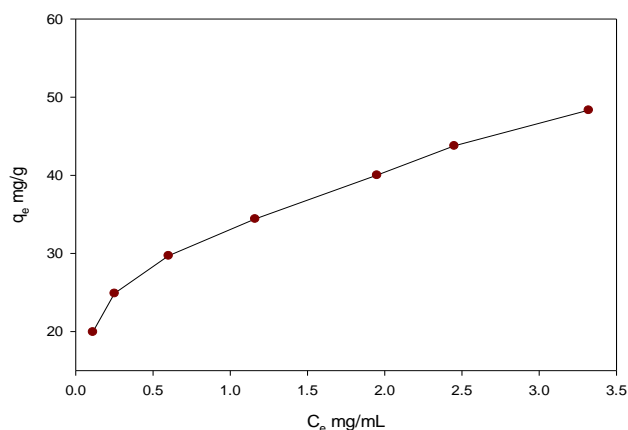
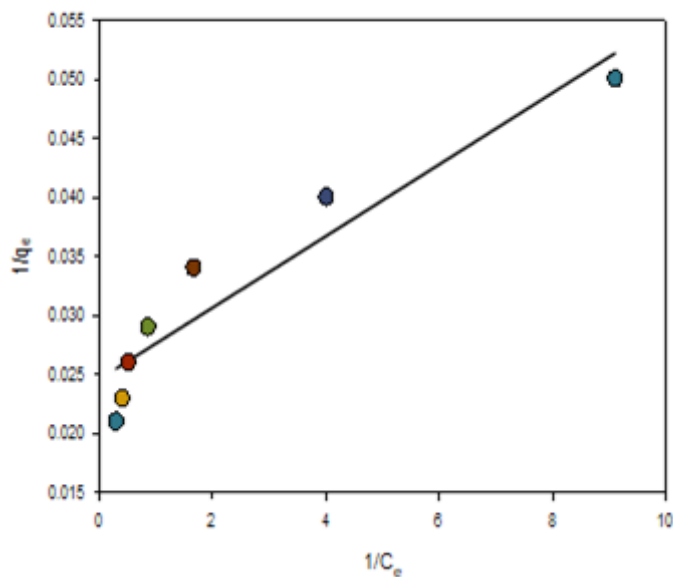


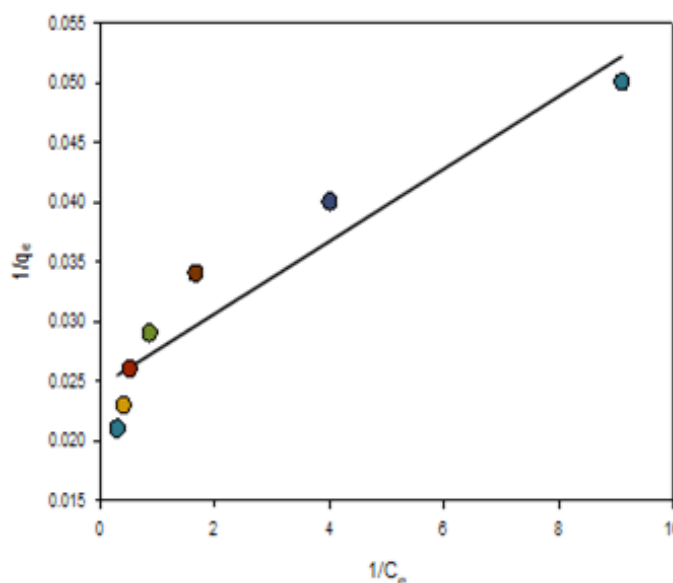
Fig. 8. The Adsorption Isotherms of Cd²⁺ on DPAC with Experimental Conditions: DPAC Dosage 10 g/50 mL, Initial Cd²⁺ Concentration 40–100 mg/L, pH = 6

Table 1. Langmuir and Freundlich Adsorption Isotherm Models Parameters of Cd²⁺ Removal on DPAC

Isotherm model	Model parameters	Parameter value	R ²
Langmuir	q_{max} , mg/g	41.15	0.8971
	b , L/mg	7.84	
Freundlich	K_F , mg ¹⁻ⁿ l ⁿ /g	34.35	0.9903
	n	4	



(a)



(b)

Fig. 9. The Adsorption Isotherms of Cd²⁺ on DPAC (a) Langmuir Isotherm Model and (b) Freundlich Isotherm Model

Table 2. Activated Carbon Date Pits for Different Heavy Metal Ions Adsorption

Activation Type	Adsorbate	Maximum capacity (mg/g)	References
Chemical activation: Cs ₂ CO ₃	Cr ⁺⁶	Cr ⁺⁶ q _m : 4.112 mg/g	[49]
Physical activation: muffle furnace, N ₂ / 600 °C	Pb ²⁺	Pb ²⁺ q _m : 0.004 mg/g	
Chemical activation: 60% H ₃ PO ₄ , 50% ZnCl ₂ IR 1:1, 24 h	Pb ²⁺	Pb ²⁺ q _m : 34.18 mg/g	[50]
Physical activation: muffle furnace 500 °C,50-70 min	Cd ²⁺	Cd ²⁺ q _m : 32.9 mg/g	
Chemical activation: 85% H ₃ PO ₄ IR 1:2.5	Pb ²⁺	Pb ²⁺ q _m : 128.21 mg/g	[28]
Physical activation: N ₂ / 650 °C,120 min			
Chemical activation: 60 % H ₃ PO ₄ IR 1:1.75	Cu ²⁺	q _m : 31.25 mg/g	[51]
Physical activation: carbonization, N ₂ / 450 °C,2 h			
Chemical activation: 85% H ₃ PO ₄ IR 1:3	Cu ²⁺	Cu ²⁺ q _m :33.44 mg/g	[27]
Physical activation: air carbonization 600 °C,30 min	Cd ²⁺	17.24 mg/g	
Physical activation: N ₂ atmosphere carbonization 700 °C, 2h and CO ₂ flush/ 500-900 °C	Cd ²⁺	q _m : 6.5 mg/g	[48]

5- Conclusion

The goal of the current study was to determine the performance of DPAC produced from date pits that had undergone chemical activation with H_3PO_4 . The DPAC was used to remove Cd^{2+} through an adsorption process from simulated wastewater. Thermodynamics, kinetics, and isotherms of adsorption were investigated. Acid functional groups were created when DP was activated with H_3PO_4 . The FTIR spectra of the adsorbent exhibited that hydroxyl, carbonyl/carboxylic, and amine groups involved in the adsorption processes were present. SEM images for DPAC showed surface morphologies that were suitable for metal adsorption with rough, porous surfaces, which increased its surface area and enhanced the adsorption phenomenon. In comparison to raw date pits, the date pit activated carbon has a higher specific area, measuring $1700\text{ m}^2/\text{g}$. The DPAC exhibited the highest Cd^{2+} adsorption ability at a low temperature of 48.34 mg/g at $30\text{ }^\circ\text{C}$ and the lowest Cd^{2+} adsorption at a high temperature and 39.74 mg/g at $40\text{ }^\circ\text{C}$. DPAC has a total pore volume and average pore diameter of $0.694\text{ cm}^3/\text{g}$ and 3.78 nm , respectively. Different parameters, including initial pH, initial concentrations of Cd^{2+} , and temperature, affected adsorption. At an optimal pH of 6, the adsorption of Cd^{2+} reached its maximum value of 48.34 mg/g . The efficiency of the Cd^{2+} elimination is conversely linked to the rise in starting Cd^{2+} concentration. Hence, the greatest removal efficiency was reached at 40 mg/L and was found to be 99.73% . The experimental data were better modeled using the Freundlich adsorption isotherm in comparison to the Langmuir isotherm model for DPAC, indicating multilayer coverage with a 41.15 mg/g maximum adsorption capacity.

References

- [1] A. N. Ghanim, 'Utilization of date pits derived bio-adsorbent for heavy metals in wastewater treatment: Review', *Al-Qadisiyah Journal for Engineering Sciences.*, vol. 16, pp. 58–69, 2023. <https://doi.org/10.30772/qjes.v16i1.910>
- [2] K. Al-Kaabi, A. Al-Khanbashi, and A. Hammami, 'Date palm fibers as polymeric matrix reinforcement: DPF/polyester composite properties', *Polymer Composites.*, vol. 26, no. 5, pp. 604–613, 2005. <https://doi.org/10.1002/pc.20130>
- [3] V. C. Goyal, O. Singh, R. Singh, K. Chhoden, and S. K. Malyan, 'Appraisal of heavy metal pollution in the water resources of Western Uttar Pradesh, India and associated risks', *Environ. Adv.*, vol. 8, no. April, p. 100230, 2022. <https://doi.org/10.1016/j.envadv.2022.100230>
- [4] J. Briffa, E. Sinagra, and R. Blundell, 'Heavy metal pollution in the environment and their toxicological effects on humans', *Heliyon*, vol. 6, no. 9, p. e04691, 2020. <http://dx.doi.org/10.1016/j.heliyon.2020.e04691>
- [5] Q. J. M. Slaiman, C. Kh. Haweel, and Y. R. Abdulmajeed, 'Removal of Heavy Metals Ions from Aqueous Solutions Using Biosorption onto Bamboo', *Iraqi Journal of Chemical and Petroleum Engineering*, vol. 11, no. 3, pp. 23–32, 2010. <http://dx.doi.org/10.31699/ijcpe.2010.3.4>
- [6] P. K. Rai, S. S. Lee, M. Zhang, Y. F. Tsang, and K. H. Kim, 'Heavy metals in food crops: Health risks, fate, mechanisms, and management', *Environment International*, vol. 125, no. November 2018, pp. 365–385, 2019. <https://doi.org/10.1016/j.envint.2019.01.067>
- [7] A. H. Sulaymon, S. E. Ebrahim, S. M. Abdullah, and T. J. Al-Musawi, 'Removal of lead, cadmium, and mercury ions using biosorption', *Iraqi Journal of Chemical and Petroleum Engineering*, vol. 11, no. 2, pp. 1–13, 2010. <https://doi.org/10.31699/IJCPE.2010.2.1>
- [8] P. B. Tchounwou, C. G. Yedjou, A. K. Patlolla, and D. J. Sutton, 'Heavy Metal Toxicity and the Environment', *Molecular, Clinical and Environmental Toxicology*, pp. 133–166, 2012. <https://doi.org/10.1007/978-3-7643-8340-4>
- [9] M. Vatandoost, D. Naghipour, S. Omidi, and S. D. Ashrafi, 'Survey and mapping of heavy metals in groundwater resources around the region of the Anzali International Wetland; a dataset', *Data in Brief*, vol. 18, pp. 463–469, 2018. <https://doi.org/10.1016/j.dib.2018.03.058>
- [10] G. K. Kinuthia, V. Ngunjiri, D. Beti, R. Lugalia, and A. Wangila, 'Open Levels of heavy metals in wastewater and soil samples from open drainage channels in Nairobi, Kenya: community health implication', *Scientific Reports*, pp. 1–13, 2020. <https://doi.org/10.1038/s41598-020-68286-7>
- [11] V. S. Cherednichenko, A. V. Cherednichenko, A. V. Cherednichenko, A. K. Zheksenbaeva, and A. S. Madibekov, 'Heavy metal deposition through precipitation in Kazakhstan', *Heliyon*, vol. 7, no. 1, p. e05844, 2021. <https://doi.org/10.1016/j.heliyon.2020.e05844>
- [12] T. K. Tran, N. Kim, Q. C. Le, M. T. Nguyen, H. J. Leu, and K. N. Vo Thi, 'Electrochemical preparation and characterization of polyaniline enhanced electrodes: An application for the removal of cadmium metals in industrial wastewater', *Materials Chemistry and Physics*, vol. 261, no. January, p. 124221, 2021. <https://doi.org/10.1016/j.matchemphys.2021.124221>
- [13] N. Mohammad and Y. Atassi, 'Enhancement of removal efficiency of heavy metal ions by polyaniline deposition on electrospun polyacrylonitrile membranes', *Water Science and Engineerin.*, vol. 14, no. 2, pp. 129–138, 2021. <https://doi.org/10.1016/j.wse.2021.06.004>

- [14] J. Kończyk, 'Selective solvent extraction of some heavy metal ions from aqueous solutions by octafunctionalized resorcin[4]arenes', *Physicochemical Problems of Mineral Processing*, vol. 56, no. 2, pp. 271–285, 2020. <https://doi.org/10.37190/ppmp20001>
- [15] H. A. Qdais and H. Moussa, 'Removal of heavy metals from wastewater by membrane processes: A comparative study', *Desalination*, vol. 164, no. 2, pp. 105–110, 2004. [https://doi.org/10.1016/S0011-9164\(04\)00169-9](https://doi.org/10.1016/S0011-9164(04)00169-9)
- [16] T. M. Zewail and N. S. Yousef, 'Kinetic study of heavy metal ions removal by ion exchange in batch conical air spouted bed', *Alexandria Engineering Journal*, vol. 54, no. 1, pp. 83–90, 2015. <http://dx.doi.org/10.1016/j.aej.2014.11.008>
- [17] M. Medfu Tarekegn, F. Zewdu Salilih, and A. I. Ishetu, 'Microbes used as a tool for bioremediation of heavy metal from the environment', *Cogent Food and Agriculture*, vol. 6, no. 1, 2020. <https://doi.org/10.1080/23311932.2020.1783174>
- [18] N. S. Al-Kadhi *et al.*, 'Preparation of NiO/MWCNTs nanocomposite and its application for cadmium ion removal from aqueous solutions', *Journal of Materials Research and Technology*, 2022. <https://doi.org/10.1016/j.jmrt.2022.05.149>
- [19] M. Nageeb, 'Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater', in *Organic Pollutants - Monitoring, Risk and Treatment Efficient*, M. N. Rashed, Ed. Intech open science| open mind, 2013. <https://doi.org/10.5772/54048>
- [20] M. S. Ismail, M. D. Yahya, M. Auta, and K. S. Obayomi, 'Facile preparation of amine - functionalized corn husk derived activated carbon for effective removal of selected heavy metals from battery recycling wastewater', *Heliyon*, vol. 8, no. 5, p. e09516, 2022. <https://doi.org/10.1016/j.heliyon.2022.e09516>
- [21] N. C. Joshi and P. Gururani, 'Advances of graphene oxide based nanocomposite materials in the treatment of wastewater containing heavy metal ions and dyes', *Current Research in Green and Sustainable Chemistry*, vol. 5, no. December 2021, p. 100306, 2022. <https://doi.org/10.1016/j.crgsc.2022.100306>
- [22] G. Li *et al.*, 'Hydrothermal synthesis of zeolite-calcium silicate hydrate composite from coal fly ash with co-activation of Ca(OH)₂-NaOH for aqueous heavy metals removal', *International Journal of Mining Science and Technology*, vol. 32, no. 3, pp. 563–573, 2022. <https://doi.org/10.1016/j.ijmst.2022.03.001>
- [23] B. G. Fouda-Mbanga, E. Prabakaran, and K. Pillay, 'Carbohydrate biopolymers, lignin based adsorbents for removal of heavy metals (Cd²⁺, Pb²⁺, Zn²⁺) from wastewater, regeneration and reuse for spent adsorbents including latent fingerprint detection: A review', *Biotechnology Reports*, vol. 30, p. e00609, 2021. <https://doi.org/10.1016/j.btre.2021.e00609>
- [24] M. Ibrahim, A. A. AbdulRazak, and A. Dari Jaafar, 'Removal of Copper (II) from Wastewater Using Modified Carbon Nanotubes', *Engineering and Technology Journal*, vol. 31, no. 12, pp. 2228–2241, 2013. <https://doi.org/10.30684/etj.31.12a.2>
- [25] K. Hummadi, 'Optimal Operating Conditions for Adsorption of Heavy Metals from an Aqueous Solution by an Agriculture Waste', *Iraqi Journal of Chemical and Petroleum Engineering*, vol. 22, no. 2, pp. 27–35, 2021. <https://doi.org/10.31699/IJCPE.2021.2.4>
- [26] A. Gil *et al.*, 'A review of organic-inorganic hybrid clay based adsorbents for contaminants removal: Synthesis, perspectives and applications', *Journal of Environmental Chemical Engineering*, vol. 9, no. 5, p. 105808, 2021. <https://doi.org/10.1016/j.jece.2021.105808>
- [27] N. M. Hilal, I. A. Ahmed, and R. E. El-Sayed, 'Activated and Nonactivated Date Pits Adsorbents for the Removal of Copper(II) and Cadmium(II) from Aqueous Solutions', *ISRN Physical Chemistry*, vol. 2012, pp. 1–11, 2012. <https://doi.org/10.5402/2012/985853>
- [28] R. Krishnamoorthy, B. Govindan, F. Banat, V. Sagadevan, M. Purushothaman, and P. L. Show, 'Date pits activated carbon for divalent lead ions removal', *Journal of Bioscience and Bioengineering*, vol. 128, no. 1, pp. 88–97, 2019. <https://doi.org/10.1016/j.jbiosc.2018.12.011>
- [29] C. J. Geankoplis, 'Liquid-Liquid and Fluid-Solid Separation Processes', in *Transport processes and unit operations*, Third., vol. 20, no. 1, C. J. Geankoplis, Ed. UK: Prentice-Hall International, Inc., 1980, pp. 697–743. [https://doi.org/10.1016/0300-9467\(80\)85013-1](https://doi.org/10.1016/0300-9467(80)85013-1)
- [30] M. Hamid Khashan and A. K. Mohammad, 'Comparative study for Pb²⁺ adsorption from simulated wastewater of battery manufacture on activated carbon prepared from rice husk with different activation agents', *Al-Qadisiyah Journal for Engineering Sciences*, vol. 15, no. 3, pp. 147–155, 2022. <https://doi.org/10.30772/qjes.v15i3.827>
- [31] S. A. Yousif and S. Al-Mosawi, 'Adsorptive separation of dissolved cadmium from aqueous solution using (Ziziphus Spina-Christi) leaves as an adsorbent', *South African J. Chem. Eng.*, vol. 42, no. April, pp. 12–22, 2022. <https://doi.org/10.1016/j.sajce.2022.07.002>
- [32] I. Langmuir, 'The Constitution and fundamental properties of solids and liquids. Part I. Solids', *Journal of the American Chemical Society*, vol. 38, no. 11, pp. 2221–2295, 1916. <https://doi.org/10.1021/ja02268a002>
- [33] A. Islam, M. R. Khan, and S. I. Mozumder, 'Adsorption Equilibrium and Adsorption Kinetics: A Unified Approach', *Chemical Engineering & Technology*, vol. 27, no. 10, pp. 1095–1098, 2004. <https://doi.org/10.1002/ceat.200402084>

- [34] A. P. Meneghel, A. C. Gonçalves, L. Strey, F. Rubio, D. Schwantes, and J. Casarin, 'Biosorption and removal of chromium from water by using moringa seed cake (*Moringa oleifera* Lam.)', *Química Nova*, vol. 36, no. 8, pp. 1104–1110, 2013. <https://doi.org/10.1590/S0100-40422013000800005>
- [35] W. J. Thomas and B. Crittenden, *Adsorption Technology and Design*, no. April. Elsevier Science & Technology Books, 1998.
- [36] C. S. T. Araújo, I. L. S. Almeida, H. C. Rezende, S. M. L. O. Marcionilio, J. J. L. Léon, and T. N. de Matos, 'Elucidation of mechanism involved in adsorption of Pb(II) onto lobeira fruit (*Solanum lycocarpum*) using Langmuir, Freundlich and Temkin isotherms', *Microchemical Journal*, vol. 137, no. II, pp. 348–354, 2018. <http://dx.doi.org/10.1016/j.microc.2017.11.009>
- [37] C. T. Chiou, 'Fundamentals of the Adsorption Theory', in *Partition and Adsorption of Organic Contaminants in Environmental Systems*, John Wiley & Sons, Inc., 2003, pp. 39–52. <http://dx.doi.org/10.1002/0471264326.ch4>
- [38] H. Freundlich, 'Über die Adsorption in Lösungen', *Zeitschrift für Physikalische Chemie*, vol. 57U, no. 1, pp. 385–470, 1906. <https://doi.org/10.1515/zpch-1907-5723>
- [39] M. Azam, M. R. Khan, S. M. Wabaidur, S. I. Al-Resayes, and M. S. Islam, 'Date pits waste as a solid phase extraction sorbent for the analysis of lead in wastewater and use in manufacturing brick: An eco-friendly waste management approach', *Saudi Chemical Society*, vol. 26, no. 5, p. 101519, 2022. <https://doi.org/10.1016/j.jscs.2022.101519>
- [40] M. Azam, S. M. Wabaidur, M. R. Khan, S. I. Al-Resayes, and M. S. Islam, 'Heavy Metal Ions Removal from Aqueous Solutions by Treated Ajwa Date Pits: Kinetic, Isotherm, and Thermodynamic Approach', *Polymers (Basel)*, vol. 14, no. 5, 2022. <https://doi.org/10.3390/polym14050914>
- [41] M. A. Khan *et al.*, 'Unary and binary adsorption studies of lead and malachite green onto a nanomagnetic copper ferrite/drumstick pod biomass composite', *Hazardous Materials*, vol. 365, pp. 759–770, 2019. <https://doi.org/10.1016/j.jhazmat.2018.11.072>
- [42] M. Azam, S. M. Wabaidur, M. R. Khan, M. S. Islam, and S. I. Al-Resayes, 'Removal of chromium(III) and cadmium(II) heavy metal ions from aqueous solutions using treated date seeds: An eco-friendly method', *Molecules*, vol. 26, no. 12, 2021. <https://doi.org/10.3390/molecules26123718>
- [43] B. Kayranli, 'Cadmium removal mechanisms from aqueous solution by using recycled lignocelluloses', *Alexandria Engineering Journal*, vol. 61, no. 1, pp. 443–457, 2022. <https://doi.org/10.1016/j.aej.2021.06.036>
- [44] M. F. F. Sze and G. McKay, 'An adsorption diffusion model for removal of para-chlorophenol by activated carbon derived from bituminous coal', *Environmental Pollution*, vol. 158, no. 5. Elsevier Ltd., Hong Kong, pp. 1669–1674, 2010. <https://doi.org/10.1016/j.envpol.2009.12.003>
- [45] K. Nabil, N. Abdelmonem, M. Nogami, and I. Ismail, 'Preparation of composite monolith supercapacitor electrode made from textile-grade polyacrylonitrile fibers and phenolic resin', *Materials (Basel)*, vol. 13, no. 3, 2020. <https://doi.org/10.3390/ma13030655>
- [46] M. I. Kandah *et al.*, 'Adsorption of cadmium onto activated and non-activated date pits', *World Academy of Science, Engineering and Technology*, vol. 62, no. February 2010, pp. 204–208, 2010. <https://doi.org/10.5281/zenodo.1082736>
- [47] B. Abbar *et al.*, 'Experimental investigation on removal of heavy metals (Cu²⁺, Pb²⁺, and Zn²⁺) from aqueous solution by flax fibres', *Process Safety and Environmental Protection*, vol. 109, no. June, pp. 639–647, 2017. <http://dx.doi.org/10.1016/j.psep.2017.05.012>
- [48] F. Banat, S. Al-Asheh, and L. Al-Makhadmeh, 'Kinetics and equilibrium study of cadmium ion sorption onto date pits - An agricultural waste', *Adsorption Science & Technology*, vol. 21, no. 3, pp. 245–260, 2003. <http://dx.doi.org/10.1260/026361703322404395>
- [49] A. Bumajdad and P. Hasila, 'Surface modification of date palm activated carbonaceous materials for heavy metal removal and CO₂ adsorption', *Arabian Journal of Chemistry*, vol. 16, no. 1, p. 104403, 2023. <https://doi.org/10.1016/j.arabjc.2022.104403>
- [50] W. A. Al-Onazi, M. H. H. Ali, and T. Al-Garni, 'Using Pomegranate Peel and Date Pit Activated Carbon for the Removal of Cadmium and Lead Ions from Aqueous Solution', *Journal of Chemistry*, vol. 2021, 2021. <https://doi.org/10.1155/2021/5514118>
- [51] F. Bouhamed, Z. Elouear, and J. Bouzid, 'Adsorptive removal of copper(II) from aqueous solutions on activated carbon prepared from Tunisian date stones: Equilibrium, kinetics and thermodynamics', *Journal of the Taiwan Institute of Chemical Engineers*, vol. 43, no. 5, pp. 741–749, 2012. <http://dx.doi.org/10.1016/j.jtice.2012.02.011>

نوى التمور كمادة ماصة رخيصة لتطهير ايونات الكاديوم من مياه الصرف الصحي لمصانع البطاريات

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الخلاصة

الكاديوم هو معدن ثقيل شديد الخطورة يتم إطلاقه بشكل أساسي في البيئة من خلال العمليات الصناعية وقد ثبت أن له آثارًا سلبية على كل من البشر والبيئة. تم استخدام حامض الفوسفوريك في التنشيط الكيميائي لنوى التمر غير السامة والحيوية. تم فحص الكربون المنشط لنوى التمر، وهو مادة ماصة جديدة وصديقة للبيئة، وتم استخدامه بنجاح كمادة ماصة بيولوجية لامتصاص الكاديوم من محلول ملوث. يتم تحديد نوى التمر الخام والكربون المنشط المحضر من خلال التشكل السطحي والمجموعات الوظيفية باستخدام بعض تقنيات التوصيف المختلفة. تم تمييز الكربون المنشط لنوى التمر لإظهار المجموعات الوظيفية النشطة التي تمت إضافتها إلى سطح جزيئات الامتصاص الصلبة، مما أدى إلى إنشاء مواقع أكثر نشاطًا، ومساحة سطح امتصاص أعلى، وحجم مسام أكبر. يحتوي الكربون المنشط المحضر على مساحة سطح ممتاز وقيم مسامية تبلغ ١٧٠٠ م^٢ / جم و ٣,٧٨ نانومتر، وهذا يشير إلى أكبر زيادة في مساحة السطح. تأثرت كفاءة إزالة أيون الكاديوم على الكربون المنشط لنوى التمر بعدة متغيرات. أظهرت النتائج أنه كلما ارتفع الرقم الهيدروجيني الأولي للمادة الممتازة إلى ٦ وانخفض التركيز الأولي لأيون الكاديوم، زادت كفاءة امتصاص أيون الكاديوم على الكربون المنشط في حفر التمر. تم تأكيد البيانات التجريبية باستخدام نماذج متساوي الحرارة لانجمير و فروندلش. عند درجة حرارة معينة تبلغ ٣٠ درجة مئوية، ثبت أن متساوي الحرارة فروندلش هو الأكثر قابلية للتكيف، معامل تصحيح يساوي ٠,٩٩٠٣، بينما نموذج لانجمير للكربون المنشط لنوى التمر يشير إلى تغطية متعددة الطبقات مع قدرة امتصاص قصوى تبلغ ٤١,١٥ مجم / جم. وللحصول على أفضل امتزاز، كان عامل الفصل في حدود ٠,٠٠١ إلى ٠,٠٠٣. بعد ذلك، أظهرت النتائج أن كفاءة الإزالة قد تأثرت سلبًا بارتفاع درجة حرارة المعالجة من ٣٠ إلى ٤٠ درجة مئوية.

الكلمات الدالة: نوى التمر، المعادن الثقيلة، مياه الصرف الصحي، الكاديوم، الإمتزاز.