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# Utilization of date pits derived bio-adsorbent for heavy metals in wastewater treatment: Review

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## ABSTRACT

This article provides an overview of the role of raw and burnt date pits as bio-waste for heavy metal removal. In recent years, many studies on the adsorption properties of various low-cost adsorbents, such as agricultural waste and activated carbons based on agricultural waste, have been published. This review summarizes recent research demonstrating the utility of raw and modified date pits biomass-based adsorbents in the removal of heavy metal pollutants from wastewater. Additionally, the chemical compositions, the derived activated carbon, and the proposed mechanism of heavy metal ions were discussed. It thoroughly showed how essential variables including pH, adsorbent dosage, initial metal ion concentration, physical and chemical properties, and temperature affect the adsorption of heavy metals. The significant application of date pits as a bio-adsorbent of heavy metal ions was demonstrated. According to the literature, date pit-based adsorbents are the most promising adsorbents for removing toxic materials because they adsorb heavy metals from aqueous solutions with high capacity in a short period.

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## 1. Introduction

Most industrial activities associated with human scientific progress and revolution have resulted in massive amounts of heavy metals being released into the environment. Heavy metal pollution has steadily increased in tandem with global population, industrialization, and urbanization, particularly in developing countries.

Heavy metals, such as lead (Pb), mercury (Hg), zinc (Zn), cadmium (Cd), copper (Cu), nickel (Ni), chromium (Cr), and others, are extremely poisonous and hazardous to human health and the environment, thus their removal from water and wastewater has received a lot of attention in recent years. Because they are typically poisonous by nature, heavy metals cannot be easily broken down by simple chemical or biological processes like other organic components [1]. They frequently bioaccumulate and can slowly leak into water bodies, posing grave risks to the health of living things. Therefore, before releasing it into the environment, metal-polluted wastewater must be treated.

The adsorption process has been demonstrated to be one of the best water

treatment technologies worldwide and activated carbon is unquestionably regarded as a universal adsorbent for the removal of various types of contaminants from water. Commercial activated carbon's extensive use is occasionally constrained, nevertheless, by its greater price. Innovative, affordable, renewable adsorbents have been developed using a variety of agro-industrial and municipal waste sources. Due to its role in lowering waste disposal costs and hence promoting environmental conservation, the use of waste materials as inexpensive adsorbents is appealing [2]. Some common heavy metals, along with their sources and health concerns, are mentioned in Table 1.

Since these heavy metals are typically carcinogenic in nature, their toxicity is well established. Environmental protection is aided by the fact that chronic exposure to arsenic, for instance, can harm the skin, liver, endocrine, cardiovascular, and central nervous systems (CNS), as well as cause anemia, diarrhea, and the emergence of several cancer kinds [3].

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Because it is poisonous and highly persistent, heavy metal lead can harm the kidney, stomach, and nervous system [4]. High mercury exposure can have harmful effects on the thyroid glands, reproductive system, cardiovascular, immunological, and central neurological systems in addition to serious cognitive impairments like blindness and deafness [5]. The toxic effects of cadmium are severe and frequently lead to high blood pressure, as well as damage to the kidneys, lungs, testicular tissue, and red blood cells. [6]. Chromium levels that are rising above the maximum allowable limit have been linked to digestive tract cancer, acute renal failure, impaired immune systems, and respiratory issues [7]. Similarly, exposure to nickel above the maximum allowable level frequently results in pulmonary fibrosis, eye discomfort, kidney, and lung Adsorption has received a lot of attention because of its low cost, easy availability of bio-waste materials, simple operation, reuse, and regeneration abilities, higher removal capacity over a wide pH range, and ability to remove complex metals [8].

A wide range of unconventional adsorbents has been thoroughly tested for their ability to remove various types of heavy metals from water and wastewater [2, 9-11].

Various low-cost adsorbents derived from various sources have been reported to have little or poor adsorption potential for the removal of various pollutants when compared to commercial activated carbon. As a result, the search for low-cost materials as adsorbents and precursors for the production of activated carbon is ongoing.

However, most studies are increasingly focusing on low-cost and eco-friendly adsorbents. Industrial and agricultural waste, among other basic materials, could be used to create these adsorbents [12-14].

Date palm biomass has been studied extensively as an adsorbent for the removal of various types of pollutants among several agricultural wastes. Due to their availability and significant adsorption potential for the removal of various pollutants, date palm-based agricultural wastes have gained widespread attention as effective adsorbents. Date pits have recently attracted a lot of attention as biomass wastes for the creation of green adsorbents, because of their low cost, bio-cellulose content, and abundance. This article provides an overview of the adsorption capacities of date pits as bio-adsorbents for the removal of heavy metal pollutants in wastewater.

## 2. History of date palm and its properties

The date palm (*Phoenix dactylifera* L.) has long been regarded as one of the most important fruit crops in the Arabian Peninsula, North Africa, and the Middle East. The date is one of the oldest known fruit crops, having been cultivated for at least 5000 years in North Africa and the Middle East. Date culture was probably established as early as 3000 BCE, according to the earliest record from Iraq (Mesopotamia) [15].

More than 100 million date palm trees cover approximately 1.3 million ha of the earth's surface. The exact origin of the date is unknown due to the long history of date culture and the wide distribution and exchange of date cultivars, but it most likely originated in ancient Mesopotamia (southern Iraq) or western India.

Egypt is currently the leading producer of dates, followed by Iran, Algeria, Saudi Arabia, Iraq, Pakistan, Sudan, Oman, UAE, and Tunisia. Date production in the world (including the top 20 producing countries) increased from 3.5 million metric tons in 1990 to 7.5 million metric tons in 2014 [16].

**Table 1.** Allowable limits, sources, and health effects of toxic heavy metals in wastewater

Heavy metal	Allowable limit* (mg/l)	Adverse health effect	Sources of contamination
Lead (Pb)	0.1	Anemia, vomiting, kidney damage, high blood pressure	Corrosion of household plumbing systems, erosion
Copper(Cu)	0.2	Gastrointestinal (GI) distress, GI irritation, liver, and kidney damage	Corrosion of household and plumbing, erosion of natural deposits
Nickel (Ni)	0.2	Allergy, cardiovascular and kidney diseases, lung fibrosis, lung, and nasal cancer	Combustion of coal, and fuel oil, and the incineration of waste and sewage
Cadmium (Cd)	0.01	Kidney damage, lung cancer, proteinuria	Pipes, erosion of metal refineries, waste batteries, paints
Mercury (Hg)	0.005	Hypersensitivity, fever, vomiting, neurasthenia	Erosion of natural deposits, discharge from industry, runoff from landfills, croplands
Zinc (Zn)	0.2	Corrosive to skin and eye, zinc pox, s taste, throat dryness, cough, weakness, generalized aching, chills, fever, nausea, vomiting	Electroplating industry, galvanized metal surfaces, motor oil and hydraulic fluid, tire dust
Chromium (Cr)	0.1	Allergic dermatitis, hemolysis, renal failure	The steel industry, pulp mills, erosion
Arsenic (As)	0.05	Cancer, skin damage, circulatory system problems	Erosion of natural deposits, runoff from orchards, glass and electronics waste
Selenium (Se)	0.05	Hair and fingernail loss, red skin, numbness in fingers and toes, caustic burns, circulatory problems	Petroleum refineries, erosion, discharge from mines
Barium (Ba)	0.4	Breathing difficulties, elevated blood pressure, changes in heart rhythm, skin irritation, muscle weakness, changes in reflexes, brain and liver swelling, kidney heart damage	Mining, refining, and production of barium and barium chemicals, fossil fuel combustion
Manganese(Mg)	0.5	The respiratory tract and the brains Manganese poisoning causes hallucinations, forgetfulness, and nerve damage	Ferroalloy production and steel foundries, power plants, and coke ovens, combustion of fossil fuels
Aluminium (Al)	0.5	Dementia, Alzheimer's disease, and hyperactivity and learning disabilities in children	Air emissions, wastewater effluents, and solid waste primarily associated with industrial production

\* Iraqi Environmental Standards, 2011 [92].

Iraq is the world's largest producer of dates, with over 21 million date palm

trees and an annual production of approximately 400,000 tons. In 2006, the world production of dates was approximately 7 million tons, with Egypt, Saudi Arabia, Iran, the United Arab Emirates, Pakistan, Algeria, Sudan, Oman, Libya, and Tunisia ranking first through tenth [17]. About 14% of the fruit is waste material in the form of seeds. Date stones account for about 10% of total date weight. Date palm is a major fruit grown in many parts of the world, and date pits account for 6–12 percent of the fruit.

The date fruit goes through four distinct stages of ripening. These four stages are commonly referred to in terms derived from Iraqi Arabic as "Kimri," "Khalal" (also known as "Bisir," "Rutab," and "Tamar," to represent the immature green, mature full colored, soft brown, and hard raisin-like stages, respectively [15].

Fruit loses a lot of water during the Tamar stage, and the sugar-to-water ratio is high enough to prevent fermentation. Water content is 75–80 percent in young fruit, 40–60 percent at the start of ripening, and rapidly decreasing later. During early Kimri, the sugar content is about 20% dry matter, gradually increasing to 50% dry matter at the start of Khalal, and then accumulating at a faster rate until it reaches 72–88% dry matter at maturity. Date fruit sizes and shapes vary according to cultivar, culture, and environment [15]. The typical date palm yields 40 kg of fruit per year, while rigorous treatment could increase yields to over 100 kg.

Over the centuries, the date palm has produced a wide range of products, in addition to fruit, that has been widely used by humans in all aspects of life. When pitted dates are produced in packing plants or industrial date-processing plants based on juice extraction, date pits are abundant. Date pit waste has been a major issue for the dating industry. As a result, repurposing it is a promising step [18].

### 3. Chemical composition of date pits

Many researchers found that date pit waste has a higher capacity for heavy metal ions removal than other natural waste materials due to its chemical composition. However, date pit fibers are lignocellulosic materials made up of three essential components: cellulose (40–50%), hemicellulose (20–35%), and lignin (15–35%) [19]. Most researchers claim that when compared to other natural low-cost adsorbents, heavy metals, and other pollutants can be removed more effectively with a small number of date pits adsorbents and a short contact time for equilibrium [20].

Date pit moisture, protein, oil, and carbohydrate contents ranged from 3.1–12.5, 2.3–6.9, 5.0–12.5, and 70.9–86.9 g/100 g, respectively. The moisture content of BET-monolayer (i.e. strongly bound), solids-melting peak (at moisture: 6.7 g/100 g date-pits), and the melting point of oil were 4.3 g/100 g dry-solids, 106°C, and 1.8°C, respectively. The major fatty acids were lauric, myristic, palmitic, stearic, oleic, and linoleic acids and the polyphenol content ranged from 21.0–62.0 mg/g date pits depending on the variety, solvent type, and extraction temperature [21].

As a three-dimensional polymer of phenyl propane units linked together by C-C or C-O-C bonds, lignin is the most important constituent and has complex chemical constituents within the date pits waste material. Hence, the elemental composition has a high carbon percentage (62 wt%) and a low oxygen percentage (32 wt%). A higher number of carbon atoms is generally associated with lower polarity and thus a higher potential for adsorption; additionally, lignin has a significant impact on the adsorption process due to its high number of carbon atoms. As a result, the preferred

adsorbent for adsorption techniques is lignocellulosic material [22].



Figure 1. Photograph of Date Pits.

### 4. Date pits derived activated carbons

Date pits are frequently utilized as bio-adsorbent since they are readily available as agricultural wastes. These agricultural wastes have the ability to synthesize and produce cheap and eco-friendly activated carbon as an alternative substitution for commercial type, as well as the ability to use these precursors in non-carbonized form.

Many researchers have used date pits, both raw and burned, as agricultural waste to remove the majority of heavy metals from wastewater. In order to remove heavy metals, raw date pits with minimal physical processing have been utilized routinely [23–31].

Activated carbon is greatly used for the removal of various pollutants and is widely regarded as a universal adsorbent for effluent treatment. Activated carbon has been recommended as a viable adsorbent due to its high adsorption capacity, small particle sizes, maximum internal surface area, and high porosity [32–33]. Despite this, because of its high production costs, it was unable to be used as an adsorbent for extensive water treatment. Additionally, it is challenging to regenerate activated carbon because it necessitates the use of costly chemicals and has limited commercial feasibility.

The methods used to prepare different date pits as adsorbents have a direct impact on how effectively hazardous heavy metals are removed from contaminated wastewater. Below is a summary of some typical processes for creating date pits biomass-based activated carbon.

For the synthesis of bio-adsorbents, several methods have been developed, including hydrothermal activation, pyrolysis, precipitation, and carbonization. Adsorbents are treated with acids and alkalis such as NaOH, KOH, ZnCl<sub>2</sub>, FeCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and others to create activated carbons [34–43].

There are many techniques used to understand the physical and chemical properties of bio-adsorbents, their adsorption capacity, and their interactions with pollutants; these include scanning electron microscopy (SEM), the Brunauer–Emmett–Teller method (BET), the Barrett–Joyner–Halenda method (BJH), Fourier transform infrared spectroscopy (FTIR), and energy-dispersive X-ray (EDX), among others [44].

The choice of activation method and the activating agent is influenced by the type of biomass waste and its physiochemical properties. For example, Merzougui and Addoun (2008) [45] produce three types of activated carbon from date pits: carbonization without adjuvant, chemical activation with ZnCl<sub>2</sub> and KOH, and mechanical activation. Chemical activation of date

stones with KOH results in activated carbon with the same mesoporosity as  $ZnCl_2$  activation. The activated carbons adsorption capacity was determined by the surface area and porosity of the carbon, the solubility of the organic adsorbate, and the substituent's hydrophobicity.

Another research study was conducted by El-Hendawy (2009) [37], where the removal of significant amounts of  $Pb^{2+}$  and  $Cd^{2+}$  ions using activated carbon derived from date pits with pH of solutions 3-5.9, was investigated.  $HNO_3$  acid surface treatment and carbonization temperature of  $700^\circ C$  for 3 hr increased the adsorption capacity of the investigated carbons. The findings were discussed in light of a potential chemical modification by nitric acid that would result in the formation of a large number of surface functional oxygen species.

On the other hand, date pits can be utilized as precursors to create activated carbons with well-developed porosity and specialized oxygen surface groups, according to another study by Belhachemi et al. 2009 [46]. When the burn-off is increased, both the carbon dioxide and steam activations create microporous carbons with an increasing number of CO-evolving oxygen surface groups. However, the amount of  $CO_2$  developing oxygen surface groups are not significantly different. With  $CO_2$  activation, the porosity is better developed at high levels of activation (the  $S_{BET}$  of sample C50 is  $1443\text{ m}^2\text{ g}^{-1}$  whereas it is only  $1096\text{ m}^2\text{ g}^{-1}$  for sample S49).

Similarly, Danish et al., 2011 [47] made activated carbon-based date beads from farm date stones. Soaking in  $4.2\text{ mmol/L ZnCl}_2$  for 5 hours resulted in chemical activation. The BET surface area was less than the apparatus's detection level of  $850\text{ m}^2/\text{g}$ , the average pore diameter determined by the Barrett-Joiner-Halenda method was  $1.4 \times 10^{-2}\text{ cm}$ , and the bulk density was  $1.196\text{ g/mL}$  at room temperature ( $25^\circ C$ ).

In the same sense, Bouhamed et al., 2012 [48] developed activated carbons for the removal of  $Cu^{2+}$  ions from wastewater by pyrolyzing date stones in the presence of  $H_3PO_4$  as an activating agent. The measured specific surface area of date stones derived activated carbon was  $825\text{ m}^2\text{ g}^{-1}$  and the total pore volume was  $0.46\text{ cm}^3/\text{g}$  at solution pH 3.34.

Moreover, Sekirifa et al., 2013 [49] use local date stones to produce activated carbon via physical activation as an adsorbent of the potent phenolic derivative compound 4-chlorophenol. The final product had BET surface areas ranging from  $502$  to  $604\text{ m}^2/\text{g}$  and micropore volume to total pore volume ratios ranging from  $0.76$  to  $0.85$ . In addition, chemical reagents (such as  $ZnCl_2$ , KOH, and  $CaCl_2$ ) are sometimes used to activate carbon materials in order to retain ionic impurities from wastewater.

## 5. Mechanism of heavy metals adsorption

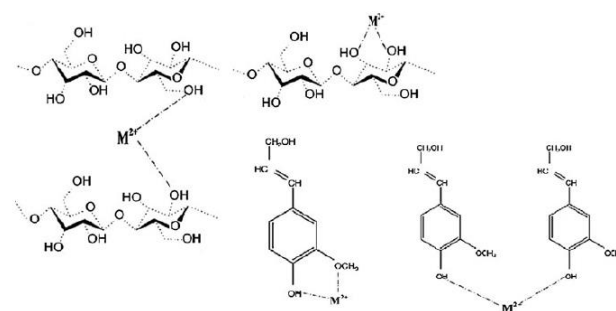
Adsorption is a mass transfer process that involves fluid elements transfer from the bulk of solution to the solid surface of adsorbents due to concentration gradient. However, solid surface is exposed to a fluid phase, molecules from the fluid phase accumulate or concentrate on the solid's surface [50]. Metal ion adsorption mechanisms include physical adsorption, chemical adsorption, electrostatic interactions, hydrogen bonding, pi-pi interactions, and precipitation. Adsorption of pollutants from wastewater comprises the diffusion of pollutant molecules to the adsorbent surface and is adherent by electrostatic attractions [32, Shaheen et al., 2019].

A comparison of copper and zinc ion adsorption on raw and burnt date pits was published by Banat et al., 2002 [52]. Raw date pits absorb more  $Zn^{2+}$  and  $Cu^{2+}$  ions than activated date pits. The surface functional group of raw and activated date pits can explain this behavior. However, the surface of

active functional groups responsible for binding with  $Zn^{2+}$  and  $Cu^{2+}$  in activated date pits was destroyed by the heat treatment used during activation.

In this sense, the adsorption mechanism of metal  $Cu^{2+}$  and  $Cd^{2+}$  ions by raw date pits was suggested by Al-Ghouti et al., 2010 [53]. The isotherms exhibited the Freundlich behavior, indicating heterogeneous surface binding. The primary mechanism for  $Cu^{2+}$  is the binding of two cellulose/lignin units together. The most likely mechanism for  $Cd^{2+}$  binding is the binding via two hydroxyl groups in the cellulose/lignin as shown in Figure 2.

The basic property of a bio-adsorbent is its affinity for toxic heavy metal pollutants. Plant biomass is primarily composed of lignin and cellulose, along with hemicellulose, extractives, lipids, proteins, starches, water, hydrocarbons, and biopolymer-containing lignocellulose and tannins. The presence of various functional groups in biomass such as amine, hydroxyl, carboxyl, carbonyl, and thiol may result in enhanced binding affinity towards metal ions and prepared bio-sorbent [54].



**Figure 2.** Possible binding mechanism of date pits, cellulose and lignin, respectively with  $Cu^{2+}$  and  $Cd^{2+}$  [53].

The electrostatic attraction between positively charged metal ions and negatively charged (functional groups) of bio-adsorbents, for example, could successfully promote adsorption capacity [32, 55].

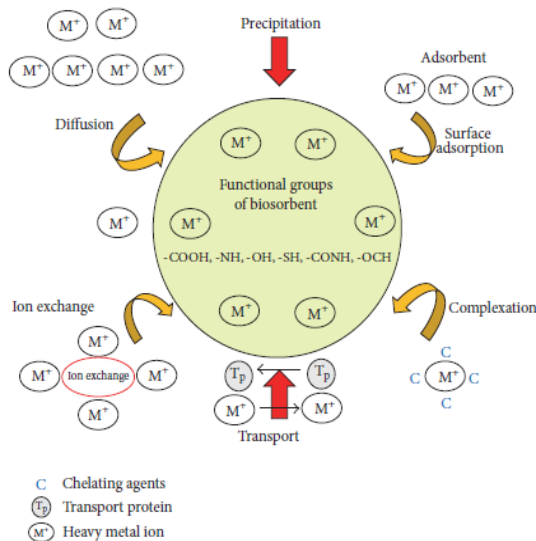
Other attractive forces, such as Van der Waal, hydrogen bonding, and hydrophobic, may also be responsible for heavy metal adsorption on the surface of bio-waste synthesized adsorbents.

However, the removal of heavy metals by bio-waste-based adsorbents is influenced not only by pore volume, pore structure, surface cation exchange capacity, and the number and type of functional groups in bio-adsorbents but also by other factors on which the adsorption process is dependent, such as bio-adsorbent dosage, pH of wastewater, temperature, pressure, adsorbent activation, adsorbent surface area, etc. [50]. Figure 3 shows the different mechanisms of heavy metal ions adsorption by functional groups of biosorbent. In another route, the mechanism of complexation involves the formation of complexes by the combination of more than one species, whereas chelation is a subset of complexation that involves the formation of rings [56]. When it comes to complexation, metals bound by ligands occupy the central position and are referred to as mononuclear complexes.

## 6. Important factors influencing heavy metal adsorption

Adsorption can be carried out as a batch, semi-batch, and continuous process. When little quantities are to be treated, batch processes are

generally carried out and the equilibrium distribution depends on the contact time in the batch process [50].



**Figure 3.** Schematic diagram of mechanisms of bio-adsorbent [50].

### 6.1. Acidity of the solution (pH)

The pH of the aqueous media is an important operational factor in heavy metal adsorption because changes in solution pH can affect adsorbate speciation, ionization of solute metal ions, and adsorbent surface chemistry [54]. The point of zero charges (PZC) or zeta potential analysis of bio-adsorbents is important because it determines the adsorbent's surface charge at different pH levels. When the pH value is lower than the PZC, the acidic water donates more  $H^+$  than  $OH^-$  groups, causing the bio-surface adsorbents to become positively charged (attracting anions). When the pH value exceeds the PZC, the surface becomes negatively charged (attracting cations/repelling anions) [57, 28].

For example, in the case of lead metal adsorption, increasing pH causes the adsorbent surface to develop a negative charge, which facilitates the sorption of positively charged heavy metal ions [58-59].

The majority of metal adsorption at pH less than 3 shows a lower percentage of metal removal, whereas increasing pH decreases  $H^+$  ion concentration, resulting in more sorption sites becoming available [60, 61]. In contrast, efficient adsorption occurs at acidic pH, though this is dependent on the nature of the adsorbate and adsorbent. Furthermore, the degree of ionization of a species is affected by pHs, such as the presence of a weak acid or a weak base, which affects adsorption [62, 63].

### 6.2 Adsorbent dosage

The adsorbent dose is another important factor that directly influences the design of an efficient adsorption system. In general, the extent of an adsorption capacity to effectively adsorb heavy metals increases with increasing adsorbent dose because more adsorbent provided a greater number of active adsorption sites. The heavy metal removal from

wastewater is greatly influenced by the partial aggregation among the binding sites at the optimum dosage of the adsorbent [64]. This is because the lack of active binding sites resulted in a decreased rate of heavy metal removal.

For example, it was observed that at increasing doses of tamarind fruit shell bio-adsorbents, the removal% of Cr(VI) and Ni(II) ions enhanced from 80% to 85% and 75 to 95% at the initial concentration of 0.01 g per 10 mL and 0.08 g per 10 mL, respectively [65]. Furthermore, it was also found that using a small adsorbent dosage of  $1.2 \text{ g L}^{-1}$ , date palm trunk fibers could remove up to 99.95 percent of chromate anions ( $Cr^{6+}$ ) from a  $100 \text{ mg L}^{-1}$  solution. At the optimal pH of 3.5, equilibrium was reached in 30 minutes [63]. They also found that as the initial Cr(VI) concentration increases from 50 to  $100 \text{ mg/L}$ , the equilibrium adsorption capacity increases from 49.8 to  $89.3 \text{ mg/g}$ .

Furthermore, Hilal et al., 2012 [25] found that increasing the adsorbent dose increases the removal efficiency percentage of Cu(II) and Cd(II) ions up to a certain point, after which it remains nearly constant. Adsorption is expected to increase with increasing adsorbent dose due to an increase in adsorbent surface area and the availability of more adsorption sites.

It is worth noting that some studies show that the removal of heavy metals such as Co(II) and Cr(VI) onto bio-sorbent increases until the adsorption equilibrium is reached, at which point further increases in adsorbent dosage will not significantly increase the removal. Another contradictory study found a reverse trend in Cr(VI) adsorption onto adsorbent derived from *Sargassum tentorium* when the dosage was increased [66]. This opposing approach occurred due to a decrease in the ratio of pollutants to the binding sites on the bio-sorbent, which resulted in a decrease in toxic metal concentrations in solution at high dosage.

### 6.3 Initial metal ion concentration

The initial concentration of metal pollutants has a direct impact on the percentage removal of heavy metallic ions. In general, as heavy metal concentrations decrease, the adsorption efficiency increases due to an increase in the probability of adsorption to the adsorbent per ion at a low concentration. But, the adsorption capacity of any adsorbent increases with increasing metal ion concentration and reaches a maximum at a certain concentration [25, 63].

However, the effect of the initial metal concentration is mostly calculated in the sorption isotherm, which provides information about a biosorbent's maximum sorption capacity. The driving force produced by the initial concentration of analyte in an aqueous solution allows most heavy metals to transfer from the aqueous solution to the biosorbent surface. Significantly higher removal of  $Cu^{2+}$  ions ( $34 \text{ mg g}^{-1}$ ) was observed with particles  $75 \mu\text{m}$  compared to larger particle size  $251 \mu\text{m}$ . Also,  $Cu^{2+}$  removal increased significantly from 6 to  $23 \text{ mg g}^{-1}$  as  $Cu^{2+}$  concentration increased from 20 to  $100 \text{ mg L}^{-1}$  [67].

More metal oxyanions are available for biosorption reaction in the solution as the initial metal concentration increases [68]. On the other hand, the percentage of metal removed decreases with increasing metal concentration. This could be due to a lack of surface area to accommodate excess metal in the solution at lower concentrations and saturation of adsorption sites at higher concentrations [69].

### 6.4 Contact time

This is yet another critical parameter that has a significant impact on the adsorption process and kinetics. In general, as contact time increases, the percentage of pollutants removed increases until an equilibrium is reached [70]. Contact time is an important factor in determining an adsorbent's efficiency since it is controlled by bulk diffusion, external mass transfer, and chemical reaction. According to Hilal et al., 2012 [25], there was rapid adsorption of Cd(II) and Cu(II) in the first 20 minutes, and then the rate of adsorption became slower; this is due to a decreased or lesser number of active sites.

Initially, maximum sorption occurs during the adsorption process due to the abundance of vacant adsorbent sites; however, the rate of adsorption eventually decreases, resulting in a straight line plotting the adsorption amount against time, indicating the saturation level of the adsorbent [71]. However, as the contact time increases, the adsorption process may be completed. Conversely, some studies explained that a few adsorbents could adsorb heavy metal pollutants in a short period [72-74].

### 6.5 Physical and Chemical Properties of Bio-adsorbent

The particle size of the bio-adsorbent has a significant impact on the adsorption of heavy metals from wastewater because smaller particle sizes reduce internal diffusional and mass transfer limitations to adsorbate penetration, i.e. the equilibrium are more easily achieved and nearly full adsorption capability can be attained [28, 64, 67, 75]. However, the specific surface area of the solid bio-adsorbent is also important because the adsorptive capacity generally increases as the specific surface area increases [53].

The physicochemical properties of bio- agriculture waste-derived adsorbents have a strong influence on the adsorption of heavy metals by bio-waste-derived adsorbents. The surface area and porosity of bio-adsorbents, surface functional groups, pore distribution, and cation exchange capacity are the most important properties of these adsorbents [25, 76, 77].

The main physical properties that influence the ability of bio-adsorbents to uptake various heavy metals are porosity and specific surface area. The specific surface area of bio-sorbents is determined by their pore structure. The presence of functional groups is an important property of bio-adsorbents that allows them to interact with pollutants. Bio-adsorbents typically contain a variety of functional groups (amino, carbonyl, carboxyl, hydroxyl, and so on) that serve as binding sites for heavy metal pollutants [18].

Another physicochemical property of developed adsorbents is zeta potential, which is influenced by changes in solution pH. It is commonly used to determine the surface charge of bio-adsorbents at different pH levels [12]. It indicates the potential interactions between metal species and adsorbent surfaces at a given pH.

### 6.6 Temperature

Several studies on the effect of temperature on pollutant adsorption by bio-adsorbents have been published in recent years [12, 78]. Temperature is a critical parameter that influences physicochemical properties and has a significant impact on heavy metal adsorption due to the enlargement of active surface functional groups. The adsorption process can be endothermic or exothermic, which means that for endothermic adsorption,

the reaction rate increases with increasing temperature [79, 80].

The high temperature reduces the mass transfer resistance of the boundary layer, allowing ions to escape from the aqueous phase more easily. At higher temperatures, most exothermic adsorption processes have a weak interaction between metal ion adsorbate and the active sites on the surface of bio-adsorbent [54]. These interactions could be caused by Van der Waals interactions or hydrogen bonding, both of which weaken at high temperatures.

In this route, Danish et al., 2011 [81] studied the effect of temperature (293-313 K) on the adsorption of Cu(II) and Ni(II) ions at optimal pH values of 6.0 and 5.5, respectively. The results indicated that Cu(II) and Ni(II) adsorption capacities increased from 19.39 to 44.79 mg g<sup>-1</sup> and from 15.77 to 40.73 mg g<sup>-1</sup>, respectively. However, at equilibrium, the total adsorption was greater at lower temperatures, and the following trend for maximum adsorption was observed: 293 K > 303 K > 313 K. The observed trend in total adsorption at equilibrium could be attributed to an increase in the kinetic energy of the ions at higher temperatures, resulting in a decrease in adsorption.

On the other hand, Krishnamoorthy et al., 2019 [82] found that the adsorption capacity of activated carbon from date pits DPAC for temperature variations ranging from 30°C to 60°C. Results confirmed the exothermic nature of the lead adsorption on DPAC. Consequently, an increase in temperature caused the Pb(II) molecules to easily migrate from the solid phase to bulk resulting in low uptake capacities for DPAC.

## 7. Application of date pits as bio-adsorbent

Heavy metals have been identified as potentially hazardous materials to human health and the environment. The removal of toxic heavy metals from wastewater is currently one of the most important environmental issues being researched.

Toxic heavy metals in untreated effluent discharged into the environment make their way into streams and rivers, affecting aquatic life and entering the food chain, posing health risks. When found above the tolerance level, this could lead to accumulative poisoning, cancer, and brain damage. Date pits, as bio-agriculture waste, have been extensively investigated as green adsorbents for the removal of various metal ions from water and wastewater by various researchers. A summary of the adsorption capacities of date pits-based bio-adsorbents for different metal ions removal has been presented in Table 2. Azam et al., 2022 [80] explained the adsorption potential of Cu<sup>2+</sup> using two types of Ajwa date pits as biosorbent ADP and TADP. The biosorbent TADP showed higher adsorption capabilities compared to ADP. The Cu<sup>2+</sup> ions adsorptions by ADP and TADP were endothermic, indicating that a pseudo-second-order kinetics model would be more appropriate in all circumstances. In addition, they stated that the Langmuir isotherm model produced somewhat better findings in comparison to the Freundlich model for both ADP and TADP.

Alhamzani A.G., 2021 [83] studied two types of date pits of date palm trees (Sukary and Klass) as bio-sorbents for Pb and Cu adsorption from aqueous solutions. The maximum adsorption capacity at room temperature of Sukary date pits was 17.53 mg g<sup>-1</sup> and 9.86 mg g<sup>-1</sup> for Pb<sup>2+</sup> and Cu<sup>2+</sup>, respectively. Whereas, Khlass date pits showed maximum adsorption capacity at 14.1 mg g<sup>-1</sup> and 7.91 mg g<sup>-1</sup> for Pb<sup>2+</sup> and Cu<sup>2+</sup>, respectively at room temperature. Furthermore, Langmuir and Freundlich models, as equilibrium isotherm models, were used for the analysis of equilibrium

experimental results.

Al-Onazi et al., 2021[84] investigate the possibility of using pomegranate peel (PP) and date pit (DP) activated carbon (PPAC and DPAC, respectively) as sorbents to remove Cd<sup>2+</sup> and Pb<sup>2+</sup> from aqueous solutions. The results showed that the maximum adsorptions of Cd<sup>2+</sup> and Pb<sup>2+</sup> were achieved at pH ranging from 6 to 6.5, 90 min contact time, and 0.5 g/L for

**Table 2.** Raw date pits and date pits derived activated carbon for different heavy metal ions adsorption.

Adsorbent	Adsorbate	Concen. Range	Contact time	pH	% Removal
Adsorption capacity		Temperature °C	Reference		
Activated C	Zn <sup>2+</sup> 5.23 mg/g	20-100mg/L	2-8 h 25, 40, 50	3.5-5	- Banat et al., 2002
Activated C	Cu <sup>2+</sup> 8.89 mg/g	10-50 mg/L	2-8 h 25, 40, 50	3.5-5	- Banat et al., 2002
Raw	Cu <sup>2+</sup> 9.53 mg/g	10-50 mg/L	2-8 h 25, 40, 50	3.5-5	- Banat et al., 2002
Raw	Cd <sup>2+</sup> 6.5 mg/g	4-90 mg/L	24 h 25, 35, 45	2-7	- Banat et al., 2003
Carbonized 500°C	Cd <sup>2+</sup> 3 mg/g	4-90 mg/L	24 h 25, 35, 45	2-7	- Banat et al., 2003
Carbonized 900°C	Cd <sup>2+</sup> 1.8 mg/g	4-90 mg/L	24 h 25, 35, 45	2-7	- Banat et al., 2003
Activated C	Pb <sup>2+</sup> 30.7 mg/g	25-300 mg/L	24 h 25	5.2	-Abdulkarim&Al-Rub,2004
Activated C	Pb <sup>2+</sup> 30.6 mg/g	25-300 mg/L	24 h 25	5.2	-Abdulkarim&Al-Rub,2004
Chem modified					
Activated C	Al <sup>3+</sup> 0.305 mg/g	5-50 mg/L	24 h 22	4	- Al-Muhtaseb et al.,2008
Activated C	Cr <sup>6+</sup> 120.48 mg/g	5-150 mg/L	3 h 25	100	El Nemr et al., 2008
Activated C	Pb <sup>2+</sup> 182 mg/g	25-250 mg/L	24 h 25	97	El-Hendawy, 2009
Activated C	Cd <sup>2+</sup> 169 mg/g	25-250 mg/L	24 h 25	83	El-Hendawy, 2009
Activated C	Pb <sup>2+</sup> 19.64 mg/g	10-30 mg/L	3 h 20	94.4	Mouni et al., 2010
Activated C	Zn <sup>2+</sup> 10.41 mg/g	10-30 mg/L	3 h 20	93.2	Mouni et al., 2010
Activated C/CaO	Cu <sup>2+</sup> 44.79 mg/g	50-200 mg/L	3h 20, 30, 40	6	- Danish et al., 2011
Activated C/CaO	Ni <sup>2+</sup> 40.73 mg/g	50-200 mg/L	3h 20, 30, 40	6	- Danish et al., 2011
Raw	Cu <sup>2+</sup> 7.4 mg/g	10-110 mg/L	3.3h 25	2.1-9.05	90 Hilal et al., 2012
Activated C	Cu <sup>2+</sup> 33.44 mg/g	10-110 mg/L	3.3h 25	2.1-9.05	96 Hilal et al., 2012
Raw	Cd <sup>2+</sup> 6.02 mg/g	10-110 mg/L	3.3h 25	2.1-9.05	66 Hilal et al., 2012
Activated C	Cd <sup>2+</sup> Cd <sup>2+</sup> 17.24 mg/g	10-110 mg/L	3.3h 25	2.1-9.05	87 Hilal et al., 2012
Activated C	Pb <sup>2+</sup> 9.91 mg/g	5-50 mg/L	2 h 25-60	2-10	99 Chaouch et al., 2014
Activated C	Cu Ions 0.1058 mg/g	10-50 mg/L	0.5-1.5 h 27	3.5-6.5	85 Esmael et al., 2014
Activated C	Cr <sup>6+</sup> 0.0557 mg/g	10-50 mg/L	0.5-1.16 h 27	3.5-7.5	65 Esmael et al., 2014
Activated C	Fe Ions 0.111 mg/g	10-50 mg/L	0.5-1.5 h 27	3.5-7.5	87 Esmael et al., 2014
Raw	Au <sup>3+</sup> 78 mg/g	1000 mg/L (HAuCl <sub>4</sub> )	0-2.5 h 25-30	1.8-10.90	Al-Saidi, 2016
Biochar	Pb <sup>2+</sup> 85.876 mg/g	24.6-328 mg/L	24 h 25	6	- Mahdi et al., 2018
Biochar	Cu <sup>2+</sup> 12.209 mg/g	8.7-116 mg/L	24 h 25	6	- Mahdi et al., 2018
Biochar	Ni <sup>2+</sup> 9.324 mg/g	4-112 mg/L	24 h 25	6	- Mahdi et al., 2018
Activated C	Pb <sup>2+</sup> 101.35 mg/g	5-50 mg/g	0.5 h 30	6	89% Krishnamoorthy et al., 2019
Raw/Treated	Cr <sup>3+</sup> 1428.5 mg/g	10-50 mg/L	0.083-5 h 20-50	2.9-11.1	- Azam et al., 2021
Raw/Treated	Cd <sup>2+</sup> 1302 mg/g	10-50 mg/L	0.083-5 h 20-50	2.9-11.1	- Azam et al., 2021
Raw	Cu <sup>2+</sup> 9.86 mg/g	50-600 mg/L	3 h 20	-	Alhamzani, 2021
Raw	Pb <sup>2+</sup> 17.53 mg/g	100-1000 mg/L	3 h 20	-	Alhamzani, 2021
Raw	Cu <sup>2+</sup> 290 mg/g	10-50 mg/L	6 h 25-55	2.7-10.5	- Azam et al., 2022
Raw	Cu <sup>2+</sup> 360 mg/g	10-50 mg/L	6 h 25-55	2.7-10.5	- Azam et al., 2022

PPAC and 1 g/L for DPAC dosage. Furthermore, the adsorption efficiencies for both Pb<sup>2+</sup> and Cd<sup>2+</sup> were higher for PPAC than for DPAC. However, the recorded Q<sub>max</sub> values for PPAC were 68.6 and 53.8 mg/g for Pb<sup>2+</sup> and Cd<sup>2+</sup> and for DPAC were 34.18 and 32.90 mg/g for Pb<sup>2+</sup> and Cd<sup>2+</sup>, respectively. Langmuir isotherm model fits the adsorption data better than the Freundlich model. Kinetically, the adsorption reaction followed a pseudo-second-order reaction model, with a<sub>ges</sub> ranging from 12.0 to 22.37 mg/g and an R<sup>2</sup> value of 0.99.

The adsorption behavior of Cr<sup>3+</sup> and Cd<sup>2+</sup> ions from wastewater using raw date pits and chemically treated date pits was demonstrated by Azam et al.,

2021 [85]. In a batch system, they investigated various parameters such as solution pH, contact time, initial metal concentrations, and adsorbent dosage. The optimum pH for achieving maximum adsorption capacity was found to be approximately 7.8. The experimental results were fitted using isotherm Langmuir and Freundlich equations, and maximum monolayer adsorption capacities for Cr<sup>3+</sup> and Cd<sup>2+</sup> at 323 K were 1428.5 and 1302.0 mg/g treated using Majdool date pits adsorbent and 1228.5 and 1182.0 mg/g treated using Sagai date pits adsorbent, respectively. The results showed that the Langmuir model gave slightly better results than the Freundlich model for the untreated and treated date pits.

Maki et al., 2020 [31] used a bio-adsorbent consisting of date palm seeds of two cultivars of the date palm fruit Hillawi and Zahdi to treat synthetic Pb wastewater. The result showed an efficient removal of Pb<sup>2+</sup> ions from the wastewater. A rapid adsorption rate, high adsorption capacity, optimum pH, contact time, temperature, and optimum mixing speed were determined. The capacity of adsorption is in the following order: Hillawi (0.598mg/g, 79.81%) is more than Zahdi (0.349mg/g, 43.65%).

Mangwandi et al., 2020 [86] studied the chemically modified date pit (CM-DP) and olive stone (CM-OS) for biosorption capacity for Cr<sup>6+</sup> removal in the aqueous phase. Results showed that at pH = 2, biosorbent dosage > 4 g/L, and low ionic strength, both biosorbents showed the best biosorption capacity of the Cr<sup>6+</sup> removal. Various isotherm models were applied to fit the experimental data and the Freundlich isotherm model was the best-fitting isotherm model for the biosorption experimental data of both biosorbents. The maximum biosorption capacities of CM-DP and CM-OS were found to be 82.63 and 53.31 mg/g respectively, which is comparable to other materials. In the kinetic study, the pseudo-second-order model can best describe the biosorption process of both biosorbents and the intraparticle diffusion was not the rate-limiting step indicating the contribution of film diffusion in the Cr<sup>6+</sup> removal processes.

Alghamdi A.A., 2019 [30] stated that the date pits powder could be used as an adsorbent to remove Pb<sup>2+</sup> ions from wastewater. Thomas model was applied to study the efficiency of the date stone powder for adsorbing Pb<sup>2+</sup> ions. It was observed that the breakthrough point was giving clear evidence of the occupancy rate of the adsorbent with Pb<sup>2+</sup> ions in all particle size ranges.

Al-Saad et al., 2019 [29] tested the adsorption of targeted heavy metals, both by raw date pits (RDP) and burnt date pits (BDP). Results showed that BDP is more efficient as an adsorbent and mostly adsorbing Cu<sup>2+</sup>. A novel approach; fractional factorial design (2<sup>k-p</sup> - FrFD) was used to build the experimental pattern of this study. The implemented design allowed studying variables impacting the adsorption with the minimum time and effort. The equilibrium study shows that the adsorption obeys the Langmuir isotherm at low concentrations while it follows the Freundlich isotherm at higher concentrations. Temkin isotherm shows that the adsorption is exothermic in segments (I and III), while it is endothermic in segment (II). Dubinin-Radushkevich shows four regions, segments (I and IV) are physisorption, while segment (II) is chemisorption.

Mohamed et al., 2019 [71] prepared an adsorbent from the powder of Ajwaa date seeds (PADS). The adsorbent was applied in removing heavy metal ions from a stock standard aqueous solution containing 1000 ppm of cadmium, lead, copper, chromium, cobalt and. The maximum removal efficiency of 93.34%, 71.06%, 92.06%, 96.96%, 95.91%, and 36.13% for Cd<sup>2+</sup> ions, Cr<sup>3+</sup> ions, Co<sup>2+</sup> ions, Cu<sup>2+</sup> ions, Pb<sup>2+</sup> ions, and Mn<sup>2+</sup> ions, respectively.

Krishnamoorthy et al., 2019 [82] studied the preparation of phosphoric acid-based activated carbon from date pits (DPAC) for the removal of  $\text{Pb}^{2+}$  ions from an aqueous solution. The adsorption capacity of DPAC was improved with incremental pH in the acid region as well as with a rise in initial feed concentration. Contact time, temperature, and adsorbent dosage were analyzed for their optimum values of 30 min, 30°C, and 2 g/L, respectively. Prepared DPAC possessed an experimental maximum of 101.35 mg/g as  $\text{Pb}^{2+}$  uptake capacity for optimal values of adsorption variables. Equilibrium studies specified the suitability of Langmuir isotherm with a theoretical adsorption capacity of 128.21 mg/g for DPAC under studied conditions. Adsorption kinetic analysis confirmed that the  $\text{Pb}^{2+}$  binding to the DPAC surface followed the pseudo-second-order model. Mahdi et al., 2019 [87] investigated the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  in binary and ternary systems using date seed biochar in batch and column adsorption experiments. The adsorption of the heavy metal ions was strongly solution pH dependent. Optimal adsorption was achieved around pH 6. Compared to single-component capacities, a reduction ranging from 48 to 75% was observed for multi-component systems due to the competitive behavior of the ions. Equilibrium isotherms were obtained and analyzed using Langmuir and modified Langmuir models. The behavior of competitive adsorption for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  combinations was successfully described by the modified Langmuir model in the studied concentration ranges. The isotherms indicated competitive adsorption, with  $\text{Pb}^{2+}$  being preferentially adsorbed followed by  $\text{Cu}^{2+}$  and then  $\text{Ni}^{2+}$ . For fixed bed competitive adsorption, the removal efficiency of the biochar followed the order of  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$ .

Mahdi et al., 2018 [88] explored the adsorption of lead ions from an aqueous solution onto biochars produced from date seed biomass. Initial evaluation of nine date seed-derived biochars showed that biochar prepared at 550 °C and heating time of 3 h (DSB550-3) was the best adsorbent for  $\text{Pb}^{2+}$  ion removal. Therefore, it was selected for further investigation in batch and column experiments. The effects of contact time, initial  $\text{Pb}^{2+}$  concentration, and solution pH were studied. The batch maximum adsorption capacity of DSB550-3 biochar was 0.360 mmol g<sup>-1</sup>. The equilibrium data were adequately fitted to Freundlich and Langmuir isotherms ( $R^2=0.97$ ). The adsorption kinetics was best described by the pseudo-second-order model ( $R^2=0.94$ ). The breakthrough curve obtained from the column experiment was best described by the modified response model ( $R^2 = 0.95$ ). The desorption efficiencies of  $\text{Pb}^{2+}$  were 2.1%, 23%, 12%, and 55% for DI water, 0.1 M HCl, 0.1 M  $\text{CaCl}_2$ , and a combination of 0.1 M HCl + 0.1 M  $\text{CaCl}_2$  eluents, respectively.

Aldawsari et al., 2017 [42] explained that Mesoporous mercerized date pit activated carbon (DPAC) having extremely high BET surface area showed promising results for the adsorption of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  from aqueous medium. Preliminary adsorption studies showed maximum adsorption of  $\text{Cd}^{2+}$  onto DPAC followed by  $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+}$ . The experimental parameters have a profound influence on the heavy metals adsorption process. A physical adsorption process having exothermic nature was observed. Maximum monolayer adsorption capacities ( $q_m$ ) for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  obtained by non-linear isotherm model at 298 K were 212.1, 133.5, 194.4, and 111 mg/g, respectively. Kinetics modeling parameters showed the applicability of the pseudo-second-order model. The activation energy ( $E_a$ ) magnitude revealed the physical nature of adsorption. Maximum elution of  $\text{Cu}^{2+}$  (81.6%),  $\text{Zn}^{2+}$  (70.1%),  $\text{Pb}^{2+}$  (96%), and  $\text{Cd}^{2+}$  (78.2%) were observed with 0.1 M HCl.

Rezgui et al., 2017 [61] showed that raw date pits can be used as a low-cost sorbent for the removal of  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$  metal ions from aqueous solutions using the batch equilibrium method. Sorption isotherms that can be accurately modeled by the Langmuir equation gave maximum sorption capacities close to 38.5 mg Hg g<sup>-1</sup> and 52.6 mg Zn g<sup>-1</sup> at monolayer coverage of the sorbent. The modeling of sorption isotherms with the Dubinin-Radushkevich allowed calculating the mean free energies for both  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$  sorption that is consistent with an ion-exchange mechanism. The thermodynamic study of metal sorption on date pits demonstrated that the sorption is exothermic and spontaneous.

Al-Saidi 2016 [27] investigated the recovery of  $\text{Au}^{3+}$  ions from aqueous solutions employing raw date pits RDPs. The adsorption of  $\text{Au}^{3+}$  onto date pits was achieved quantitatively ( $90\% \pm 3.4\%$ ) after 90 min of shaking in an aqueous medium containing 0.5 mol L<sup>-1</sup> HCl. The process of gold(III) ion recovery using RDPs was described by the adsorption coupled reduction mechanism which includes the adsorption of  $\text{Au}^{3+}$  ions onto the RDP surface, followed by the reduction of  $\text{Au}^{3+}$  to Au. The kinetic data were studied using pseudo-first order, pseudo-second order, and intraparticle diffusion models, and were found to follow closely the pseudo-second-order model.

Date pits were used as a low-cost adsorbent to study the effective removal of  $\text{Cu}^{2+}$  ions in an aqueous solution on the basis of adsorption kinetics and isotherm equations Khalil et al., 2016 [28]. The effects of the pH, zero point of charge, the adsorbent mass, and the adsorbent particle size on the adsorption of  $\text{Cu}^{2+}$  were also studied. The adsorption kinetics data were evaluated by the pseudo-first-order, second-order kinetic, Elovich, and intraparticle diffusion models. Results indicated that Freundlich adsorption isotherm was best fitted to the experimental data. The maximum adsorption capacity was found to be 3.27 mg/g. Adsorption kinetics of  $\text{Cu}^{2+}$  adsorption on date pits followed the pseudo-second-order kinetic model.

Khelaifia et al., 2016 [89] inspected if raw local date stones (D.S) waste can be successfully used as a biosorbent for removing  $\text{Cr}^{6+}$  from an aqueous solution. The experiment results in batch adsorption show that the adsorption capacity was around 70 mg g<sup>-1</sup> for; initial  $\text{Cr}^{6+}$  concentration 100 mg L<sup>-1</sup>, pH 2, equilibrium contact time 60 min, and D.S concentration 1 g L<sup>-1</sup>. These results are well modeled by Langmuir isotherm and kinetics study followed the pseudo-second-order model. The adjustment of models was confirmed by the Chi-square ( $\chi^2$ ) test and the correlation coefficient  $R^2$ . Thermodynamic parameters indicate that the adsorption process is spontaneous and endothermic.

Esmael et al., 2014 [41] studied the adsorption of heavy metals for individual elements, and for industrial wastewater samples collected from a tannery and an electroplating factory. The kinetic studies showed that Cu,  $\text{Cr}^{6+}$ , and Fe were adsorbed very rapidly within the first 30 minutes in a continuous adsorption column, while equilibrium was attained within 90min. The optimum pH range for their adsorption was found to be (4.5-6.5), the depth of the adsorbent layer (was 70-90) cm, and particle size (was 0.5-0.75) mm. The adsorption capacity and the removal efficiency for individual elements reached 89.17% for Cu, 71.30% for  $\text{Cr}^{6+}$ , and 85.17% for Fe respectively. As for the removal of heavy metals from industrial wastewater collected from the tannery, the removal efficiency reached 85.17% for Cu, 65.42% for  $\text{Cr}^{6+}$ , and 87.03% for Fe and for the electroplating factory effluent: 82.857% for Cu, 61.65% for  $\text{Cr}^{6+}$ , and 89% for Fe. Experimental data were better fitted to the Freundlich equation rather than to the Langmuir equation.



Samra et al., 2014 [26] showed the effect of pH and initial  $Pb^{2+}$  concentration and sorbent dose on the adsorption capacity of  $Pb^{2+}$  from natural water. The Freundlich and Langmuir were applied. The change in Gibbs free energy change ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) were also calculated. Under the optimum experimental conditions employed, the removal of ~95% of  $Pb^{2+}$  was attained.

Awad et al., 2013 [39] demonstrated that carbon samples with good adsorption properties could be prepared from date pits through chemical or physical activation as; (i) activated carbons by steam pyrolysis, (ii) activated carbons by single-step steam pyrolysis conditions at 700 C with the accompanying flow of  $N_2$ -activation, (iii) activated carbons by steam pyrolysis technique at 700 C was performed in presence of catalytic gasifying acetate of calcium. The produced carbon samples show a specific surface area from 290-702  $m^2/g$  and a pour volume ( $V_p$ ) of 0.248–0.321 mL/g. The prepared carbon samples were studied as adsorbents for metal ions  $Co^{2+}$ ,  $Fe^{3+}$ ,  $Pb^{2+}$ , and  $Zn^{2+}$  and showed a removal percentage of more than 95% of metal ions from the solution.

Hilal et al., 2012 [25] examined raw date pits (RDP), and activated carbon prepared from date pits (ADP) have been used as adsorbents for the removal of Cu(II) and Cd(II) from wastewater. They stated that the adsorption was influenced by various parameters such as initial pH, initial metal ions concentrations, and dose of adsorbents. The maximum uptake of two metal ions occurred at an initial pH of  $5.8 \pm 0.5$ . Adsorption was increased with increasing dose of adsorbent and decreased with increasing initial metal ions concentrations. Furthermore, the equilibrium time for the adsorption of metal ions from aqueous solutions was achieved within 60 min of contact time. The Freundlich adsorption isotherm model was better used to represent the experimental data. The adsorption kinetics fits to pseudo-second-order model.

Danish et al., 2011 [81] prepared, characterized, and used as an unconventional adsorbent for the removal of  $Cu^{2+}$  and  $Ni^{2+}$  ions from aqueous solutions in a batch process. Calcium oxide activated stone carbon (ADS) characterization of activated carbon obtained from Phoenix dactylifera stone has been done. The percent adsorption of  $Cu^{2+}$  and  $Ni^{2+}$  ions increased with an increase in contact time and initial metal ion concentration. Equilibrium data fit the Langmuir adsorption isotherm model, confirming monolayer adsorption on the surface of ADS for  $Cu^{2+}$  and  $Ni^{2+}$  ions at 293 K. The applicability of Langmuir, Freundlich, and DubininRadushkevich (D-R) adsorption isotherms was evaluated to better understand the adsorption process. The results of this study revealed that ADS has a honeycomb-like surface morphology with a large mesoporous surface area ( $645.5 m^2 g^{-1}$ ) for adsorption and removal of copper and nickel was followed by the pseudo-second-order kinetics and the Langmuir model of isotherms. Thermodynamic studies revealed that the heat of adsorption of  $Cu^{2+}$  and  $Ni^{2+}$  ions was  $-4.99 kJ mol^{-1}$  and  $10.78 kJ mol^{-1}$ , respectively. Al-Ghouti et al., 2010 [53] investigated the adsorption mechanism of removing heavy metal ions from an aqueous solution using date pits as adsorbent. The adsorption capacities of the raw date pits reported for  $Cu^{2+}$  and  $Cd^{2+}$  ions using Langmuir and Freundlich models were 35.9 and 39.5 mg/g, respectively. The pH of the solute solution is an important parameter since it affects the solute adsorption capacities on the raw date pits. The isotherms exhibited the Freundlich behavior, which indicates a heterogeneous surface binding. For  $Cu^{2+}$ , binding two cellulose/lignin units together are the predominant mechanism. For  $Cd^{2+}$ , the most predicted mechanism is, the binding of  $Cd^{2+}$  using two hydroxyl groups in the

cellulose/lignin unit.

The adsorption of  $Pb^{2+}$  and  $Cd^{2+}$  ions onto date pits activated carbons have been studied by El-Hendawy, 2009 [37]. The results revealed that all obtained isotherms follow the Langmuir equation. The investigated activated carbons exhibited higher uptake capacities for metal ions as compared to raw date pits. The surface chemistry of the activated carbon and pH of the solution was found to have the highest impact on  $Pb^{2+}$  and  $Cd^{2+}$  ions removal. Lead is removed in somewhat higher amounts than cadmium due to its lower solubility and lower pH for complexation or deposition, which promotes its removal in comparison to  $Cd^{2+}$ .

A comparative study of copper and zinc ion adsorption onto  $CO_2$ -activated and non-activated date pits was reported by Banat et al., 2002 [52]. Raw date pits show higher  $Zn^{2+}$  and  $Cu^{2+}$  ion uptake than activated date pits carbon. This behavior can be explained based on the surface functional group of raw and activated date pits. In inactivated date pits, the surface active functional groups that were responsible for binding with  $Zn^{2+}$  and  $Cu^{2+}$  were destroyed due to heat treatment given during activation. So no improvement in the adsorption capacity was observed. The removal of  $Cu^{2+}$  ions by activated date pits carbon as well as raw date pits was higher than the removal of  $Zn^{2+}$  ions. This behavior may be attributed to the fact that the  $Cu^{2+}$  ions have an ionic radius than  $Zn^{2+}$  ions so  $Cu^{2+}$  ions will be capable of greater accessibility to the surface of certain pores than  $Zn^{2+}$  ions.

The adsorption of  $Cd^{2+}$  ions onto date pits activated carbon was reported by Banat et al., 2003c [90]. They found that raw date pits possessed a metal ion sorption capacity that was two to three times greater than that of carbonized date pits. The uptake of cadmium ions by natural date pits was dependent on the experimental conditions, particularly the pH of the medium, the concentration of date pits employed, and the cadmium ion concentration. The amount of cadmium ions adsorbed increased with increasing pH as well as with an increase in the cadmium ion concentration. The Langmuir and Freundlich isotherm models were used successfully for the mathematical description of the sorption of cadmium ions onto natural and carbonized date pits. A pseudo-second-order reaction model correlated well with the kinetics of  $Cd^{2+}$  ion sorption by natural date pits.

Abdulkarim and Al-Rub, 2004 [91] reported the adsorption of  $Pb^{2+}$  onto activated carbon and 8-hydroxyquinoline-modified activated carbon prepared from date pits. The results showed that both carbons exhibited a high adsorption capacity. However, the chemical modification did not improve the adsorption of lead ions significantly. Increasing the initial pH, an increase in the removal of lead ions onto activated carbon was observed. Kinetic studies showed that the process followed pseudo-second-order kinetics. The equilibrium data for the adsorption of lead ions were found to fit both the Langmuir and Freundlich isotherms.

The adsorptions of copper from aqueous solutions by date pits and palm trees waste were investigated by Bella et al., 2011 [75]. Results show that the highest percentage of copper adsorption was obtained for the smallest size of the sorbent particles. High efficiency ranging from 60% to 80% may be obtained with particle size below 1 mm. The adsorption process was rapid, i.e., the maximum sorption capacity was reached within 20 min. The process involved pseudo-second-order kinetics with an activation energy value within the normal range considered for processes, where a physical interaction between the sorbate and the sorbent solid predominated. The thermodynamic parameters of the copper ions' uptake onto the solid sorbents indicated that the process was endothermic and proceeded

spontaneously from the date stones. However, the thermodynamic studies of the adsorption of copper on palm tree waste indicated that the process was exothermic and proceeded spontaneously.

A new activated carbon with sulphuric acid activation developed from date palm seed for the removal of toxic chromium (VI) from different kinds of the aqueous solution was reported by El Nemr et al., 2008 [62]. A strong dependence of the percentage adsorption on pH was reported, the percentage removal of chromium (VI) increased as the pH value decreased and the optimum pH value was 1.0. The adsorption process was fast and the equilibrium was reached within 180 min. The maximum adsorption capacity of chromium (VI) was reported 120.48 mg/g onto date palm seed-based activated carbon. The Elovich equation and pseudo-second-order equation provide good accuracy for the kinetic data. For adsorption isotherm, Koble–Corrigan and Langmuir models were the closest fit to the isotherm data. With the help of the Dubinin–Raduskovich isotherm model the mean free energy of adsorption has been calculated between 0.115 and 0.229 kJ/mol, which infers that the adsorption was dominated by the physisorption mechanism (the typical values of mean free energy of adsorption for ion exchange mechanism is lies between 8 and 16 kJ/mol).

## 8. Conclusion

Since heavy metals are noxious and non-degradable in nature, even trace amounts of heavy metals in wastewater frequently cause a variety of health and environmental issues. Date pits, as an agricultural waste, low cost, and ease of use materials for metal ion uptake from water, have received a lot of attention in recent years as a green adsorbent. This review focuses on recent advancements in the use of date pits as bio-waste derived adsorbents to remove toxic metal ions from water. Raw and burnt date pits have been used by many researchers as bio-adsorbents for heavy metal ions removal from wastewater. According to literature, a variety of physiochemical and heat treatment methods were used to modify biomass porosity and surface areas. As a result, the number of available sorption sites and metal ion binding functional groups on the developed bio-adsorbent surfaces increases. This review found that numerous processes such as physisorption, ion exchange, electrostatic interaction, precipitation, chelation, and complexation may be involved in the adsorption of heavy metal ions by functional groups of date pits. Date pits bio-sorbents have showed greater economic and environmental advantages than other conventional adsorbents in the removal of heavy metals from wastewater.

## Declaration of competing interest

The authors declare no conflicts of interest.

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