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Efficient Removal of Zinc and Copper from Wastewater Using Activated Carbon Derived from Date Pits in a Continuous Fixed-Bed Column

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ABSTRACT

Adsorbents based on agricultural biomass have been subjected to several investigations in recent years owing to their low cost and promising adsorption capabilities. This paper aimed to demonstrate the efficiency of date pits activated with phosphoric acid as common activating agent that increases the porosity and surface area of date pits. This results in a greater number of binding sites for the heavy metals to attach to improving the bio-adsorbent's effectiveness. To get rid of heavy metals such as zinc and copper ions from industrial wastewater using a fixed bed with a continuous flow configuration, the derived adsorbent was tested under a variety of operating conditions, including a flow rate of 4-12mL/min, an initial metal ion concentration of 30-60mg/L, and temperatures ranging from 20 to 50℃, which were chosen based on industrial conditions and available data**.** The results revealed that the removal efficiency of heavy metals increased with an increase in the initial metal ion concentration, but conversely, it decreased with an increase in flow rate and temperature. Also, the results indicated that with the optimum conditions of 15cm static bed height, 60mg/L initial metal concentration, 8mL/min flow rate, and 25℃ temperature, determining the ideal conditions results in the efficient removal of pollutants in less time and the treatment of larger quantities. Mathematical modeling of the fixed bed column was achieved using the kinetic models of Adams Thomas, Yoon-Nelson, Bohar, and Modified Dose-Response, in this regard, the Thomas model is the closest to the experimental values, it is supposed that the adsorption mechanism was a Langmuir type adsorption followed by a pseudo-second-order chemical sorption. The Yoon-Nelson approach was employed on experimental data to predict breakthrough curves through nonlinear regression. This made it easier to determine the crucial characteristic column parameters for process design. According to thermodynamic studies, heavy metals spontaneously and exothermally adsorb activated carbon in date pits. Firstly, spontaneous adsorption indicates efficient processes that occur favorably without external energy input, offering cost-effective solutions for various applications. Secondly, the exothermic nature of adsorption suggests that lower temperatures may be sufficient, reducing energy consumption and preserving the stability of sensitive materials. Additionally, the process's exothermicity facilitates desorption at higher temperatures, enhancing the efficiency of regeneration processes. This study has shown that BDP can successfully remove heavy metals from aqueous solutions. Understanding these characteristics is crucial for optimizing applications, reducing costs, and improving overall efficiency in industrial and environmental contexts.

1. INTRODUCTION

Water contaminated with heavy metals is a major environmental threat that can significantly impact human health and the environment [1-3]. Heavy metals are natural elements with high toxicity to humans and other living organisms, even at low concentrations, and remain for a longer time owing to their non-biodegradable character [4-6]. the exact contribution of each source can vary depending on location, scale of operations, and other factors, here's a general overview based on available data and research. industrial waste is a major contributor to heavy metal contamination, stemming from activities such as mining, metallurgy, manufacturing, and chemical production. These industries discharge wastewater containing high concentrations of heavy metals, which can significantly impact water quality if not properly treated. Agricultural runoff also plays a significant role due to the widespread use of fertilizers, pesticides, and animal manure, which can introduce heavy metals into water bodies. Mining operations are a substantial source of heavy metal pollution, particularly in regions with active mining activities. While urban runoff contributes to contamination through the cumulative effect of numerous urban centers, its individual impact may be smaller compared to other sources.

Landfills contribute to heavy metal contamination primarily through improper disposal of products containing heavy metals, though their individual contribution may not be as significant. Finally, while natural sources of heavy metals exist, their contribution to overall contamination is generally lower compared to anthropogenic sources, but can vary depending on geological factors [5, 7, 8]. Heavy metals might accumulate in fish and other aquatic organisms when released into water streams. Humans could then be subjected to these heavy metals by consuming polluted food and water [9-11].

Chemical precipitations [12], ion exchanges [13], and membrane filtration [14] are effective methods for removing heavy metals from water, but they have limitations. Chemical precipitation can generate large volumes of sludge and may not be cost-effective for treating water with low metal concentrations. Ion exchange requires regular resin regeneration and may not be suitable for treating large volumes of water or fluctuating metal concentrations. Membrane filtration is capital-intensive, energy-intensive, and prone to fouling. These limitations justify exploring alternative approaches like adsorption, which offers simplicity, versatility, and cost-effectiveness, making it a promising solution for heavy metal removal, especially at low concentrations. Adsorption processes can utilize various adsorbent materials and benefit from ongoing advancements in technology for enhanced efficiency and sustainability. Therefore, considering the drawbacks of conventional methods, exploring alternatives like adsorption is crucial for developing effective and sustainable solutions for heavy metal removal from water. To successfully remove all heavy metals from water at concentrations less than 100mg. L-1, these methods might be costly and energy-intensive [15-17].

Adsorption is a promising alternative treatment method for heavy metal ion removal from wastewater [18, 19]. This separation process relies on surface phenomena where a pollutant material (the adsorbate) is adhered to and kept on the surface of another material (the adsorbent) by attracting forces, active functional groups, and occupying the pores over the adsorbent surface [20-22]. When removing heavy metals, the adsorbent is usually a solid substance with a strong affinity for the heavy metals [18, 23].

Natural adsorbents are natural materials that could be employed for removing heavy metals from water [24-26]. A thorough analysis of the effectiveness of several natural materials derived from plants in eliminating heavy metals from tainted water sources has been performed. These include orange peel [27, 28], wheat-based materials [29, 30], brown algae [31], eucalyptus bark [32, 33], sugar beet pulp [34], olive stone [35, 36], and papaya seed [37, 38]. The bio-adsorbent potential of these materials in addressing heavy metal-induced water contamination has been the subject of extensive investigation.

Date pits offer natural biomass, date pit is a cheap and plentiful waste product from date palm resources. Lead [39], zinc [19], copper [40], cadmium [41], and mercury [42] are just a few of the heavy metal ions that it effectively removed from water using date pit-based adsorbents.

There is growing research on the potential of date pits as a natural bio-adsorbent that efficiently eliminates heavy metals from water. More research is required to determine the long-term environmental impact of using date Pits derived activated carbons for heavy metal removal and to maximize their use.

Date pits offer several distinct advantages as an adsorbent material for heavy metal removal. Firstly, date pits are readily available as a byproduct of date fruit processing industries, making them a sustainable and environmentally friendly option. This abundance contributes to their low cost compared to some commercial adsorbents, making date pits an economically viable choice for large-scale water treatment applications. Additionally, date pits possess a high adsorption capacity due to their porous structure and abundant functional groups, such as hydroxyl and carboxyl groups, which facilitate the binding of heavy metal ions. Studies have demonstrated that date pit-based adsorbents exhibit comparable or even superior adsorption capacities for heavy metals compared to conventional adsorbents like activated carbon. Moreover, date pits can be easily modified or activated to enhance their adsorption properties further, offering versatility in their application for water treatment. Therefore, the utilization of date pit-based adsorbents presents a promising and sustainable approach for effective heavy metal removal from water, leveraging their availability, cost-effectiveness, and high adsorption capacity. This study uses date Pits derived activated carbons, to remove Zn (II) and Cu (II) from industrial effluents in a continuous fixed-bed column. The other aims of this study were to investigate thermodynamics to provide a complete thermodynamic description of the system and kinetics for optimal adsorption data analysis under various adsorption conditions such as temperature, initial heavy metal concentration, and feed flow rate.

2. MATERIALS AND METHODS

2.1 Raw bio-adsorbent

Al-Zahdi dates were evaluated in the current study. It is the most popular date in Iraq, the choice of Al-Zahdi dates as the bio-adsorbent source was informed by considerations of availability, cost-effectiveness, and indications of their potential efficacy based on existing knowledge. These dates are widely cultivated in Iraq and other regions, ensuring accessibility for research purposes. Moreover, Al-Zahdi dates are known for their robust physical characteristics and high fiber content, which could enhance their suitability as a bio-adsorbent material. where this study was conducted. The chemicals employed for the activation of the adsorbents and for the adsorption experiments included phosphoric acid (H_3PO_4) (85% purity), sodium hydroxide (NaOH) (98% purity), copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) (99% purity), zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) (99% purity), and deionized distilled water. Hydrochloric acid (HCL) (32% purity) was used to neutralize the pH after the chemical activation using phosphoric acid. All the chemicals were reagent-grade and were purchased from Sigma Aldrich.

2.2 Preparation of burnt date pits (BDP)

The date pits were rinsed using tap water to remove dirt and undesired byproducts. Subsequently, they were left to undergo natural drying under sunlight and then dried in a Sanyo oven at 100°C for 2 hours. The date pits were ground for about 30 minutes in an electric mill (Generic Co., JIQI, China), homogenized, and sieved at 2mm. The sieved pits were rinsed with water and dried in an oven before the activation procedures and adsorption evaluations were carried out.

The sieved date pit was soaked with (85 wt.%) H_3PO_4 and shaken for four hours to ensure a complete soaking process.

The mixture was filtered and dehydrated at 200℃ for 2 hours [43], the study followed strict environmental and safety protocols to mitigate risks associated with the use of phosphoric acid and high temperatures. This included wearing personal protective equipment, implementing proper ventilation, specialized storage and handling of chemicals, waste management procedures, temperature control measures, and emergency response protocols.

The carbonization temperature of 500℃ and duration of 90 minutes for date pit-derived adsorbents were chosen based on established practices in biomass carbonization and likely optimization experiments. While specific literature supporting these exact conditions for date pits may be limited, previous research on similar biomass-derived adsorbents and empirical evidence suggest that these parameters are conducive to achieving desirable pore structure and surface chemistry for effective adsorption. The oven was permitted to attain ambient temperature gradually after the carbonization process. Afterward, the carbonized samples were washed with distilled water until they reached a neutral pH and removed from any acidic residuals. The washed samples were subsequently dried at 105℃ for 2 hours in a hot air oven. The resultant burnt date pit (BDP) was weighed and kept in an airtight container for storage for the subsequent experiments [44].

2.3 Experimental set-up

The experimental set-up consists of a lab-scale adsorption column made of Perspex material with a length of 30cm and a 2.5cm inner diameter as show in Figure 1. In order to achieve the required adsorbent bed height, a predetermined amount of the prepared activated carbon was put in the column. A fiberglass wool supporting layer of 3mm was fixed at the bottom and top of the bed to secure it in place of constant height. This support was retained using settled stainless-steel mesh inside the column. A peristaltic pump was used to pass wastewater continuously, and a control valve and flowmeter were employed to ensure a steady-state flow operation. 5mL samples of the column effluent have been collected in a beaker every 20 minutes to determine the concentration of the residual pollutant, to ensure accurate plotting of breakthrough curves. This frequency was chosen to capture the dynamic adsorption process adequately, allowing for the detection of initial breakthrough and subsequent changes over time. By sampling at regular intervals, fluctuations in breakthrough behavior could be identified and characterized effectively, enhancing the reliability of the experimental results. Additionally, the selected sample volume ensured representative data at each sampling point, minimizing variability and improving the accuracy of the plotted breakthrough curves. Atomic absorption spectroscopy was used to measure the concentration of metal ions in the effluents, Calibration procedures and standards were likely used for the atomic absorption spectroscopy (AAS) measurements in the study to ensure accuracy and reliability. This involved establishing a calibration curve using known standards of the target heavy metals at various concentrations. The breakthrough curves were used to test how well the adsorption column worked and how well heavy metals were removed, in addition to the provided information, the experiment continued until the adsorbent reached a point of saturation with metal ions, indicating its exhaustion. This saturation point was identified when the concentration of metal ions in the final effluent column, denoted as Ct (mg/L), approached approximately 90% of the initial influent column effluent, represented as Co (mg/L). This criterion served as a reliable indicator that the adsorbent had reached its maximum adsorption capacity and that further adsorption of metal ions was negligible. Thus, the endpoint of the adsorption process was determined based on this saturation point, ensuring thorough characterization of the adsorption behavior and facilitating accurate assessment of the adsorbent's performance. The conditions were 15cm bed height, 4, 7, and 10 pH, 20, 35, and 50℃, 4, 8, and 12mL/min flowrate, 60mg/L Cu_2+and Zn_2+initial solution, and particles that were 2mm in size**,** carefully selected based on their relevance to real industrial effluents and their impact on the adsorption process. These parameters were chosen to strike a balance between practical feasibility and experimental rigor, aiming to mimic real-world conditions encountered in industrial wastewater treatment processes. By aligning the experimental setup with conditions commonly found in industrial effluents, the study aimed to provide meaningful insights into the effectiveness of the adsorbent material for practical applications in heavy metal removal.

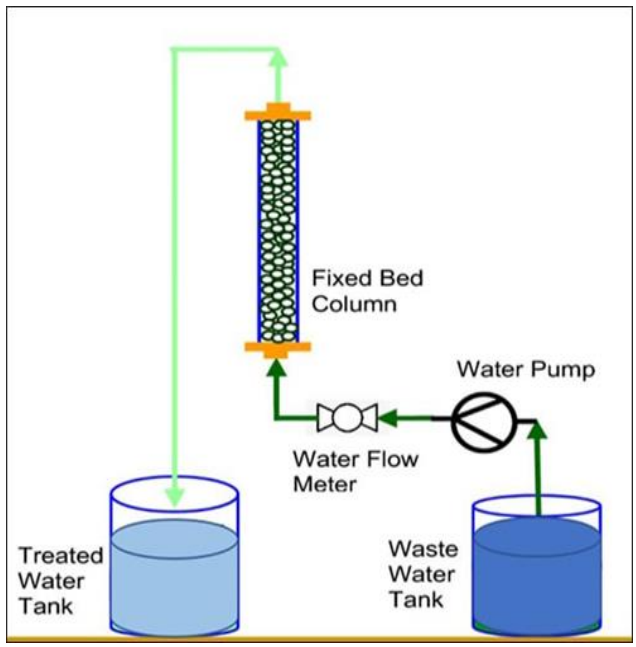


Figure 1. Schematic representation of the experimental setup

The experimental setup is complemented by a brief overview of specific data analysis methods utilized for interpreting breakthrough curves and calculating adsorption capacities. Breakthrough curves are analyzed using mathematical modeling techniques like the Thomas model or Yoon-Nelson model, which characterize dynamic adsorption behavior and estimate parameters such as breakthrough time and adsorption capacity. Equilibrium adsorption data obtained from adsorption isotherms further inform adsorption capacity calculations. These methods aim to provide comprehensive insights into adsorption behavior and evaluate the efficacy of the adsorbent material for heavy metal removal.

To ensure experiment reproducibility, duplicates or triplicates were conducted for each tested condition. This redundancy helped assess experimental variability and identify inconsistencies. Additionally, quality control measures, such as instrument calibration and standardized procedures, were implemented. Statistical analysis techniques, like calculating mean values, were applied to assess data

consistency. Overall, these steps aimed to enhance the reliability and transparency of the research findings.

3. RESULTS AND DISCUSSION

Temperature exerts a significant influence on adsorption kinetics and thermodynamics by altering the kinetic energy of molecules, thereby affecting their mobility and the likelihood of successful adsorption onto the adsorbent surface. Typically, higher temperatures lead to increased molecular mobility, which might intuitively suggest higher rates of adsorption. However, contrary to this expectation, in some cases, higher temperatures can result in a decrease in the rate of adsorption. Additionally, when adsorption is exothermic and the equilibrium adsorption capacity decreases with increasing temperature, it often signifies that the adsorption process is governed by strong intermolecular forces between the adsorbate and adsorbent. These strong intermolecular forces can hinder adsorption at higher temperatures, leading to a decrease in the overall adsorption capacity despite increased molecular mobility. Therefore, understanding the temperature dependence of adsorption behavior is crucial for elucidating the underlying mechanisms and optimizing adsorption processes for various applications.

3.1 Bio-adsorbent characterizations

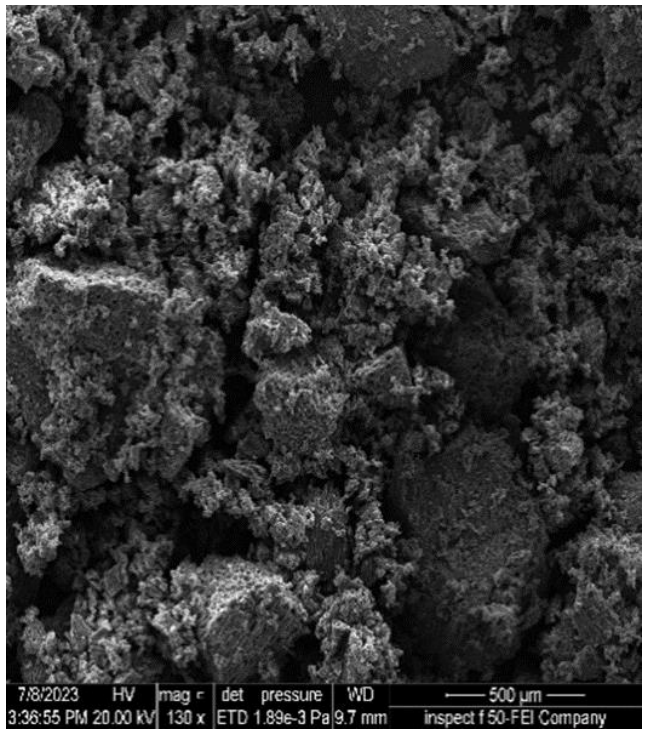
3.1.1 Scanning electron micrographs (SEM)

SEM analysis was employed to examine the morphological properties of prepared adsorbent surfaces, as shown in Figure 2. The SEM image for BDP shows that thermal activation has significantly influenced the structure of carbon by creating the surface of a spongy pore. Thermal treatment at a temperature of 500℃ results in significant morphological changes and creates more inhomogeneous and irregular pore structure due to volatilizing the organic materials that create more porosity. In addition, the acidic treatment removes impurities (i.e., ash) from the surface, increasing its porosity. As a surface phenomenon, improving activated carbon surface characteristics means improving adsorption efficiency. These organizations facilitate metal ion diffusion to adsorbent active sites.

3.1.2 Fourier transform infrared spectroscopy (FTIR)

The functional groups responsible for their binding must be identified using FTIR analysis for BDP to understand how solutes attach to the adsorbent surface. The findings of the analysis are depicted in Figure 3.

Cellulosic and hemicellulose materials are rich with functionalities such as hydroxyl, ether, and carbonyl responsible for binding with metal ions on the surface of the adsorbent [45].



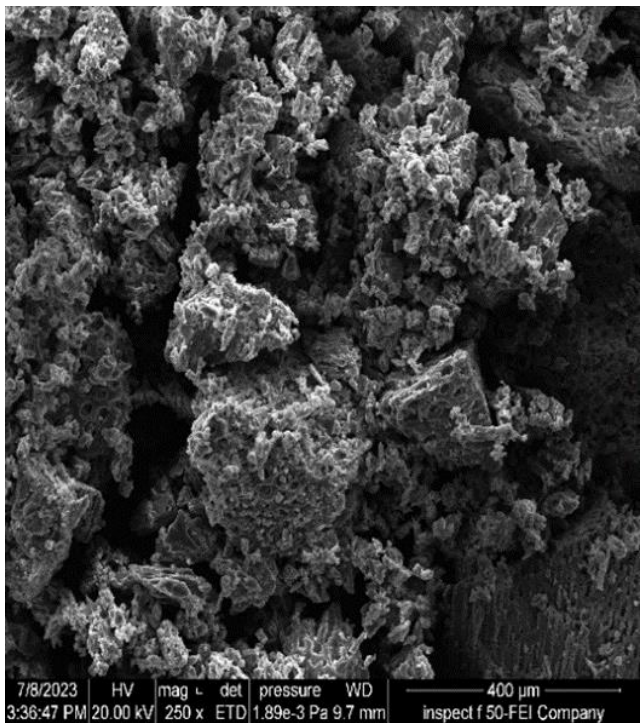


Figure 2. SEM for date pits activated with H_3PO_4 and burnt at 500℃ (BDP)

As shown in the FTIR spectrum, a broad peak at 3425.58 cm^{-1} is attributed to hydroxyl stretching vibration, characteristic of lingo cellulosic peaks, and appeared when water was used in the preparation process. The weak band aliphatic stretching vibration C-H is located between 2800 and 3000 cm^{-1}, while the vibrations at 1743.65 cm^{-1} represent the existence of unconjugated carbonyl (C=O), imine (C=C) at 1620.2 cm^{-1}, and C-O at 1242.16 and 1064.71 cm^{-1}. Some of the presenting functional groups (like hydroxyl stretching) tend to decrease during the burning process and develop after the adsorption of metals or in an aqueous environment.

The lignocellulosic organic material revealed a wide peak within the spectral range of 3230-3560 cm^{-1}, confirming the existence of hydroxyl (-OH), amino (-NH), or both functional groups [46]. Aliphatic C-H stretching vibrations can be seen by the two peaks at 2921 and 2843 cm^{-1}. Based on these results, it may be hypothesized that the NH C=O or -OH and C-O functions are largely responsible for electrostatic interactions and lone-pair transfer in binding Cu (II) and Zn (II) over the surface. However, electrostatic interactions and coordination-binding may be potential mechanisms for metal adsorption [45].

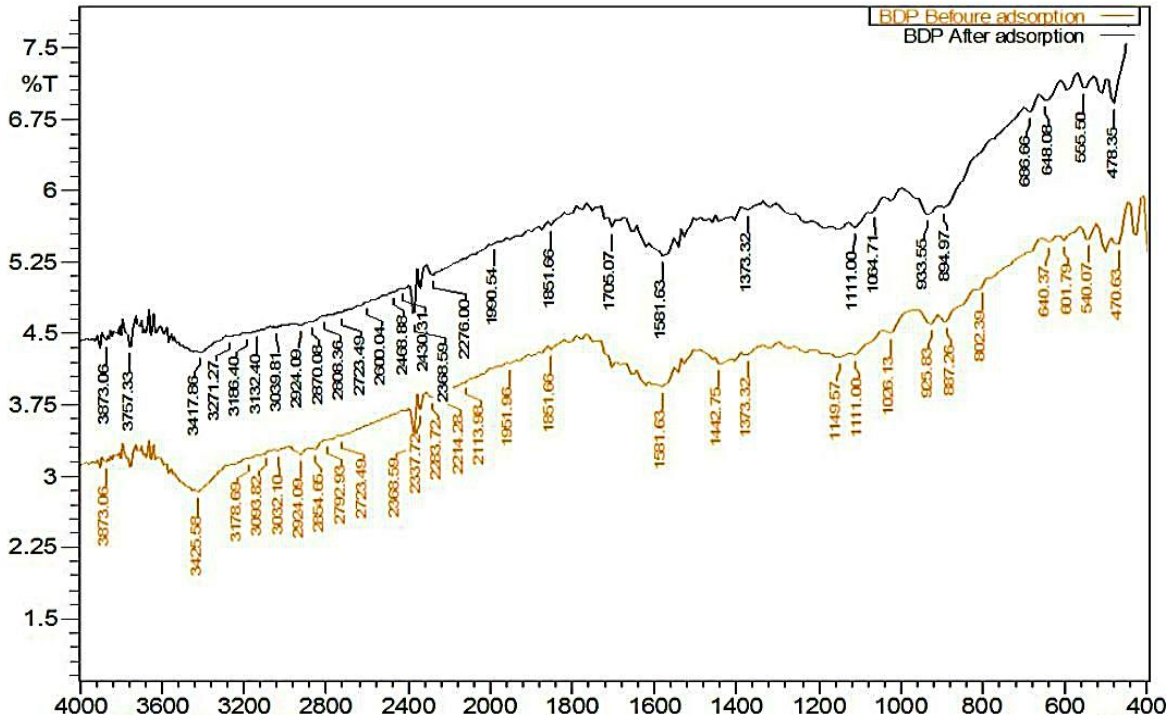


Figure 3. BDP FTIR spectra before and after Cu^{2+}, Zn^{2+} adsorption

3.2 Column kinetics study

Kinetic models like Thomas, Yoon-Nelson, Adams-Bohar, and Modified Dose-Response were applied to experimental data to analyze the adsorption efficiency at the different conditions and the column performance by breakthrough curves. The results are presented in Table 1.

Assessing the reproducibility of the adsorption process and evaluating its potential for scaling up to industrial applications are critical considerations. Reproducibility entails ensuring consistent performance under varying conditions, while scaling up involves transitioning from lab-scale experiments to large-scale operations. Factors such as uniformity in adsorbent preparation and optimization of operating parameters influence reproducibility. Scaling up requires addressing challenges like flow distribution, pressure drop, and mass transfer limitations. Pilot-scale testing and collaboration between researchers and industry stakeholders are essential for successful implementation.

3.2.1 Thomas model

The Thomas model is commonly used to describe dynamic systems. It is based on the Langmuir isotherm and second-order kinetic models [45]. The proposed model for dynamic column adsorption research has the ability to accurately estimate both the rate constants and the maximum adsorption capacity. The expression suggested by Thomas for the articulation of an adsorption column is as follows:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{K_{Th} q_{Th} M}{Q} - K_{Th} q C_0 t\right)} \quad (1)$$

The determination of the adsorption capacity of column qTh and the kinetic coefficient KTh could be attained by analyzing a plot of the natural logarithm of [(C0/Ct)-1] as a function of time (t) under a specific flow rate condition, as illustrated in Figure 4. The results are presented in Table 1.

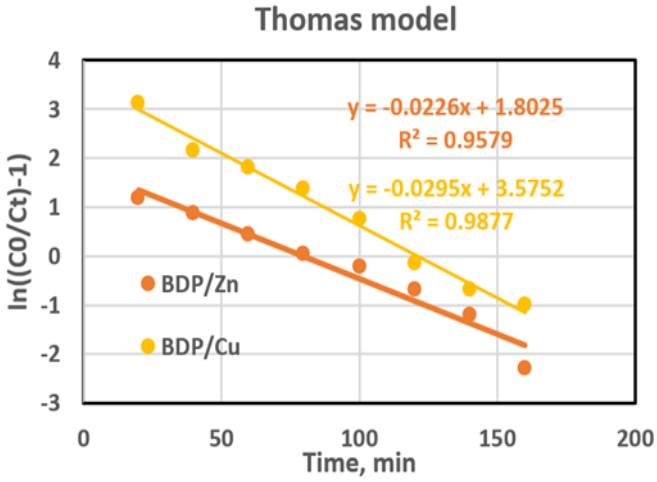


Figure 4. Breakthrough curves according to the linear form of the Thomas model

Table 1. Values of different parameters

Model/Parameters		Values	
Thomas Model	kTh (ml/mg min)	qTh (mg/g)	R^2
BDP/Zn	0.000376667	2.55221239	0.9579
BDP/Cu	0.000491667	3.87818305	0.9877
Adam- Bohart	kab (l/mg min)	N0 (mg/L)	R^2
BDP/Zn	0.000156667	1079.198723	0.9032
BDP/Cu	0.000335	1050.401194	0.9589
Yoon-Nelsoon	Kyn (L/min)	t50% (min)	R^2
BDP/Zn	0.0226	83.62389381	0.93
BDP/Cu	0.0295	121.1932203	0.98
MDR	A	qmdr (mg/g)	R^2
BDP/Zn	1.4511	2.0515419	0.8128
BDP/Cu	1.988	3.81995842	0.9219

In the majority of situations, the analysis generated high correlation coefficient values (R^2>0.95), suggesting a strong fit between the experimental outcomes and the Thomas model. The maximum capacity of adsorption of 2.55mg/g for zinc ions and 3.878mg/g for copper ions was predicted by the model at 60mg/L initial ion concentration, 8L/min feed flow rate, 7 influent pH, and temperature of 20°C.

3.2.2 Adams-Bohart model

The Adams-Bohart model presumes a direct correlation between the residual capacity, the adsorption capacity, and the initial pollutant concentrations. The Adams-Bohart approach is frequently employed to characterize the initial portion of the breakthrough curve, denoted as Ct/C0, as follows:

$$\frac{C_t}{C_0} = \exp\left(k_{AB}C_0 t - k_{AB}N_0\frac{Z}{F}\right) \quad (2)$$

In which:

kAB=kinetic constant, L/(mg.min)

N0=saturation concentration, mg/L

v=fluid velocity stated as the volumetric flow rate/bed cross-sectional area (in centimeters per minute), and Z denotes for column bed depth (in centimeters).

The time range, denoted as "t", is considered from the initial breakthrough to the end. The values of kAB and N0 were estimated in the linear format by analyzing the slope and intercept of the linear graphs depicting "ln (C0/Ct)" as a function of time, as illustrated in Figure 5. The findings are summarized in Table 1.

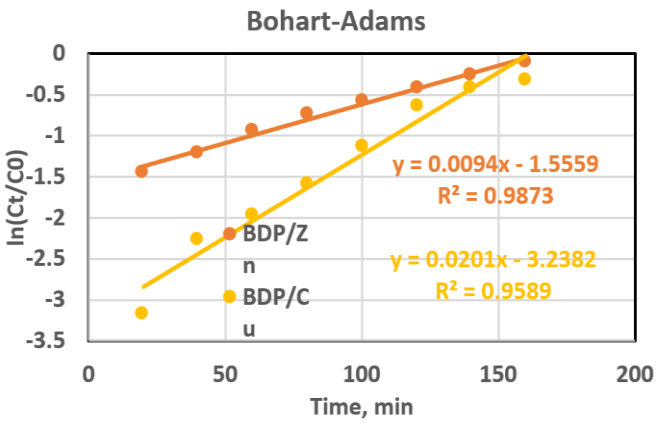


Figure 5. Breakthrough curves according to the linear form of the Bohart-Adams model

The results showed that zinc ions' saturation concentration (No) value was slightly higher than copper ions. The experimental findings strongly fit the Adams-Bohart model, as demonstrated by an R^2 value exceeding 0.90.

3.2.3 Yoon-Nelson model

Yoon and Nelson implemented a kinetic model to describe fixed bed adsorption. The model postulates a direct proportionality between the decrease in the probability of adsorption for every adsorbate molecule and the probabilities of adsorbate adsorption and breakthrough on the adsorbent. The model is depicted in the following manner:

$$\frac{C_t}{C_0} = \frac{1}{1+\exp[K_{YN}(\tau - t)]}$$

In which:

kYN=rate constant (1/minutes);

t=breakthrough time (minutes), and

τ=time required for 50% adsorbate breakthrough (minutes).

Figure 6 shows the graph of "ln (C0/Ct-1)" against time in the linear model. Table 1 provides more specific results. The time for a 50% breakthrough of adsorbate was approximately half of the total time, based on the Yoon-Nelson model. This parameter represents the time that adsorbents can adsorb half of their maximum amount of material. The Yoon-Nelson model appears to be a good fit for forecasting breakthrough behavior in this study, as evidenced by the strong correlation coefficients (R^2>0.93).

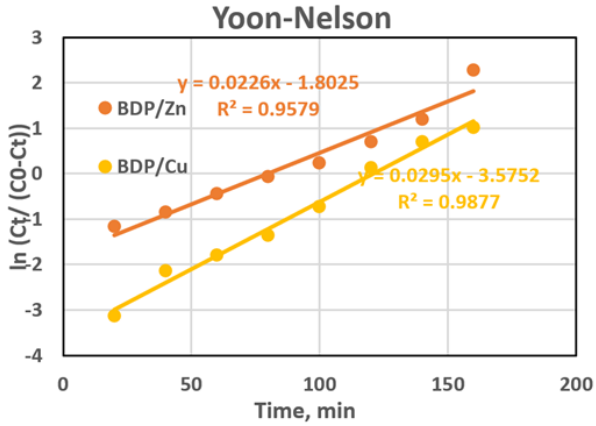


Figure 6. Measured breakthrough curves according to the linear form of the Yoon-Nelson model

3.2.4 Modified dose-response model

Another simplified numerical model employed for describing fixed-bed column adsorption data is the modified dose-response (MDR) model. This model primarily reduces the error associated with using the Thomas model, especially during the lower or higher periods of the breakthrough curve.

$$\ln\frac{C_t}{(C0 - Ct)} = a\ln(C0Qt) - a\,\ln qW$$

In its linear representation, the *a* and *qe* values were derived from the slope and intercept of linear plots of Ln(C0/Ct-1) against time, as depicted in Figure 7. The findings are outlined in Table 1, where q denotes the adsorptive capacity of the adsorbent (mg/g), w represents the adsorbent weight (g), and a is the constant specific to the modified dose-response model.

The values of both variable a and variable q can be ascertained by analyzing the slope and intercept of the linear equation derived from plotting ln[Ct/(C0-Ct)] against ln(C0Qt).

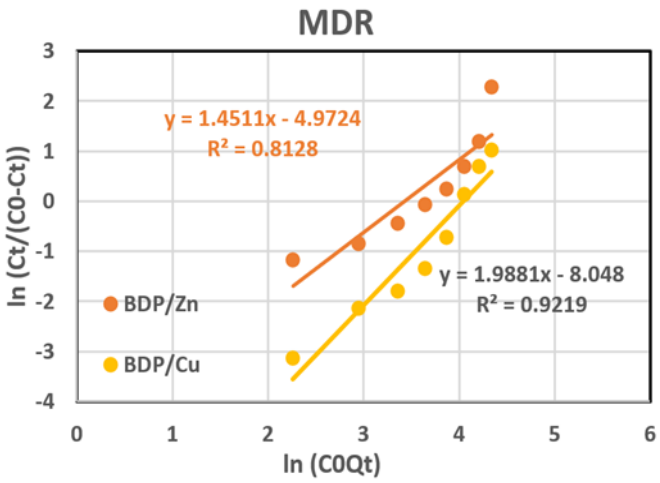


Figure 7. Breakthrough curves according to the linear form of the modified dose-response model

The model predicted a maximum adsorption capacity of 2.05mg/g for zinc ions and 3.82mg/g for copper ions at 60 mg/L initial ion concentration, 8L/min feed flow rate, 7 influent pH, and a temperature of 20°C. The analysis yielded MDR correlation coefficient values (R^2>0.8), indicating that the MDR model exhibited inferior experimental data fitting compared to the Thomas model.

3.3 Column thermodynamic study

The researchers looked into how well BDP could get rid of Cu (II) and Zn (II) at temperatures of 20, 35, and 50°C. The graphical estimation of ΔH° and ΔS° involved plotting ln [(qe/Ce)*(m/Q)] against (1/T) [48]. The experimental outcomes demonstrated temperature-dependent adsorption, as detailed in Table 2. The adsorption rate exhibited variability within the temperature range of 293K to 323K, indicating a reduction in ion adsorption on BDP at higher temperatures. Thermodynamic parameters, including free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), were computed to assess the thermodynamic feasibility and nature of the sorption process. The Gibbs free energy serves as an indicator of the spontaneity of the sorption process, with a more negative value suggesting a more energetically favorable sorption. ΔS° and ΔH° were determined from the slope and intercept of the Van't Hoff plots presented in Figures 8 and 9.

The negative values of ΔG° for the adsorption of copper metals on the BDP surface revealed the metal biosorption spontaneous nature and are energetically favorable. The ΔH° negative value revealed an exothermic sorption process. This implies that heat was released during the adsorption, signifying an exothermic reaction. In addition, the estimated ΔS° values for copper demonstrated a positive trend, suggesting an augmentation in randomness at the interface between the solid and solution phases during the sorption process. Additionally, it signifies the sorbent's propensity for binding with copper ions.

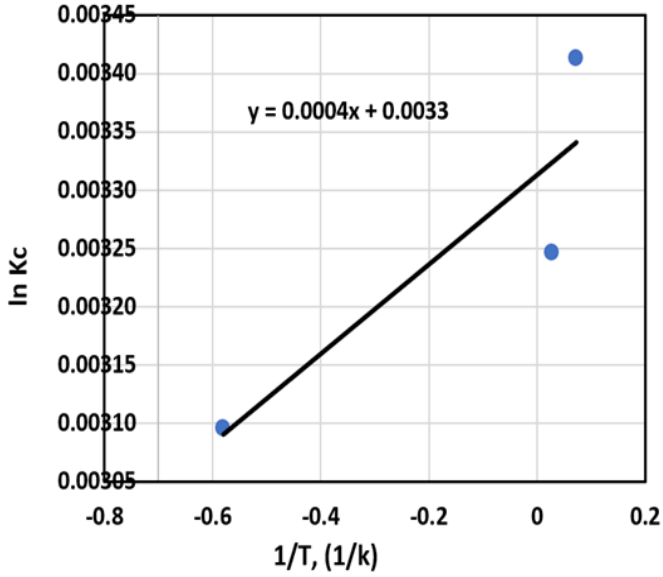


Figure 8. Van't Hoff plots for Zn (II)-BDP AC adsorption (initial pH 7; initial metal conc.: 60mg/L; bed height 15cm)

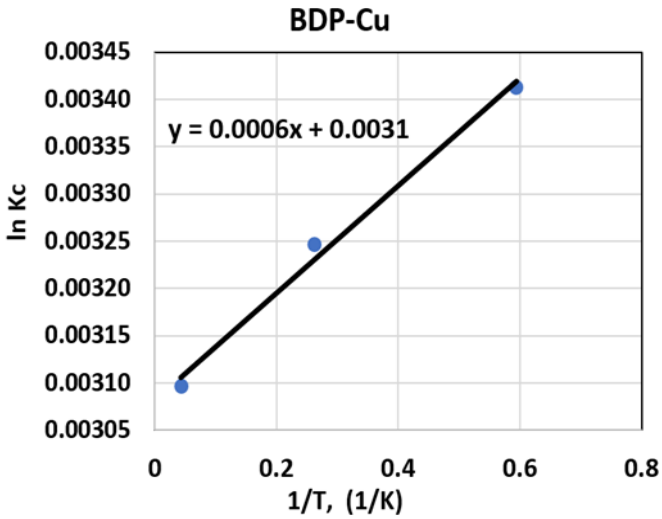


Figure 9. Van't Hoff plots for Cu (II)- BDP AC adsorption (initial pH 7; initial metal conc.: 60mg/L; bed height 15cm)

On the other hand, for the Zn-BDP ion, the Gibbs free energy change (ΔG) has the same behavior except at higher temperatures, which recorded a positive value, suggesting a non-spontaneous nature of the adsorption. Several more studies published last year show similar results for heavy metal sorption [49]. The negative value of the ΔH revealed that adsorption is an exothermic process. The increase in temperature leads to a more positive change in Gibbs free energy (ΔG), which the exothermic nature of the reaction could explain. This variation in ΔG indicates a decrease in the adsorption process feasibility [50].

Additionally, the observed low value of ΔS° suggests no significant alteration in entropy during the process of sorption of copper and zinc ions on BDP. The DS values of both adsorbents were determined to be positive, implying a random adsorption process resulting from the redistribution of energy between ions and the surface adsorbent.

Table 2. Thermodynamic parameters for the adsorption of Zn (II) and Cu (II) on BDP adsorbents

Heavy Metal	Qe (mg/g)			ΔG° (J/mol)			ΔH° (J/mol)	ΔS° (J/mol K)
	293K	308K	323K	293K	308K	323K		
Cu2+	5.5664	4.8848	4.4136	-1446.739	-673.433	-116.3865	-0.00498	0.02577
Zn2+	3.9776	3.4064	1.7224	-174.6549	-70.7289	1558.703	-0.003325	0.02743

3.4 Fixed bed column study

3.4.1 Feed flow rate impact on the bed column performance

The inlet flow rate is important in the dynamic adsorption column because it determines the interaction time between the adsorbent and the ions inside the bulk media before they are fully absorbed. The impact of wastewater flow rate on bed column performance at various rates (4, 8, 12mL/min) was examined at an initial pH of 7, an initial metal concentration of 45mg/L, a bed height of 15cm, and a temperature of 20°C. The results are presented in the breakthrough curves in Figures 10 and 11 for BDP-Zn and BRD-Cu, respectively. Generally, the breakthrough and saturation times decreased noticeably with increasing inlet flow rates, as shown in Figures 10 and 11.

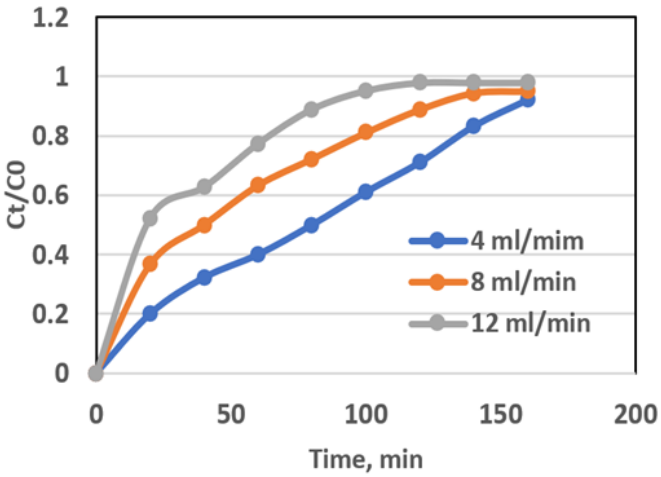


Figure 10. Breakthrough curve for Zn (II)-BDP adsorption (initial pH 7; initial metal conc.: 45mg/L; bed height 15cm, and temperature 20°C)

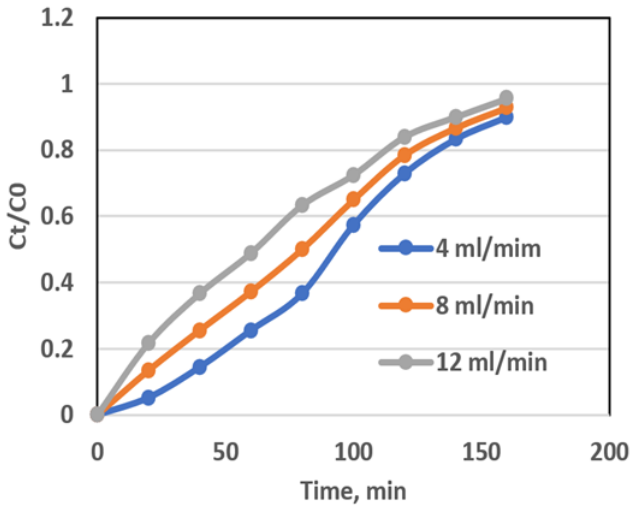


Figure 11. Breakthrough curve for Cu (II)-BDP adsorption (initial pH 7; initial metal conc.: 45mg/L; bed height 15cm, and temperature 20°C)

The break time was less than 15 minutes for the whole range. In addition, the amount of outlet metal ions was lower at a low flow rate. The recorded removal efficiency for Zn (II) ions decreased from 49.51% to 34.26% upon increasing the flow rate from 4 to 12L/min.

The flow rate in an adsorption system influences the adsorption mechanism beyond contact time by affecting boundary layer thickness and intraparticle diffusion. Higher flow rates decrease boundary layer thickness, enhancing convective transport and promoting faster mass transfer between the bulk solution and adsorbent surface. However, excessively high flow rates may reduce adsorption capacity by allowing adsorbate molecules to pass through the porous structure too quickly. Conversely, lower flow rates lead to thicker boundary layers, limiting mass transfer and prolonging the time required for adsorption equilibrium. They also allow for more thorough intraparticle diffusion, ensuring better utilization of the adsorbent material. Balancing flow rate considerations with other factors is crucial for optimizing adsorption processes in water treatment applications.

For Cu (II) ions, the removal efficiency decreased from 57.444% to 46.857% upon increasing the flow rate from 4 to 12L/min. A faster breakthrough results from the greater degree of mixing achieved with a rise in the flow rate. Furthermore, the saturation point for Zn (II) ions was decreased from 160 to 100 minutes, and for Cu (II) ions, it decreased from 160 to 140 minutes when the flow rate was increased from 4 to 12mL/min. This behavior is attributed to the fact that when the flow rate increased, more ions from the solution came into contact with the adsorbent, which takes less time to penetrate the pores of the adsorbent material and lowers mass transfer and inter-particle diffusion. Also, this result suggested that the column was not exhausted at a lower flow rate and had a longer saturation time. These findings agree with the study of Amin [51]. This indicates that the fixed time between the adsorbent and contaminated solution is significant for the adsorption process at lower than higher flow rates. The decrease in removal efficiency with increasing flow rate is not solely due to decreased contact time but also involves other flow-related phenomena. While reduced contact time is a major factor, channeling, flooding, and non-uniform flow distribution within the adsorption bed can also contribute to this effect. However, this is out of the scope of the current research.

3.4.2 Effect of temperature on the bed column performance

Temperature is a significant parameter affecting dynamic adsorption because it determines the reaction kinetics between the adsorbent and the ions inside the bulk media. The impact of changing contaminated wastewater temperature on bed column performance at various values (20, 35, and 50°C) was examined at an initial pH of 7, an initial metal concentration of 60mg/L, a biosorbent dose of 10g, and a flow rate of 8mL/min. The breakthrough curves in Figures 12 and 13 present the results for BDP-Zn and BRD-Cu, respectively. The experimental outcomes indicated a dependency of adsorption column performance on temperature, and the breakthrough

time and saturation time decreased noticeably with increasing solution temperature, as shown in Figures 12 and 13. The break time was less than 30 minutes for the whole range. In addition, increasing the
temperature shows a reduction in the adsorption capacity of BDP toward metal ions existing in the solution, Elevated temperatures may induce alterations in the surface chemistry and structure of the BDP adsorbent, such as thermal degradation of functional groups and changes in pore structure. These alterations could reduce the availability of active sites for adsorption and diminish the surface area accessible for adsorbate binding. Further characterization techniques like scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) could provide valuable insights into these mechanisms.

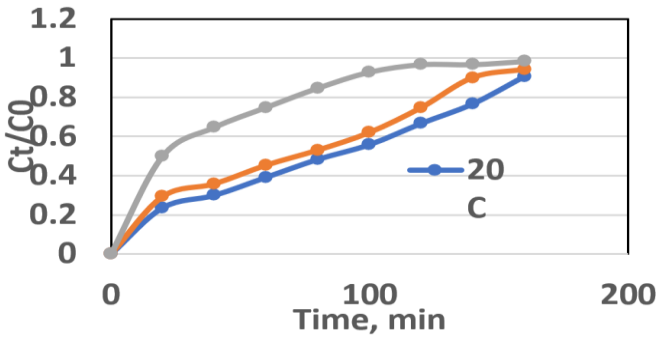


Figure 12. Breakthrough curve for Zn (II)-BDP adsorption (initial pH 7; initial metal conc.: 60mg/L; bed height 15cm, and flow rate 8ml/min)

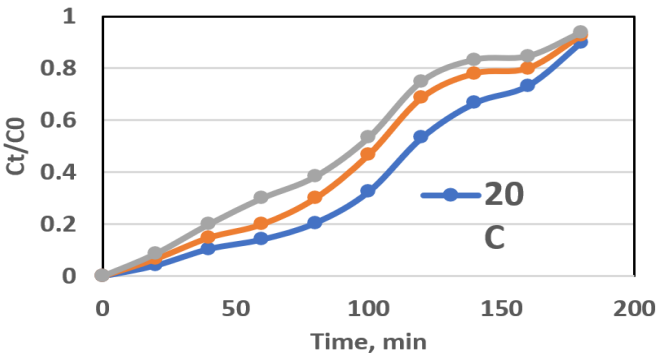


Figure 13. Breakthrough curve for Cu (II)-BDP adsorption (initial pH 7; initial metal conc.: 60mg/L; bed height 15cm, and flow rate 8mL/min)

The recorded removal efficiency for Zn (II)-BDP decreased from 51.79% to 35.8% upon increasing the solution temperature from 20 to 50°C. For Cu (II)-BDP, the removal efficiency decreased from 64.42% to 51.08% upon increasing the solution temperature from 20 to 50°C. As per the principles of adsorption theory, the adsorption mechanism weakens as the temperature rises, leading to the tendency of molecules previously adhered to a surface to detach at elevated temperatures. The decline in adsorption as temperature increases signifies a weak interaction between the biomass surface and the metal ion [51]. The increase in temperature resulted in a reduction in the removal of ions from wastewater, which means the process was exothermic. Further temperature increases caused the dissociation of active sites, directly affecting the number of sites available for adsorption and weakening the electrostatic force between metal ions and BDP [53]. These findings agree with the study of Krishnamoorthy

3.4.3 Effect of initial concentration on the bed column performance

The pollutant concentration affects the adsorption performance of adsorbent materials because it determines the limited concentration that can be handled. The impact of changing pollutant concentrations on bed column performance at various values (30, 45, and 60mg/L) was examined at an initial pH of 7, flow rate of 8ml/min, biosorbent dose of 10g, and 20°C. The breakthrough curve in Figures 14 and 15 presents the results for BDP-Zn and BRD-Cu, respectively. The experimental results indicated a dependency of adsorption column performance on initial concentration, and the saturation time increased with increasing solution concentration, as shown in Figures 14 and 15. As the concentration of metal ions in the solution increased, saturation was achieved more slowly.

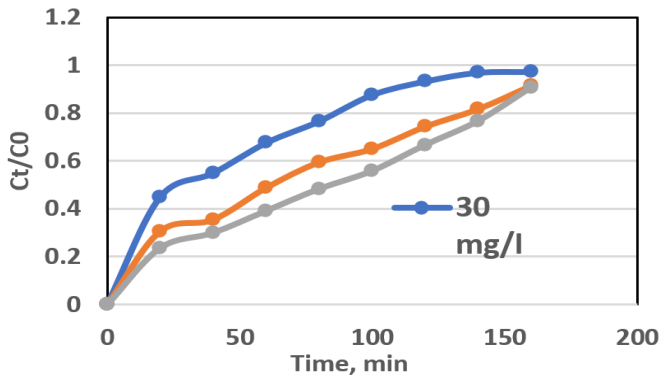


Figure 14. Breakthrough curve for Zn (II)-BDP adsorption (initial pH 7; flow rate 8mL/min; bed height 15cm, and temperature 20 C)

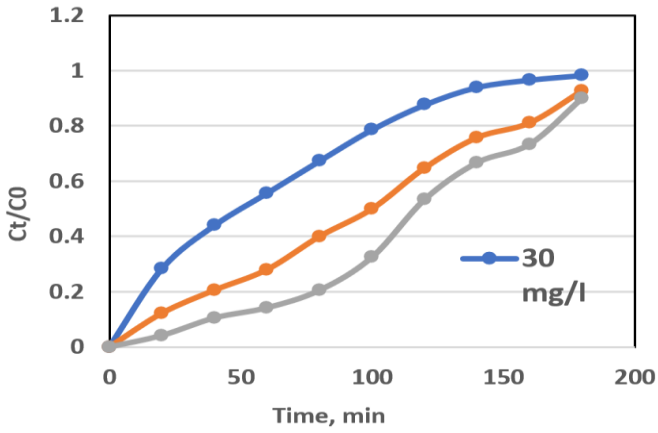


Figure 15. Breakthrough curve for Cu (II)-BDP adsorption (initial pH 7; flow rate 8mL/min; bed height 15cm, and temperature 20°C)

In addition, increasing the pollutant concentration shows an increase in the adsorption capacity of BDP toward metal ions existing in the solution. The recorded removal efficiency for Zn (II)-BDP increased from 36.889% to 51.792% upon increasing the solution concentration from 30 to 60mg/L. For Cu (II)-BDP, the removal efficiency increased from 41.619% to 64.426% upon increasing the solution concentration from 30 to 60mg/L. Generally, there may be more adsorption sites

on the adsorbent at low concentrations, leading to higher adsorption efficiency. However, at high concentrations, the adsorption capacity may become saturated. The metal ion adsorption mechanism significantly connected positively with the initial metal concentration until equilibrium was reached [52]. At elevated initial concentrations of the adsorbate, there's an increased risk of pore blockage within the adsorbent material, hindering access to active adsorption sites. Additionally, surface saturation occurs when all available adsorption sites on the adsorbent surface are occupied by adsorbate molecules, limiting further adsorption capacity. Understanding these phenomena is essential for optimizing adsorption systems and ensuring effective water treatment processes. As a result, the concentration gradient formed a higher driving force to pass the adsorbate mass transfer resistance between the bulk phase and adsorbent surface [52, 53].

4. CONCLUSION

This study assessed the efficiency of using charred date pits to eliminate metal ions, specifically Cu (II) and Zn (II), from industrial effluents in continuous dynamic columns. Various kinetic models were employed to examine the influence of the modeling method on the dynamic adsorption system. The results indicated that the performance of the column was significantly affected by adsorption conditions, including flow rate, initial metal concentration, and temperature. A higher initial metal ion concentration rate (between 30-60 ppm) was associated with a higher removal efficiency, while it decreased with higher flow rates (4-12) mL/min and temperature from 20 to 50℃. In this study, the highest adsorption at conditions of bed height of 15cm, initial metal concentration of 60mg/L, flow rate of 8mL/min, and temperature of 20℃, after 160 min the maximum adsorption removal efficiency for copper and zinc ions were approximately (51.792% for BDP/Zn), and (64.426% for BDP/Cu).

The data were analyzed for Thomas, Adams-Bohar, Modified Dose-Response, and Yoon-Nelson column kinetic models with higher correlation coefficient values (R^2>0.95) for the Thomas model, (R^2>0.97). According to the Thomas model, the maximum column adsorption capacity (q) were found for Zn2+/BDP and Cu2+/BDP, (1.901 and 3.878) mg g-1, respectively. demonstrating Langmuir isotherm behavior and the second-order kinetic reaction. The adsorption of copper metals on BDP surface shows negative values for Gibbs free energy change (ΔG), indicating spontaneous and energetically favorable metal bio sorption. The negative value of ΔH indicates exothermic sorption, with heat released during the reaction. The positive ΔS values indicate increased randomness and sorbent affinity towards Cu ions. The negative enthalpy change indicates exothermic adsorption, decreasing feasibility with temperature, On the other hand, for Zn ion on BDP, the Gibbs free energy change (ΔG) has the same behavior except at higher temperature which recorded a positive value, suggesting a non-spontaneous nature of the adsorption Several more research published in the last year's show similar results for heavy metal sorption. While the negative value of change in enthalpy (ΔH) indicates that the adsorption is an exothermic process. The exothermic nature of the reaction explains why the value of (ΔG) becomes more positive with the rise in temperature indicating a decrease in the feasibility of the adsorption process So, reduce the temperature from (50 to 20)℃ was preferred to drive the adsorption process. In this study, the highest adsorption was at 20℃, to drive the adsorption process. This work has affirmed that BDP is an effective bio-adsorbent for removing heavy metals and industrial effluents. Increasing the surface area of the adsorbent can potentially improve adsorption capacity. Further research is needed to explore surface modification methods and investigate their effectiveness with the aim to reduce the overall cost and improve the eco-efficiency of the resulting product. However, the harmless disposal of bio char contaminated with heavy metals remains a challenge. Therefore, more studies on bio char desorption and regeneration are still required. Based on the available data, it can be inferred that the utilization of BDP, based materials holds significant promise for removing pollutants. Nevertheless, further research is imperative to address existing gaps and broaden the research scope.

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NOMENCLATURE

Tb	Breakthrough time (min) k_Th constant of Thomas model (L min^{-1} mg^{-1})
Ts	Saturation (exhausted) time (min)
Cb	Breakthrough concentration (mg ml^{-1})
Cs	Saturation concentration (mg ml^{-1})
ΔG	Gibbs free energy change (J mol^{-1})
Qb	Adsorption capacity at breakthrough (mg)
ΔH	Change in enthalpy (J mol^{-1})
Q	Total capacity adsorbed by the column (mg g^{-1})
ΔS	The entropy of adsorption (J mol^{-1} k^{-1})
m-in	Total loaded ions in the column (mg)
m-ad	The total adsorbed metal ion fed to the system (mg)
T	time required for 50% adsorption breakthroughs (min)
RE (%)	Removal percentage (%)

Greek symbols

-1	constant rate of Yoon and Nelson model (min^{-1})

$k_{(AB)}$	constant rate of Bohart-Adams model (L min^{-1} mg^{-1})
Kd	Distribution coefficient (dimensionless)