Journal Homepage: http://ijcpe.uobaghdad.edu.iq
Iraqi Journal of Chemical and Petroleum Engineering
Vol. 25 No. 2 (June 2024) 139 – 150
EISSN: 2618-0707, PISSN: 1997-4884

Removal of Copper and Zinc Metal Ions from Industrial Effluents in Continuous Mode using Modified Date Pits

Huda A. Mohsen [a], **Alaa N. Ghanim** [a, *]

a Chemical Engineering Department, College of Engineering, University of Babylon, Al-Hilla, Iraq

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 utilizing date pits modified with hydrogen peroxide as agricultural biomass in extracting heavy metals from polluted water in a column continuous flow system. The resulting modified adsorbent (MDP) has a surface area of 278.18 m^2/g. The derived adsorbent was investigated under changed operating parameters including the flow rate (4-12) ml/min, pH (4-10), initial metal ion concentration (30-60) mg/L, and temperature (20-50) °C to determine their effect on heavy metals adsorption efficiency. The response surface methodology (RSM) experimental design was utilized to study the primary and combined influence of four key parameters, including (A) initial metal ion concentration, (B) pH solution, (C) solution temperature, and (D) flow rates of the influent, on the metal removing efficiency (Re%). optimization in fact, an analysis of variance (ANOVA) revealed a high coefficient of regression, or R2 > 0.90. Furthermore, the removal efficiency was positively influenced by reducing the initial ion concentration, flow rate, and temperature. in addition, the pH shows maximum effectiveness at a neutral state. In general, Cu (II) adsorption shows a higher affinity to adsorb over the MDP surface compared to Zn (II). The MDP adsorbents exhibited a promising removal efficiency for metal ions and further investigations are needed.

Keywords: Heavy metals; Adsorption; Fixed bed Column; Date pits; Wastewater.

Received on 16/09/2023, Received in Revised Form on 04/11/2023, Accepted on 05/11/2023, Published on 30/06/2024

https://doi.org/10.31699/IJCPE.2024.2.13

1- Introduction

Freshwater is the most valuable natural resource available on earth and it is essential for every living creature on the planet the Earth has a surface that is 71% covered by water, yet freshwater, crucial for drinking, bathing, and irrigation, is scarce, constituting only 3% of the total water on the planet, much of which is inaccessible [1-3]. Heavy metals are organic compounds that, despite their small amounts, cause significant pollution to people and other living things, and they persist for a long time due to their unsustainable nature [4-6]. As soon as heavy metals enter streams, they can accumulate in fish and other aquatic animals. Humans may then become exposed to these pollutants through the consumption of contaminated water and food [9-11].

Many techniques, including ion exchange systems [13], adsorption, evaporation, chemical precipitations [12], reverse osmosis (RO), Nano filtration membranes [14], and ion exchange systems [13], are frequently used to treat wastewater streams contaminated with heavy metals. The unique properties of the heavy metal pollutants and the wastewater's composition can affect how effective each treatment method is [15–17].

Adsorption process based on surface separation phenomenon in which the substances that stuck in a fluid attach or adhere to a solid material called the adsorbent over its both exterior and interior surfaces. Essentially, it employs interphase transfer to eliminate surface-active substances [18, 19]. In other words, this process is selectively separation (kinetic and/or thermodynamic selectivity) of pollutants over an adsorbent surface due to specific interactions, basically mass transfer between the fluid-solid phases [20-22], It is a highly efficient method for treating water contaminated with heavy metals. It has gained widespread recognition and popularity due to its capability to effectively eliminate inorganic pollutants, even at low concentrations Typically, the material that absorbs the heavy metals is a solid that has a strong attraction to the metals [18, 23].

Materials that can be found in nature, known as natural adsorbents, can be used to extract heavy metals from water [24–26]. Orange peel [27, 28], leaves, wheat-based materials [29, 30], brown algae [31], eucalyptus bark [32, 33], sugar beet pulp [34], olive stone [35, 36], papaya seed [37, 38], These materials are plentiful, carbon-rich, and easily processed into adsorbents with high surface area and porosity. Natural clays, zeolites, fly ash, sawdust, miscellaneous, and sludge have also been discovered to be effective heavy metal adsorbents. One natural adsorbent that is offered is raw date pits. A cheap and abundant waste product from the dates industry. hazardous metals elements as an instance nickel (Ni), arsenic (As), lead [39], (Pb), iron (Fe), cobalt (Co), cadmium (Cd), zinc (Zn) [19], copper (Cu) [40], and

---

*Corresponding Author: Email: eng.alaaghanim@uobabylon.edu.iq

mercury (Hg) [41, 42] …etc. are discharged into water bodies and environment by various human activities, including manufactory industrial processes, mining, agriculture, and improper disposal of waste.

There is currently little research on the potential of raw date pits as a natural bio-adsorbent that can efficiently remove heavy metals from water. To optimize the use of raw date pits for heavy metal removal and to ascertain the long-term environmental impact of doing so, more research is needed. This study makes use of date pits, a readily available, reasonably priced, and underutilized plant material, to extract Zn(II) and Cu(II) from an aqueous solution in a fixed-bed column. The study examined the statistical relationship and impacts of different operating parameters, including temperature, feed flow rate, pH of the initial solution, and initial metal concentration, on the bio-adsorbents of these metals.

2- Materials and Methods

Al-Zahdi, Iraqi date pits, were obtained from the Al-Hour area in the Karbala governorate. De-ionized distill water, CuSO4.5H2O, ZnSO4.7H2O, HCl, and NaOH were purchased from Sigma Aldrich and utilized in this study. All of these chemicals have a purity level of 99%.

2.1. Experimental Procedure

- Preparation of Raw Date Pits

The Zahdi date pits were rinsed using de-ionized water to remove residual edible components and particulate matter. Subsequently, they were left to undergo natural drying under sunlight for an extended period. Finally, the pits were 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 2-3 mm Fig. 1 displays the raw and ground date pits. The main features included actual density, surface area, porosity, and apparent density of 1.3 g/cm^3, 0.416 m^2/g, 0.45, and 0.75 g/cm^3, respectively, and moisture content and ash of 12.49% and 1.24%, respectively [43].

Fig. 1. Date Pits before and after Grinding

Hydrogen peroxide (H_2O_2, 1M) was used to modify the resulting adsorbent to enhance the surface functionalities (OH). The treatment includes adding 100 mL of 30% H2O2 solution (to provide the adsorbent surface with negative functionalities (-OH)) [44], into a beaker containing 10 g of dried biomass with continued mixing for 24 hours, filtering, washing with DI water, and drying. The resultant charcoal was labeled as MDPs.

Laboratory-grade hydrogen peroxide 30% contains intermediate purity and is suitable for educational or research laboratories. Higher purity can be dangerous because hydrogen peroxide is a very strong oxidizing agent. In addition, peroxide treatment may have a different outcome, such as destroying or eliminating part of the functional groups in charge of adsorption [45].

2.2. Experimental Set-up

A fixed bed column was used for bio-sorption experiments. The schematic diagram of the experimental setup is shown in Fig. 2. The setup has a 20 L closed feed tank filled with metal ions solution at a specific concentration for the selected experiments. A Perspex column with a length of 30 cm and a 2.5 cm inner diameter was employed. Fiberglass wool layers of 3 mm were fixed at the bottom and top of the bed adsorbent to stabilize the bed height constant, support the bed, and keep the bed at a constant amount. This support was retained using a fixed stainless steel sieve during the experiment.

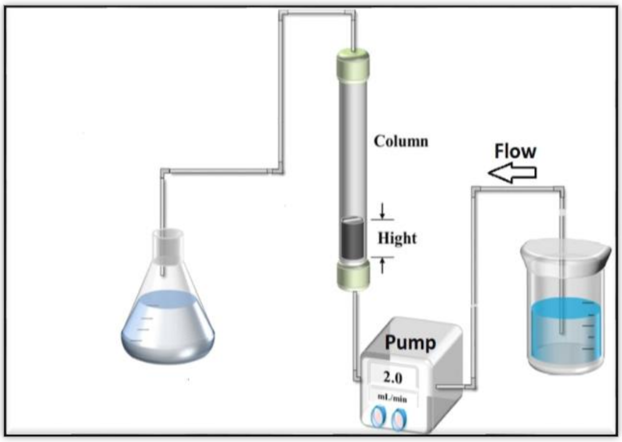


Fig. 2. Schematic Representation of the Experimental Setup

The contaminated water was delivered to the bottom of the column via a peristaltic pump (Model: BT100-1J Longer Pump).

A valve and flow meter were employed to guarantee a steady flow rate passed through the system. The column was packed with adsorbents to achieve a bed height of 15 cm. 5 ml samples of the column effluent were collected in a beaker after 20 min to determine the concentration of the residual pollutant for determining the metal ion removal efficiency (Re%). The concentration measurement of metal ions in the effluents was performed using atomic absorption spectroscopy.

The experiments were carried out to investigate the effect of changing common operating parameters by determining the metal ion removal efficiency (Re%) which is defined by Eq. 1.

$$Re\% = \frac{mass\ of\ metal\ ions\ adsorbed\ in\ the\ column\ (mg)}{mass\ of\ metal\ ions\ loaded\ in\ the\ column\ (mg)} * 100 = \frac{c_0 Q \int_0^t \left(1 - \frac{c_t}{c_0}\right) dt}{c_0 Q t} * 100 \qquad (1)$$

Where C0 and Ct represent the metal ion concentration (mg/l) at entering and at sampling time (t, min) respectively. Q is the flow rate (l/min).

2.3. experimental design

- response surface methodology (RSM)

In the present research, response surface methodology (RSM) was utilized to study the primary and combined influence of four key parameters, including (A) initial metal ion concentration, (B) pH solution, (C) solution temperature, and (D) flow rates of the influent, on the metal removing efficiency (Re%). Table 1. presents the design factors and their values. ANOVA analysis was performed in Design Expert 13.0 to imply a regression equation for the response. The primary impacts of the independent variables are denoted as A, B, and C, whereas the interplay between factors could be characterized as AB, AC, and BC interaction effects.

Table 1. Factors and their Levels

			Levels		
Factors	**Unit**	**Symbol**	**Low Level (-1)**	**Intermediate Level (0)**	**High Level (1)**
Initial concentration (C),	**mg/lit**	A	30	45	60
Ph.		B	4	7	10
Temperature (T),	**°C**	C	20	35	50
Flow rate (Q),	**lit/min**	D	4	8	12

3- Results and Discussion

3.1. Bio-adsorbent Characteristics

A- Scanning Electron Micrographs (SEM)

SEM analysis was employed to examine the morphological properties of prepared adsorbent surfaces, as shown in Fig. 3. The SEM image for RDP shows that the low or no significant pores in the adsorbent surface while the porosity of the modified date pits (MDP) is greater than that of the raw material (RDP) with the mean surface area of (278.18 m^2/g). However, it can be seen from the figure that MDP has a narrow size distribution and a regular shape with a greater tendency to agglomerate. The produced MDP adsorbent particles generated a large porous structure that is suited for target metal adsorption [39]. Hydrogen peroxide (H_2O_2) modification improved the surface functionalities (–OH) of the produced DP by establishing negative functionalities (-OH) over the surface, decomposing organic parts, avoiding cellulose degradation, and reducing biomass resistance. The (H_2O_2) treatment produces a larger porosity surface and higher contents of O_2 due to hydroxyl functionalities compared to the raw material [40].

B- Fourier transform infrared spectroscopy (FTIR)

Fig. 4 show the FTIR analysis within region of 400-4000 cm−1 wavelength that carried out before and after adsorption to identify the surface functionalities and possible adsorption mechanism for MDP. The FTIR spectrum of MDP was measured, a broad peak at 3200-3600 cm-1 is attributed to hydroxyl group stretching vibration which is characteristic lingo cellulosic peaks and appeared when water used in the preparation process and due to modifying agent used [46]. The weak band aliphatic stretching vibration C–H that suggest presence of hemicellulose and cellulose is located between 2800-3000 cm-1 and become weak after burning process, while the vibrations at 1743 cm-1 represents the existence of unconjugated carbonyl (C=O), imine (C=C) at 1635 cm1, C-O at 1242.16 and C-N bands showed at 1373cm-1. Carboxylic acids groups COOH stretching can also be located at band of 1242 cm-1. In addition, C-O-C vibrations is assigned to the bands appearing at and 1157cm-1 [47].

After metal ions adsorption, some bands have been shifted, developed, or disappeared as a result of adhesion of metal ions over MDP surface. Moreover, a new peak at 586 cm_1 was created as stretching vibration of Ion-O bond, indicating the adsorption of ions to MDP surface. The effective binding of ions on MDP was confirmed by FTIR investigations, and the functional groups -COO, -CO, and -CH were actively involved in the zinc and copper adsorption.

These results could lead to the hypothesis that the C-O and -OH or NH C=O functions played a major role in lone-pair transfer and electrostatic interactions during the binding of Cu(III) and Zn(II) across the surface. Therefore, coordination-binding and electrostatic interactions might be viable mechanisms for metal adsorption [46].

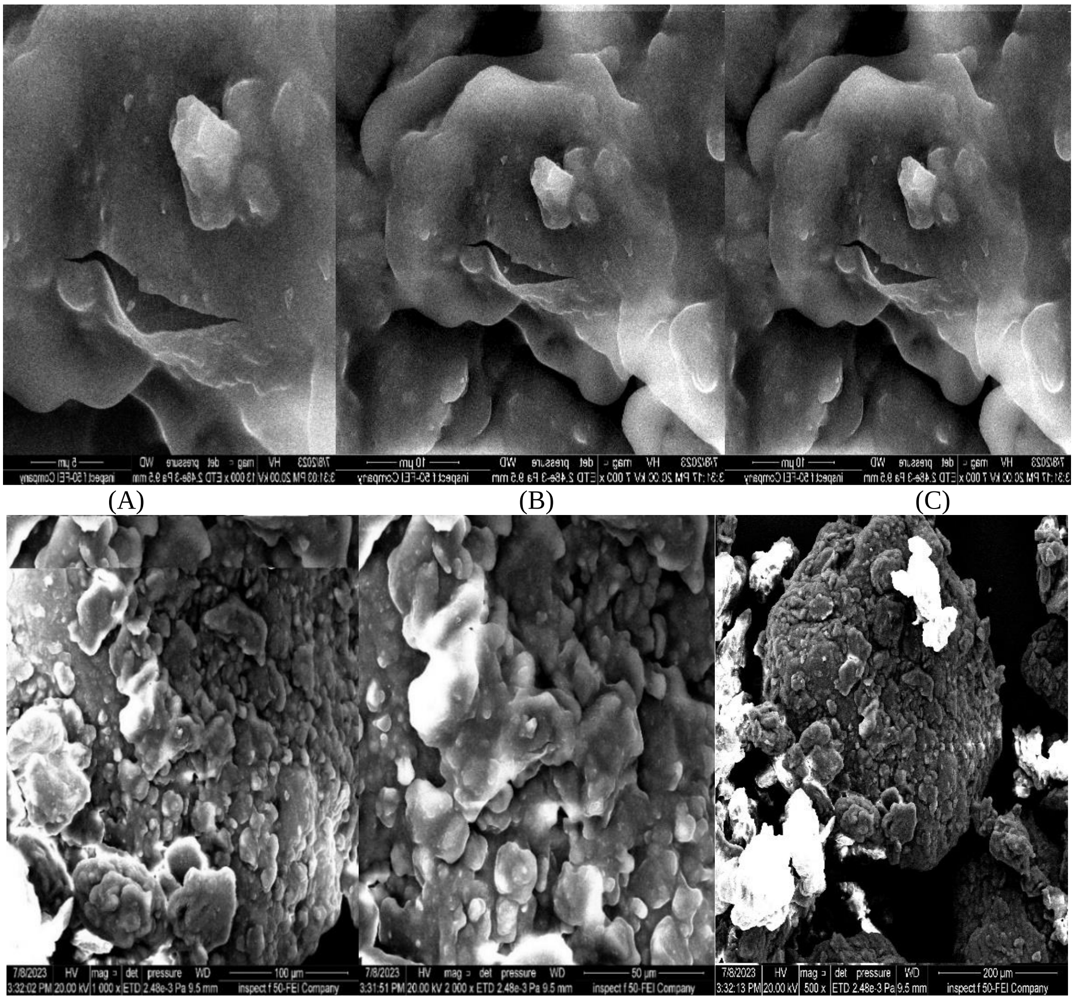
3.2. Response Surface Methodology(RSM)

The response results (removal efficiency (Re%)) are depicted in Table 2, indicating that the investigated factors at different levels substantially affected removal efficiency.

A- Statistical Analysis

In this study, the ANOVA analysis indicates that the regression equation successfully captures the relationship between the response variable and the independent variables and their interactions. Furthermore, the variables included in the equation demonstrate statistical significance in explaining the variations observed in the response variable. By examining the F-values and p-values, the variables with higher F-values and p-values of less than 5% are identified as the key contributors in this relationship [10, 11, 48].

ANOVA analysis illustrated in Table 3 and Table 4 indicates that the suggested model has p-values less than 0.05, so the models can desirably represent the statistical outcomes and study the optimal conditions for a metal adsorption process [49]. Furthermore, variables with p-values less than 5% had statistical significance and were considered contributors to the implied model. According to their p-values, A (initial Cu+2 conc.), C (Temperature), D (Flow rate), BD (pH and Flow rate), B2 (second-order PH), and B2 (second-order pH), AD (initial Cu+2 conc. and flow rate), were taken as the most significant model variables as compared to B (pH). Also, those variables with higher F-values describe their influence [50].


(A) (B) (C)

(D) (E) (F)

Fig. 3. SEM Images of RDP (A–C) and MDP (D–F) at Various Magnification: 1000x and 10 µm;3000x and 5 µm: and 6000x Magnification with 2 µm Diameter

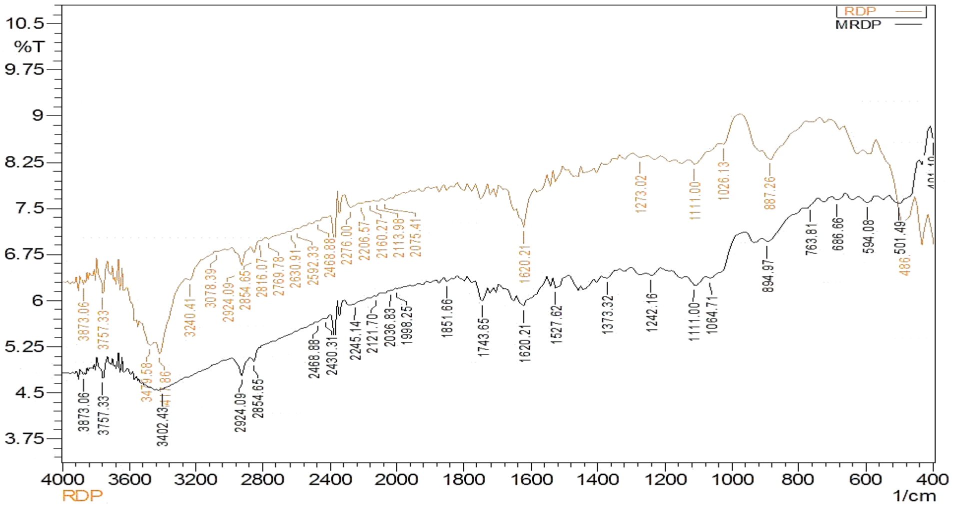


Fig. 4. FTIR Spectra of RDP and MDP

Table 2. Summary of Factorial Design Experimental Data for Heavy Metals Adsorption Using MDPs

Std	Factor (1) A: Conc. (ppm)	Factor (2) B: pH	Factor (3) C: Temp. (ºC)	Factor (4) D: Flowrate (l/min)	Zn Re%	Cu RE%
1	30	4	35	8	46.8	57.4
2	60	4	35	8	66.7	87.2
3	30	10	35	8	42.4	55.5
4	60	10	35	8	62.5	85.1
5	45	7	20	4	67.2	90.6
6	45	7	50	4	59.6	76.5
7	45	7	20	12	59.6	82.3
8	45	7	50	12	39.5	56.8
9	30	7	35	4	60.9	74.5
10	60	7	35	4	67.1	91.1
11	30	7	35	12	40.6	44.8
12	60	7	35	12	60.6	82.6
13	45	4	20	8	65.4	85.4
14	45	10	20	8	63.7	85.3
15	45	4	50	8	45.4	59.5
16	45	10	50	8	40.5	51.7
17	30	7	20	8	59.2	77.9
18	60	7	20	8	69.3	93.7
19	30	7	50	8	39.6	51.6
20	60	7	50	8	59.5	81.3
21	45	4	35	4	66.9	64.5
22	45	10	35	4	62.4	82.4
23	45	4	35	12	46.7	62.9
24	45	10	35	12	42.4	60.7
25	45	7	35	8	60.6	79.6
26	45	7	35	8	60.6	79.6
27	45	7	35	8	60.6	79.6

Table 3. Analysis of Variance (ANOVA) Results for Quadratic Model (Cu2+) Removal

Source	Sum of Squares	Df	Mean Square	F.value	p.value	
Model	5022.23	14	358.73	19.09	< 0.0001	Significant
A-concentration	2114.71	1	2114.71	112.54	< 0.0001	
B-Ph	1.20	1	1.20	0.0640	0.8045	
C- Temperature	1582.40	1	1582.40	84.21	< 0.0001	
D-Flow rate	667.52	1	667.52	35.52	< 0.0001	
AB	0.0100	1	0.0100	0.0005	0.9820	
AC	48.30	1	48.30	2.57	0.1349	
AD	112.36	1	112.36	5.98	0.0309	
BC	14.82	1	14.82	0.7888	0.3919	
BD	101.00	1	101.00	5.38	0.0389	
CD	32.49	1	32.49	1.73	0.2131	
A^2	21.69	1	21.69	1.15	0.3038	
B^2	312.46	1	312.46	16.63	0.0015	
C^2	3.24	1	3.24	0.1723	0.6854	
D^2	70.73	1	70.73	3.76	0.0762	
Residual	225.49	12	18.79			
Lack of Fit	225.49	10	22.55			
Pure Error	0.0000	2	0.0000			
Cor Total	5247.72	26				

Table 4. Analysis of Variance (ANOVA) Results for Quadratic Model (Zn2+) Removal

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2684.42	14	191.74	28.30	< 0.0001	Significant
A-concentration	803.60	1	803.60	118.61	< 0.0001	
B-ph.	48.00	1	48.00	7.08	0.0207	
C-temperature	838.34	1	838.34	123.74	< 0.0001	
D-Flow rate	779.24	1	779.24	115.01	< 0.0001	
AB	0.0100	1	0.0100	0.0015	0.9700	
AC	24.01	1	24.01	3.54	0.0842	
AD	34.81	1	34.81	5.14	0.0427	
BC	2.56	1	2.56	0.3778	0.5502	
BD	0.0100	1	0.0100	0.0015	0.9700	
CD	39.06	1	39.06	5.77	0.0334	
A^2	9.54	1	9.54	1.41	0.2583	
B^2	108.60	1	108.60	16.03	0.0018	
C^2	31.36	1	31.36	4.63	0.0525	
D^2	12.81	1	12.81	1.89	0.1942	
Residual	81.30	12	6.78			
Lack of Fit	81.30	10	8.13			
Pure Error	0.0000	2	0.0000			
Cor Total	2765.72	26				

The experiential relation between the response, which is the removal percentage, and the independent variable is shown in Table 5. The positive terms show the synergistic effect of variables and the negative terms represent the antagonistic effect. The R^2 value is the variability between the predicted data and the experimental data. R^2 values for all regression equations were often closer to 1, indicating that the models may be used to predict responses in terms of chosen variables. Additionally, the little difference between adjusted R^2 and anticipated R^2 can be used to demonstrate the relevance of the constructed regression equations. In general, the predicted R^2 is in reasonable agreement with the adjusted R^2; i.e., the difference is less than 20%.

For the regression equation of copper removal via MDP, the attained R^2 is 92.41%, which explains that 92.41% of experimental data agreed well with the predicted data. The removal efficiency was directly correlated with the initial ion concentration, linear pH, and the interaction between concentration and flow rate, according to the model equations. Additionally, it exhibited an inverse relationship with the following variables: temperature, feed flow rate, square PH, interaction between concentration and flow rate, and pH and flow rate.

For the regression equation of zinc removal via MDP, the attained R^2 is 94.7%, which explains that 94.7% of experimental data agreed well with the predicted data. According to model equations, the removal efficiency was directly proportional to the initial ion concentration, linear pH, and the interaction between concentration and flow rate. Furthermore, it was inversely proportional to the temperature, feed flow rate, square PH, interaction between concentration and flow rate, and interaction between temperature and flow rate.

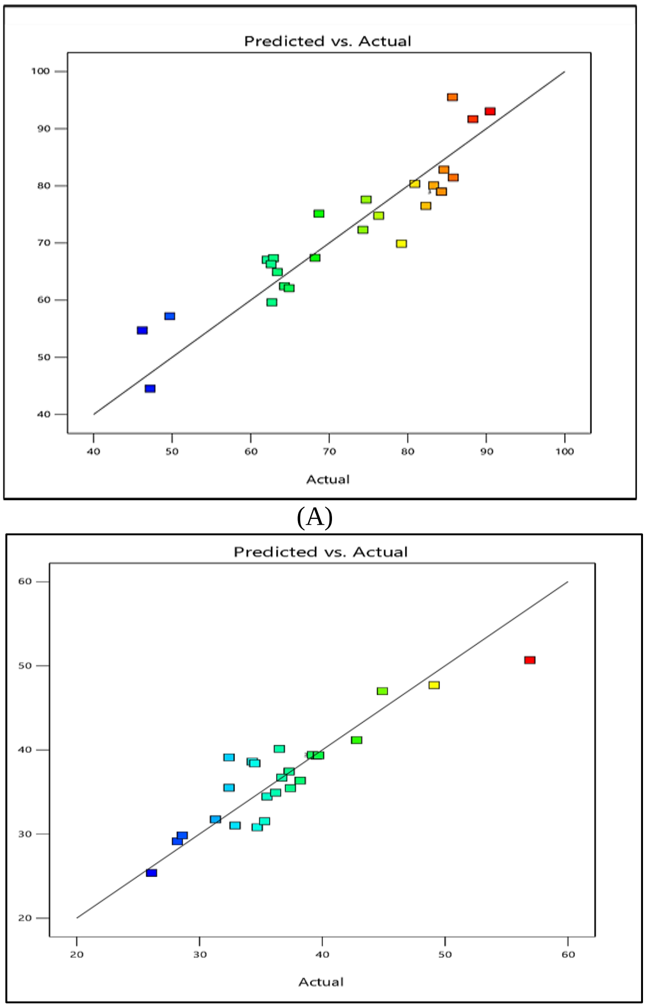
Table 5. Model Summary and Modified Regression Equations

Type of metals	The Equation	R2	Adjusted R^2	Predicted R^2
Cu+2	51.0+ 0.178 A (conc.)+ 13.36 B (pH)- 0.7656 C (Temp.)- 2.91 D (Flow rate)- 0.707 B (pH)*B (pH)+ 0.0883 A (conc.)*D (Flow rate) - 0.419 B (pH)*D (Flow rate)	92.41%	89.61%	81.7%
Zn+2	59.0 + 0.129 A (conc.) + 4.64 B (pH) - 0.141 C (Temp.) – 2.50 D (Flow rate) - 0.379 B (pH)*B (pH) + 0.0517 A (conc.)*D (Flow rate) - 0.0521 C (Temp.)*D (Flow rate)	94.7%	92.74%	89.16%

The statistical approximations in Fig. 5 were determined to be a sufficient fit with the experimental data, as evidenced by a distribution of actual and projected values closer to the diagonal line for model responses. Simply put, this aids in determining the robustness of an empirical model based on outliers or data point noise. The greater the number of outliers, the less useful and dependable the model. The data points were distributed rectilinearly, as illustrated in Fig. 5, with no discernible patterns obtained. As a result, the already developed models were satisfactory in terms of accuracy and could predict responses that were compatible with real data [51]. Similarly, in Fig. 6, the highest divergence between projected and measured metal ion removal is less than 4%, indicating that the model's assumptions have been met and the model is operating well.

B- Interactive Effect of Variables

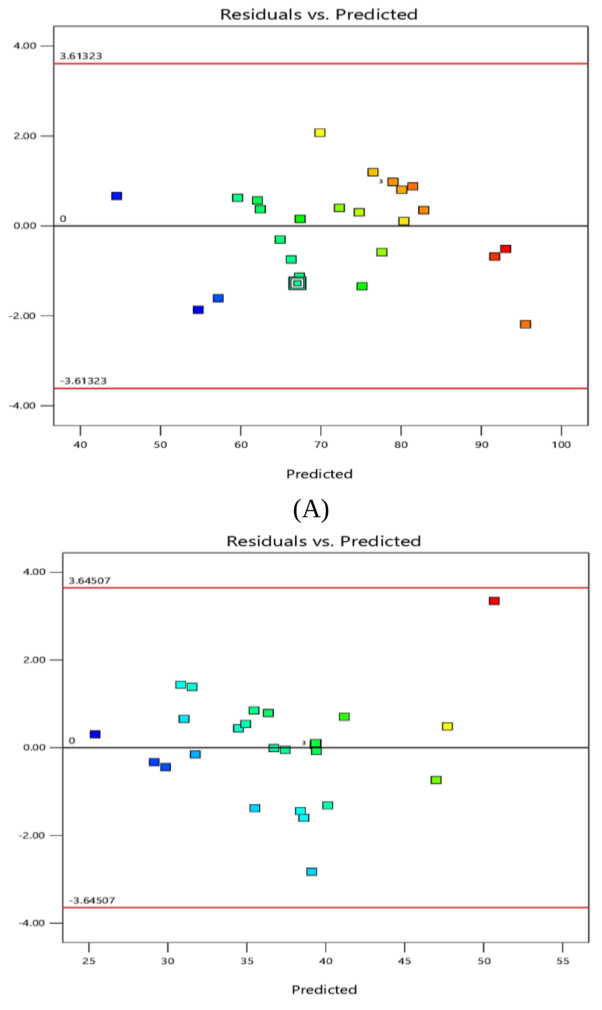
The 3D surface plots presented in Fig. 7 and Fig. 8 for Cu and Zn removal, respectively, depict how individual and interactive effects of initial metal concentration, pH, temperature, and feed flow rate influence metal removal efficiency. These plots provide empirical evidence that supports the relationships between the responses and the model variables as proposed by regression models.



(A)

(B)

Fig. 5. The actual versus predicted values for copper (A) and zinc (B) removal efficiency



(A)

(B)

Fig. 6. Plot Between Residuals and Predicted for Copper (A) and Zinc (B)

The main effects of the process parameters on removal efficiency for Copper and Zinc metals are shown in Fig. 7 and Fig. 8 respectively. The removal efficiencies were significantly increased by increasing the initial concentration from 30 to 60 ppm, resulting in an 18% and 8.38% increase in Cu (II) and Zn (II) removal efficiency, respectively indicating a larger concentration gradient and improved adsorption process, resulting in an increased driving force for the adsorption process. These findings are in good agreement with the study of Azam [40]. Increasing the temperature and feed flow rate had a negative effect. The removal efficiencies were decreased by increasing the system temperature from 20 to 50°C, which resulted in a 10.2166% and 8.3% decrease in Cu (II) and Zn (II) removal efficiencies, respectively, as temperature increases, adsorption decreases due to weak interaction between biomass surface and metal ions, resulting in exothermic nature and dissociation of active sites for adsorption [52, 53]. In addition, increasing the flow rate from 4 to 12 l/min resulted in a 15.167% and 6.867% decrease in Cu (II) and Zn (II) removal efficiencies, respectively, the higher feed flow rate affected the retention time of pollutants in the aqueous phase, causing a reduction of interaction of the adsorbates surface and the adsorbents, thereby resulting in higher effluent concentrations before equilibrium is reached. Also, this result suggested that the column was not exhausted at a lower flow rate and had a longer saturation time. These findings are in good agreement with the study of Amin [53]. Furthermore, increasing the pH of the feed solution resulted in the development of three main regions, with the highest values for the neutral solution being Cu (II) at 93.7% and Zn (II) at 69.3% removal, this means that when the concentration of H^+ increases, the surface of the biosorbent becomes more positively charged, lessening the attraction between adsorbent and metal ions. In contrast, as pH rises, more negatively charged surfaces become available, allowing for increased metal uptake. At higher pH levels, the ions precipitate as hydroxides, reducing the rate of adsorption and, as a result, the percent removal of metal ions [54].

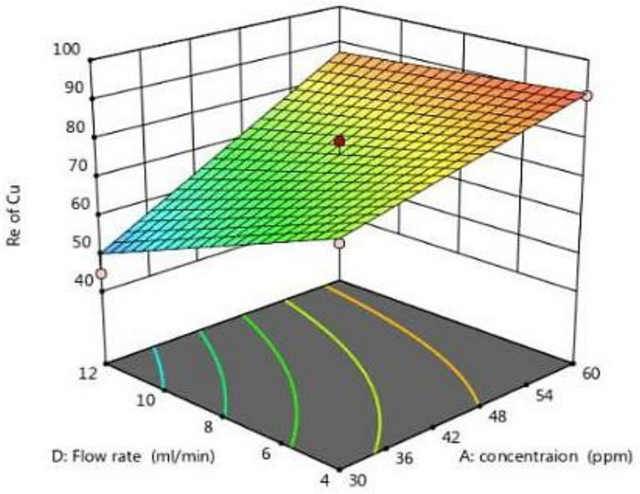


Fig. 7. Response Surface Plots for (Cu) Removals Using MDP as Adsorbent (R %) is the Response Measured, Data were Obtained Following Response Transformation

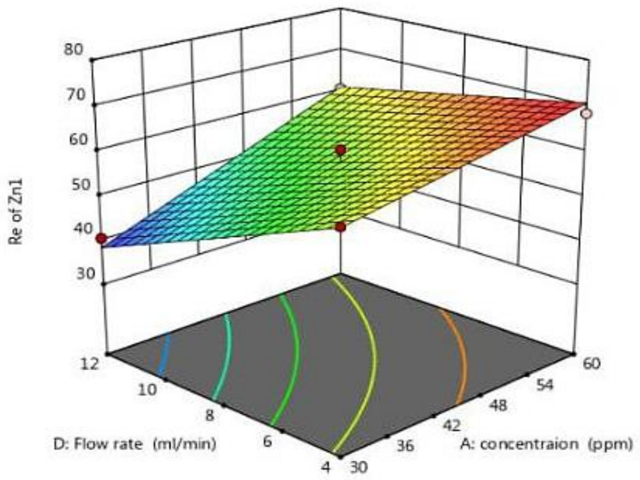


Fig. 8. Response Surface Plots for (Zn) Removals Using MDP as Adsorbent (R%) is The Response Measured, Data were Obtained Following Response Transformation

4- Conclusions

This study investigated the removal effectiveness of modified date pits (MDPs) from water contaminated with heavy metals using a column bed dynamic mode since it is a low-cost, abundant, and locally available adsorbent. The SEM image for MDP shows a narrow size distribution a regular shape a greater tendency to agglomerate and interestingly a higher porosity structure than (RDP) that is suited for target metal adsorption. Hydrogen peroxide (H_2O_2) modification improved the surface functionalities (–OH) of the produced DP by establishing negative functionalities (-OH) over the surface. RSM was discovered to be a highly useful technique for the optimization of metal adsorption parameters. In fact, an analysis of variance (ANOVA) revealed a high coefficient of regression, or $R^2 > 0.90$, which supported the model's good fit with the experimental data. Furthermore, the removal efficiency was positively influenced by reducing the initial ion concentration, flow rate, and temperature. However, the pH shows maximum effectiveness in at neutral solution. In general, Cu (II) adsorption shows a higher affinity to adsorb over the MDP surface compared to Zn (II).

References

[1] M. Vhahangwele and L. M. Khathutshelo, "Environmental Contamination by Heavy Metals," in *Heavy Metals*, vol. 10, M. S. Hosam El-Din and F. A. Refaat Eds. Rijeka: IntechOpen, 2018, ch. 7, pp. 115-133. https://dx.doi.org/10.5772/intechopen.76082

[2] M. M. Ali, D. Hossain, A. Al-Imran, M. Khan, M. Begum, and M. Osman, "Environmental pollution with heavy metals: A public health concern," in *Heavy metals-their environmental impacts and mitigation*, M. Nazal and H. Zhao Eds. Rijeka: IntechOpen, 2021, ch. 1, pp. 771-783. https://dx.doi.org/10.5772/intechopen.96805

[3] Kiran, R. Bharti, and R. Sharma, "Effect of heavy metals: An overview," *Materials Today: Proceedings*, vol. 51, no. 1, pp. 880-885, 2022/01/01/ 2022, https://doi.org/10.1016/j.matpr.2021.06.278

[4] J. Narjala Rama, "Heavy Metal Sources and Their Effects on Human Health," in *Heavy Metals*, vol. 10, N. Mazen Khaled and Z. Hongbo Eds. Rijeka: IntechOpen, 2020, ch. 2, pp. 1-12. https://doi.org/10.5772/intechopen.95370

[5] K. H. Vardhan, P. S. Kumar, and R. C. Panda, "A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives," *Journal of Molecular Liquids*, vol. 290, no. 1, p. 111197, 2019/09/15/ 2019, https://doi.org/10.1016/j.molliq.2019.111197

[6] T. Nachana'a and W. Ezekiel Tagui, "Environmental Pollution by Heavy Metal: An Overview," *International Journal of Environmental Chemistry*, vol. 3, no. 2, pp. 72-82, 2019, https://doi.org/10.11648/j.ijec.20190302.14

[7] A. Anderson, A. Anbarasu, R. R. Pasupuleti, S. Manigandan, T. R. Praveenkumar, and J. Aravind Kumar, "Treatment of heavy metals containing wastewater using biodegradable adsorbents: A review of mechanism and future trends," *Chemosphere*, vol. 295, no. 1, p. 133724, 2022/05/01/ 2022, https://doi.org/10.1016/j.chemosphere.2022.133724

[8] A. Daripa, L. C. Malav, D. K. Yadav, and S. Chattaraj, "Chapter 7 - Metal contamination in water resources due to various anthropogenic activities," in *Metals in Water*, S. K. Shukla, S. Kumar, S. Madhav, and P. K. Mishra Eds. Amsterdam: Elsevier, 2023, ch. 7, pp. 111-127. https://doi.org/10.1016/B978-0-323-95919-3.00022-7

[9] Z. Hao *et al.*, "Heavy metal distribution and bioaccumulation ability in marine organisms from coastal regions of Hainan and Zhoushan, China," *Chemosphere*, vol. 226, no. 1, pp. 340-350, 2019/07/01/ 2019, https://doi.org/10.1016/j.chemosphere.2019.03.132

[10] M. Zaynab *et al.*, "Health and environmental effects of heavy metals," *Journal of King Saud University - Science*, vol. 34, no. 1, p. 101653, 2022/01/01/ 2022, https://doi.org/10.1016/j.jksus.2021.101653

[11] G. Y. Zaghloul, H. M. Ezz El-Din, L. I. Mohamedein, and K. M. El-Moselhy, "Bio-accumulation and health risk assessment of heavy metals in different edible fish species from Hurghada City, Red Sea, Egypt," *Environmental Toxicology and Pharmacology*, vol. 95, no. 1, p. 103969, 2022/10/01/ 2022, https://doi.org/10.1016/j.etap.2022.103969

[12] M. C. Benalia, L. Youcef, M. G. Bouaziz, S. Achour, and H. Menasra, "Removal of Heavy Metals from Industrial Wastewater by Chemical Precipitation: Mechanisms and Sludge Characterization," *Arabian Journal for Science and Engineering*, vol. 47, no. 5, pp. 5587-5599, 2022/05/01 2022, https://doi.org/10.1007/s13369-021-05525-7

[13] A. Bashir *et al.*, "Removal of heavy metal ions from aqueous system by ion-exchange and biosorption methods," *Environmental Chemistry Letters*, vol. 17, no. 2, pp. 729-754, 2019/06/01 2019, https://doi.org/10.1007/s10311-018-00828-y

[14] H. Xiang, X. Min, C.-J. Tang, M. Sillanpää, and F. Zhao, "Recent advances in membrane filtration for heavy metal removal from wastewater: A mini review," *Journal of Water Process Engineering*, vol. 49, no. 1, p. 103023, 2022/10/01/ 2022, https://doi.org/10.1016/j.jwpe.2022.103023

[15] M. R. R. Ashutosh Tripathi, "Heavy metal removal from wastewater using low cost adsorbents," *Journal of Bioremediation and Biodegradation*, vol. 6, no. 6, p. 315, 2015, https://doi.org/10.4172/2155-6199.1000315

[16] G. Crini and E. Lichtfouse, "Advantages and disadvantages of techniques used for wastewater treatment," *Environmental Chemistry Letters*, vol. 17, no. 1, pp. 145-155, 2019/03/01 2019, https://doi.org/10.1007/s10311-018-0785-9

[17] R. Shrestha *et al.*, "Technological trends in heavy metals removal from industrial wastewater: A review," *Journal of Environmental Chemical Engineering*, vol. 9, no. 4, p. 105688, 2021/08/01/ 2021, https://doi.org/10.1016/j.jece.2021.105688

[18] W. S. Chai *et al.*, "A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application," *Journal of Cleaner Production*, vol. 296, no. 1, p. 126589, 2021/05/10/ 2021, https://doi.org/10.1016/j.jclepro.2021.126589

[19] S. Bouranene, N. Sedira, L. Zeghadnia, and A. E. K. Guebail, "Kinetic Study of the Adsorption of Zinc and Copper Ions on to Activated Carbon Prepared from Date Pits," *International Journal of New Chemistry*, vol. 9, no. 1, pp. 21-35, 2022, https://doi.org/10.22034/ijnc.2022.1.3

[20] S. Kulkarni, "Synthesis, characterization and performance of low-cost unconventional adsorbents derived from waste materials," *Biointerface Research in Applied Chemistry*, vol. 10, no. 6, pp. 7243-7256, 2020, https://doi.org/10.33263/BRIAC106.72437256

[21] S. Afroze and T. K. Sen, "A Review on Heavy Metal Ions and Dye Adsorption from Water by Agricultural Solid Waste Adsorbents," *Water, Air, & Soil Pollution*, vol. 229, no. 7, p. 225, 2018/06/20 2018, https://doi.org/10.1007/s11270-018-3869-z

[22] M. Ruthiraan *et al.*, "An Overview of Magnetic Material: Preparation and Adsorption Removal of Heavy Metals from Wastewater," in *Magnetic Nanostructures : Environmental and Agricultural Applications*, K. A. Abd-Elsalam, M. A. Mohamed, and R. Prasad Eds. Cham: Springer International Publishing, 2019, ch. 8, pp. 131-159. https://doi.org/10.1007/978-3-030-16439-3_8

[23] C. Duan, T. Ma, J. Wang, and Y. Zhou, "Removal of heavy metals from aqueous solution using carbon-based adsorbents: A review," *Journal of Water Process Engineering*, vol. 37, no. 1, p. 101339, 2020/10/01/ 2020, https://doi.org/10.1016/j.jwpe.2020.101339

[24] L. Joseph, B.-M. Jun, J. R. V. Flora, C. M. Park, and Y. Yoon, "Removal of heavy metals from water sources in the developing world using low-cost materials: A review," *Chemosphere*, vol. 229, no. 1, pp. 142-159, 2019/08/01/ 2019, https://doi.org/10.1016/j.chemosphere.2019.04.198

[25] P. O. Oladoye, "Natural, low-cost adsorbents for toxic Pb(II) ion sequestration from (waste)water: A state-of-the-art review," *Chemosphere*, vol. 287, no. 1, p. 132130, 2022/01/01/ 2022, https://doi.org/10.1016/j.chemosphere.2021.132130

[26] R. Chakraborty, A. Asthana, A. K. Singh, B. Jain, and A. B. H. Susan, "Adsorption of heavy metal ions by various low-cost adsorbents: a review," *International Journal of Environmental Analytical Chemistry*, vol. 102, no. 2, pp. 342-379, 2022/01/26 2022, https://doi.org/10.1080/03067319.2020.1722811

[27] R. Lakshmana Naik, M. Rupas Kumar, and T. Bala Narsaiah, "Removal of heavy metals (Cu & Ni) from wastewater using rice husk and orange peel as adsorbents," *Materials Today: Proceedings*, vol. 72, no. 1, pp. 92-98, 2023/01/01/ 2023, https://doi.org/10.1016/j.matpr.2022.06.112

[28] H. Tang, Y. Zhang, Y. Zhang, Q. Xiao, X. Zhao, and S. Yang, "Turning waste into adsorbent: Modification of discarded orange peel for highly efficient removal of Cd(II) from aqueous solution," *Biochemical Engineering Journal*, vol. 185, no. 1, p. 108497, 2022/07/01/ 2022, https://doi.org/10.1016/j.bej.2022.108497

[29] U. Farooq, J. A. Kozinski, M. A. Khan, and M. Athar, "Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature," *Bioresource Technology*, vol. 101, no. 14, pp. 5043-5053, 2010/07/01/ 2010, https://doi.org/10.1016/j.biortech.2010.02.030

[30] F. Haq *et al.*, "Role of Starch Based Materials as a Bio-sorbents for the Removal of Dyes and Heavy Metals from Wastewater," *Journal of Polymers and the Environment*, vol. 30, no. 5, pp. 1730-1748, 2022/05/01 2022, https://doi.org/10.1007/s10924-021-02337-6

[31] Y. Liu, Q. Cao, F. Luo, and J. Chen, "Biosorption of Cd2+, Cu2+, Ni2+ and Zn2+ ions from aqueous solutions by pretreated biomass of brown algae," *Journal of Hazardous Materials*, vol. 163, no. 2-3, pp. 931-938, 2009/04/30/ 2009, https://doi.org/10.1016/j.jhazmat.2008.07.046

[32] I. Anastopoulos, M. J. Ahmed, and E. H. Hummadi, "Eucalyptus-based materials as adsorbents for heavy metals and dyes removal from (waste)waters," *Journal of Molecular Liquids*, vol. 356, no. 1, p. 118864, 2022/06/15/ 2022, https://doi.org/10.1016/j.molliq.2022.118864

[33] M. Matouq, M. Saleh, O. Al-Ayed, T. El-Hasan, Y. Hiroshi, and T. Tagawa, "Biosorption of chromium and nickel from aqueous solution using pine cones, eucalyptus bark, and moringa pods: a comparative study," *Water Practice and Technology*, vol. 16, no. 1, pp. 72-82, 2021, https://doi.org/10.2166/wpt.2020.096

[34] E. Pehlivan, B. H. Yanık, G. Ahmetli, and M. Pehlivan, "Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp," *Bioresource Technology*, vol. 99, no. 9, pp. 3520-3527, 2008/06/01/ 2008, https://doi.org/10.1016/j.biortech.2007.07.052

[35] G. Blázquez, F. Hernáinz, M. Calero, M. A. Martín-Lara, and G. Tenorio, "The effect of pH on the biosorption of Cr (III) and Cr (VI) with olive stone," *Chemical Engineering Journal*, vol. 148, no. 2, pp. 473-479, 2009/05/15/ 2009, https://doi.org/10.1016/j.cej.2008.09.026

[36] M. B. Amar, K. Walha, and V. Salvadó, "Evaluation of Olive Stones for Cd(II), Cu(II), Pb(II) and Cr(VI) Biosorption from Aqueous Solution: Equilibrium and Kinetics," *International Journal of Environmental Research*, vol. 14, no. 2, pp. 193-204, 2020/04/01 2020, https://doi.org/10.1007/s41742-020-00246-5

[37] P. Paranjape and P. Sadgir, "Removal of Heavy Metals from Water Using Low-cost Bioadsorbent: A Review," in *Recent Trends in Construction Technology and Management*, Singapore, B. B. D. M. S. Ranadive, Yusuf A. Mehta, Rishi Gupta, Ed., 2023, vol. 260: Springer Nature Singapore, in Recent Trends in Construction Technology and Management, pp. 527-546, https://doi.org/10.1007/978-981-19-2145-2_40

[38] H. Lim, "A Study on Removal of Cu (Ii) and Ni (Ii) From Synthetic Wastewater Using Agro-waste as Low-cost Potential Adsorbent," M.Sc., Chemical Engineering Department, Universiti Tunku Abdul Rahman (UTAR), Perak, Malaysia, 2019.

[39] R. Krishnamoorthy, B. Govindan, F. Banat, V. Sagadevan, M. Purushothaman, and P. L. Show, "Date pits activated carbon for divalent lead ions removal," *Journal of Bioscience and Bioengineering*, vol. 128, no. 1, pp. 88-97, 2019/07/01/ 2019, https://doi.org/10.1016/j.jbiosc.2018.12.011

[40] M. Azam, S. M. Wabaidur, M. R. Khan, S. I. Al-Resayes, and M. S. Islam, "Heavy Metal Ions Removal from Aqueous Solutions by Treated Ajwa Date Pits: Kinetic, Isotherm, and Thermodynamic Approach," *Polymers*, vol. 14, no. 5, p. 914, 2022, https://doi.org/10.3390/polym14050914

[41] A. A. H. Faisal, Z. S. Nassir, H. M. Rashid, O. A. Al-Hashimi, A. Shubbar, and B. Saleh, "Neural network for modeling the capture of lead and cadmium ions from wastewater using date palm stones," *International Journal of Environmental Science and Technology*, vol. 19, no. 11, pp. 10563-10576, 2022/11/01 2022, https://doi.org/10.1007/s13762-021-03883-1

[42] M. A. Al-Ghouti, D. Da'ana, M. Abu-Dieyeh, and M. Khraisheh, "Adsorptive removal of mercury from water by adsorbents derived from date pits," *Scientific Reports*, vol. 9, no. 1, p. 15327, 2019/10/25 2019, https://doi.org/10.1038/s41598-019-51594-y

[43] A. D. Alsulaili, A. A. Refaie, and H. A. Garcia, "Adsorption capacity of activated carbon derived from date seeds: Characterization, optimization, kinetic and equilibrium studies," *Chemosphere*, vol. 313, no. 1, p. 137554, 2023/02/01/ 2023, https://doi.org/10.1016/j.chemosphere.2022.137554

[44] M. Azam, S. M. Wabaidur, M. R. Khan, S. I. Al-Resayes, and M. S. Islam, "Removal of Chromium(III) and Cadmium(II) Heavy Metal Ions from Aqueous Solutions Using Treated Date Seeds: An Eco-Friendly Method," *Molecules*, vol. 26, no. 12, p. 3718, 2021, https://doi.org/10.3390/molecules26123718

[45] G. Z. Qu, H. B. Ji, R. Xiao, and D. L. Liang, "Effect of Modification with Nitric Acid and Hydrogen Peroxide on Chromium (VI) Adsorption by Activated Carbon Fiber," *Advanced Materials Research*, vol. 518-523, no. 1, pp. 2099-2103, 2012, https://doi.org/10.4028/www.scientific.net/AMR.518-523.2099

[46] M. A. Khan *et al.*, "Unary and binary adsorption studies of lead and malachite green onto a nanomagnetic copper ferrite/drumstick pod biomass composite," *Journal of Hazardous Materials*, vol. 365, no. 1, pp. 759-770, 2019/03/05/ 2019, https://doi.org/10.1016/j.jhazmat.2018.11.072

[47] P. Doondani, D. Panda, V. Gomase, K. R. Peta, and R. Jugade, "Novel Chitosan-ZnO nanocomposites derived from Nymphaeaceae fronds for highly efficient removal of Reactive Blue 19, Reactive Orange 16, and Congo Red dyes," *Environmental Research*, vol. 247, no. 1, p. 118228, 2024/04/15/ 2024, https://doi.org/10.1016/j.envres.2024.118228

[48] T. K. Trinh and L. S. Kang, "Application of Response Surface Method as an Experimental Design to Optimize Coagulation Tests," *Environmental Engineering Research*, vol. 15, no. 2, pp. 63-70, 6 2010, https://doi.org/10.4491/eer.2010.15.2.063

[49] D. T. C. Nguyen, D.-V. N. Vo, T. T. Nguyen, T. T. T. Nguyen, L. T. T. Nguyen, and T. V. Tran, "Optimization of tetracycline adsorption onto zeolitic–imidazolate framework-based carbon using response surface methodology," *Surfaces and Interfaces*, vol. 28, no. 1, p. 101549, 2022/02/01/ 2022, https://doi.org/10.1016/j.surfin.2021.101549

[50] M. Hosseinpour, M. Soltani, A. Noofeli, and J. Nathwani, "An optimization study on heavy oil upgrading in supercritical water through the response surface methodology (RSM)," *Fuel*, vol. 271, no. 1, p. 117618, 2020/07/01/ 2020, https://doi.org/10.1016/j.fuel.2020.117618

[51] Z. A. Solangi, I. Bhatti, and K. Qureshi, "A Combined CFD-Response Surface Methodology Approach for Simulation and Optimization of Arsenic Removal in a Fixed Bed Adsorption Column," *Processes*, vol. 10, no. 9, p. 1730, 2022, https://doi.org/10.3390/pr10091730

[52] R. Surkatti, M. H. Ibrahim, and M. H. El-Naas, "Date pits activated carbon as an effective adsorbent for water treatment," in *Sorbents Materials for Controlling Environmental Pollution*, A. Núñez-Delgado Ed. Lugo, Spain: Elsevier, 2021, ch. 7, pp. 135-161. https://doi.org/10.1016/B978-0-12-820042-1.00007-9

[53] M. Amin, A. Alazba, and M. Shafiq, "Batch and fixed-bed column studies for the biosorption of Cu (II) and Pb (II) by raw and treated date palm leaves and orange peel," *Global NEST Journal*, vol. 19, no. 3, pp. 464-478, 2017.

[54] L. Mouni, D. Merabet, A. Bouzaza, and L. Belkhiri, "Removal of Pb2+ and Zn2+ from the aqueous solutions by activated carbon prepared from Dates stone," *Desalination and Water Treatment*, vol. 16, no. 1-3, pp. 66-73, 2010/04/01 2010, https://doi.org/10.5004/dwt.2010.1106

إزالة أيونات النحاس والزنك المعدنية من النفايات السائلة الصناعية في وضع مستمر باستخدام نوى التمر المعدلة: طريقة صديقة للبيئة

هدى عبد المهدي محسن [١] ، علاء نور غانم [١، *]

١ قسم الهندسة الكيمياوية، كلية الهندسة، جامعة بابل، بابل، العراق

الخلاصة

خضعت المواد الماصة المعتمدة على الكتلة الحيوية الزراعية لعدة تحقيقات في السنوات الأخيرة بسبب تكلفتها المنخفضة وقدراتها الواعدة على الامتزاز. يهدف هذا البحث إلى بيان كفاءة نواة التمر المعدلة ببيروكسيد الهيدروجين ككتلة حيوية زراعية في استخلاص المعادن الثقيلة من المياه الملوثة في نظام الجريان المستمر العمودي. تبلغ مساحة سطح المادة المازة المشتقة (278.18) م^{٢}/جم. تم فحص المادة الممتزة المشتقة في ظل معلمات تشغيل متغيرة بما في ذلك معدل التدفق (٤–١٢) مل/دقيقة، ودرجة الحموضة (٤–١٠)، وتركيز أيون المعدن الأولي (٣٠–٦٠) ملجم/لتر، ودرجة الحرارة (٢٠–٥٠) درجة C .لتحديد تأثيرها على كفاءة امتصاص المعادن الثقيلة. تم استخدام التصميم التجريبي RSM لإنشاء مجموعة من التجارب المبنية باستخدام برنامج Design-Expert لتحليل البيانات بأقل قدر من التجارب. تم اكتشاف أن RSM هي تقنية مفيدة للغاية لتحسين معلمات امتزاز المعادن. في الواقع، كشف تحليل التباين (ANOVA) عن وجود معامل انحدار مرتفع، أو R2> 0.90 ، مما يدعم ملاءمة النموذج بشكل جيد مع البيانات التجريبية. علاوة على ذلك، تأثرت كفاءة الإزالة بشكل إيجابي من خلال تقليل تركيز الأيون الأولي ومعدل التدفق ودرجة الحرارة. ومع ذلك، يظهر الرقم الهيدروجيني أقصى قدر من الفعالية في الحالة المحايدة. بشكل عام، يظهر امتزاز النحاس (II) تقارب أعلى للامتصاص على سطح MDP مقارنة بالزنك .(II) أظهرت الممتزات MDP كفاءة إزالة واعدة للأيونات المعدنية وهناك حاجة إلى مزيد من التحقيقات.

الكلمات الدالة: المعادن الثقيلة، الامتزاز، مفاعل الطبقة الثابتة، نوى التمر، مياه الصرف الصحي.