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FACILE ULTRASONIC-ASSISTED ZIF-67 SYNTHESIS AND USE IN PHENOL REMOVAL FROM AQUEOUS SOLUTIONS

BASIT ULTRASONIK-DESTEKLI ZIF-67 SENTEZI VE SULU ÇÖZELTILERDEN FENOLÜN UZAKLAŞTIRILMASINDA KULLANIMI

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ABSTRACT

Recently, water-stable ZIF MOFs, a new material class with a very large surface area, have attracted attention for the removal of organic pollutants. This type of MOF's excellent adsorption capacities, large pore volumes, and recyclability performances stand out compared to many other adsorbents. In this work, the ZIF-67 structure, a cobalt-containing ZIF, was synthesized using the ultrasound-assisted solvothermal method, and its phenol adsorption performance was investigated. The characterization of the ZIF-67 structure was carried out by SEM-EDS, XRD, FTIR, and nitrogen adsorption analyses. Nitrogen adsorption data showed that ZIF-67 had microporosity, and the surface area calculated from the BET model was 1656 m^2/g. To synthesize ZIF-67, optimization of phenol adsorption, one of the important pollutants in water, was investigated by response surface method (RSM) for initial phenol concentration, adsorbent concentration, pH, and temperature variables. At the operating levels determined by RSM, the most effective removal of 92.2% was obtained at 30°C, 1 g/L adsorbent concentration, 20 mg/L initial phenol concentration, and pH 6.5. The adsorption isotherm of phenol onto ZIF-67 was fit to the Langmuir model, which is a monolayer interaction. According to the Langmuir isotherm model, the maximum phenol adsorption capacity of ZIF-67 was determined as 303.0 mg/g.

Keywords: Experimental design, phenol adsorption, zeolitic imidazole framework, ultrasonic-assisted synthesis

ÖZET

Oldukça geniş yüzey alanına sahip yeni bir malzeme sınıfı olan suya dayanıklı ZIF MOF'lar, organik kirleticilerin uzaklaştırılması konusunda son yıllarda dikkat çekmektedir. Bu tip MOF'ların mükemmel adsorpsiyon kapasiteleri, geniş gözenek hacimleri ve geri dönüştürülebilirlik performansları diğer birçok adsorbanla karşılaştırıldığında öne çıkmaktadır. Bu çalışmada da kobalt içerikli bir ZIF yapısı (ZIF-67) ultrasonik destekli solvotermal yöntem kullanılarak sentezlendi ve fenol adsorpsiyon performansı araştırıldı. Sentezlenen ZIF yapısının karakterizasyonu SEM-EDS, XRD, FTIR ve nitrojen adsorpsiyon analizleri ile gerçekleştirildi. Azot adsorpsiyon verileri, ZIF-67'nin mikro gözenekliliğe sahip olduğunu ve Brauner Emmet Teller (BET) modelinden hesaplanan yüzey alanının 1656 m^2/g olduğunu gösterdi. ZIF-67'yi sentezlemek için sudaki önemli kirleticilerden biri olan fenol adsorpsiyonunun optimizasyonu, başlangıç fenol derişimi, adsorbent derişimi, pH ve sıcaklık değişkenleri için yanıt yüzey yöntemi (RSM) ile araştırıldı. RSM ile belirlenen çalışma seviyelerinde %92,2'lik en etkili giderim 30°C'de, 1 g/L adsorban derişiminde, 20 mg/L başlangıç fenol derişiminde ve pH 6,5'te elde edildi. Fenolün ZIF-67 üzerine adsorpsiyon izotermi, tek katmanlı bir etkileşim olan Langmuir modeline uyuyordu. Langmuir izoterm modeline göre ZIF-67'nin maksimum fenol adsorpsiyon kapasitesi 303,0 mg/g olarak belirlendi.

Anahtar Kelimeler: Deneysel tasarımı, Fenol adsorpsiyonu, Zeolitik imidazol kafesler, Ultrasonik destekli sentez

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INTRODUCTION

Metal-organic frameworks (MOFs) are a new type of nanoporous crystalline material constructed by metal ions (or metal nodes) and organic binders. They have shown great potential as materials for gas separation and storage, sensing, catalysis, and biomedicine due to their large surface area, adjustable pore size, and good physicochemical characteristics. Zeolitic imidazole frameworks (ZIF) are also a subset of MOFs that are topologically similar to zeolites. ZIFs have an anionic structure as opposed to MOFs' neutral structures. It is the extra cage ions that balance the negative charge in their structure, and ion exchange occurs thanks to these ions (Czaja et al., 2009; C. Duan et al., 2022). Because they can maintain chemical stability in a humid environment, unlike many MOFs, they have potential applications in areas like heterogeneous catalysis, separation processes, and sensors in aqueous mediums.

ZIFs constitute a distinct and intriguing subclass of porous MOFs, consisting of imidazolate ligands and tetrahedral metal cations (M ¼ Zn or Co) (Qian et al., 2012; C. Duan et al., 2022). For the synthesis of ZIFs, several synthesis methods have been developed. The principal techniques include Sono-chemical, Electrochemical, Mechano-chemical, Solvo-thermal, Hydro-thermal, and Microwave methods (Kalauni et al., 2022). Reaction time, temperature, pressure, solvent type, starting material ratio, and initial pH are crucial parameters to consider when using MOF synthesis techniques (Czaja et al., 2009). In terms of the applicability of MOFs, it is also desired that the synthesis be environmentally friendly and economical. Producing MOFs quickly and with minimal harm to the environment is possible with sonochemically-assisted synthesis.

Phenol is an organic compound that is discharged from wastewater from various industries, including the coal processing, petrochemical, pharmaceutical, polymeric resin, and pesticide industries (Xie et al., 2020). It belongs to the class of organic compounds that are toxic and can lead to either acute or chronic illnesses (Gundogdu et al., 2012). Serious problems with the environment and human health can result from even very low concentrations of phenol in water. Furthermore, the potential for phenol to convert into more harmful substances through interactions with other compounds is considered a significant concern, in addition to its inherent toxicity (Gundogdu et al., 2012). International regulatory agencies do not want low levels of phenol in surface waters because of this.

MOFs have been extensively researched for their potential to remove a variety of dangerous organic compounds, including dyes, pesticides, and aromatic hydrocarbons (G. Liu et al., 2018; Dai et al., 2021; Kouser et al., 2022; Garg & Sabouni, 2023). In this study, the phenol adsorption ability of the ZIF-67 synthesized was examined. The effect of process variables on phenol removal, such as temperature, initial phenol concentration, adsorbent dose concentration, and pH, was investigated with the response surface method face-centered composite design. The isotherms of phenol to ZIF-67 were examined to determine the adsorption mechanism. Facile and rapid ultrasonic-assisted synthesis of ZIF-67 structure is a relatively new technique. This study, in which the characterization of the synthesized ZIF-67 is presented and its phenol removal performance is evaluated, will contribute to the literature for studies in these areas.

MATERIALS AND METHODS

ZIF-67 Synthesis

In the synthesis of the ZIF-67 structure, 2-methylimidazole (MeIM) was used as the linker, cobalt nitrate salt as the metal source, and ultrapure water as the solvent. For the synthesis of ZIF structures, 2 mmol of $Co(NO_3)6H_2O$ (Sigma Aldrich, 99%) salt and 2 mmol of MeIM (Acros-Organics, 99%) were mixed in 50 mL of ultrapure water until a clear solution was obtained. It was kept in an ultrasonic bath for 30 minutes and then in an oven at 80 °C for 2 hours. At the end of the period, the mixture was centrifuged, washed several times with water, and dried in methanol in a vacuum oven kept at room temperature.

Characterization of ZIF-67

The synthesized ZIF-67 structure was characterized by scanning electron microscopy- energy dispersive X-ray spectroscopy (SEM-EDS), X-ray diffraction (XRD), Fourier-transform infrared analysis (FTIR), and nitrogen adsorption measurements. The SEM images and chemical analysis of ZIF-67 were recorded with a Zeiss Supra 55 field emission instrument (Carl Zeiss, Germany). The XRD pattern was obtained using a Rigaku Smartlab model XRD (Japan) at Cu-Kα radiation (λ = 1.54 Å). The analysis was carried out in continuous scans from 2° to 50° at a scan rate of 2 theta min−1. The FTIR spectra were recorded with the MIR mode at room temperature by accumulating 10 scans at a 1 cm^{-1} resolution in the 4000–400 cm−1 region by a Perkin Elmer/MIR spectrometer with a Pike Technologies Gladi ATR accessory. The nitrogen adsorption isotherm was analysed at 77 K using a Micromeritics

Tristar Orion II 3020 surface area and porosimetry analyzer (Micromeritics, Norcross, USA). The sample was degassed at 573 K for 12 h using a sample degas system (Micromeritics VacPrep 061, Norcross, USA) before N2 adsorption measurement. Density functional theory (DFT), Barrett-Joyner-Halenda (BJH), t-plot, Langmuir, and Brunauer-Emmett-Teller (BET) models were employed to analyze the surface properties based on the resulting isotherms.

Phenol Adsorption Experiments

The face-centered central composite design (FCCD) model was utilized in the design of adsorption experiments to extract phenol from water using the synthesized ZIF-67. The experimental design was created at 3 levels for 4 independent variables temperature (A), adsorbent concentration (B), initial phenol concentration (C), and pH (D). Phenol removal (%) adsorption was determined as a response. Table 1 includes independent variables, codes, and levels for the used model design.

Table 1. Face-Centred Central Composite Design Variables, Codes, and Levels

Variables, unit	Codes	Levels		
Temperature, (°C)	A	-1	0	+1
Initial Phenol concentration, (mg/L)	B	-1	0	+1
Adsorbent concentration, (g/L)	C	-1	0	+1
pH	D	-1	0	+1

Experiments on phenol adsorption were conducted in a 250 mL erlenmayer with a 100 mL working volume. The desired initial phenol concentration (Ci) was prepared by diluting the 200 mg phenol/L solution. In preliminary studies, the equilibrium time was determined to be 120 minutes. The concentration of phenol in the aqueous solution was detected using a gas chromatography flame ionization detector (GC-FID Agilent 6890A). GC-FID was equipped with a polyethylene glycol column (HP-Innowax, 30m x 0.25 mm x 0.25 µm) and an autosampler. The GC-FID working parameters were: inlet temperature, 250 °C; carrier gas, Helium; oven conditions, isocratic 170 °C for 10 min; injection mode, 1/10 split; injection volume, 1.0 µL; detector temperature, 270 °C. In the analysis, benzyl alcohol (Benzyl alcohol; 99%) was used as an internal standard, analytical grade phenol (Sigma-Aldrich; 99.5%) was used as a reference, and acetone was used for dilutions. The calibration curve was created to be between 20-100 mg/L. The phenol (%) removal was calculated with Equation 1.

$$Removal\ of\ phenol\ (R,\%) = \frac{C_i - C_e}{C_i} x100 \quad (1)$$

where Ci and Ce are the initial and equilibrium phenol concentrations, respectively.

RESULTS AND DISCUSSION

Characterization

The morphology of ZIF-67 synthesized with ultrasonic support was first clarified by SEM and EDX analyses. Figure 1a, the image of the SEM of ZIF-67, shows that the ZIF-67 crystals are in a polyhedral shape with sizes about 1µm. ZIF-67 crystal structures with similar shapes and different sizes have been reported in the literature (Qin et al., 2017; Wu et al., 2016). It may be concluded that for ZIF-67, a compound with the chemical formula, the element distribution is consistent. EDS analysis for ZIF-67, a compound with the chemical formula $C_{24}H_{30}Co_3N_{12}O_2$, shows that the elemental distribution is consistent.

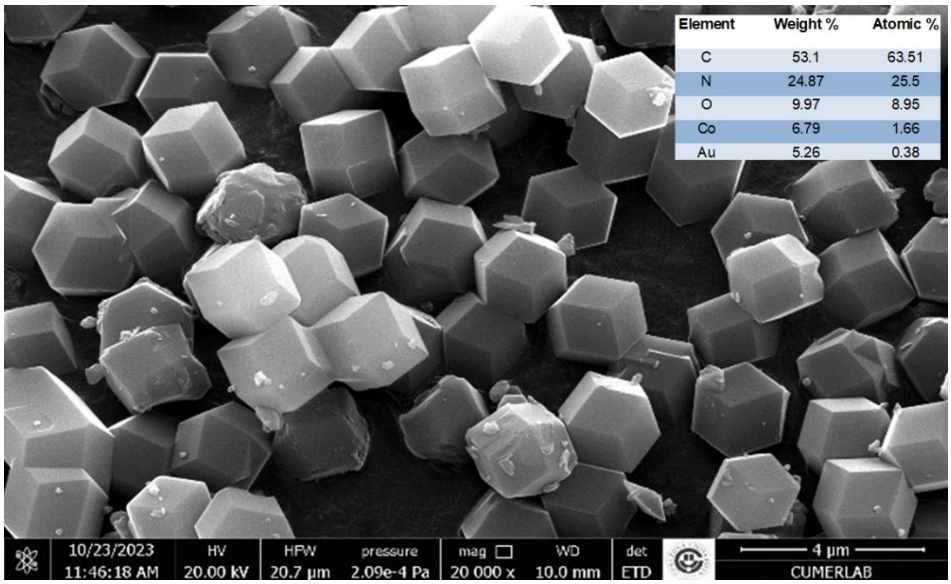

Figure 1. SEM Image and EDS Analysis of ZIF-67

Figure 2 shows the XRD pattern and FTIR spectrum of the as-synthesized ZIF-67. When the XRD pattern of the ZIF-67 structure given in Figure 2a was compared with the simulated model given in the literature, it was observed that the product was compatible with pure ZIF-67 (J. Qian et al., 2012; L. Qian et al., 2018; S. Duan et al., 2024). The ZIF-67 structure contains many diffraction peaks in the range of 2–40° in the 2θ. Selectable diffraction peaks 2θ=7.3°, 10.3°, 12.7°, 14.7°, 16.4°, 18.0°, 22.1°, 24.5°, 26.6°, 29.6°, 30.5°, and 32.3° crystal planes are fully compatible (0 1 1), (0 0 2), (1 1 2), (0 2 2), (0 1 3), (2 2 2), (1 1 4), (2 3 3), (1 3 4), (0 4 4), (2 4 4), and (2 3 5), respectively. Analysis of the surface functional groups of the ZIF-67 structure was evaluated by FTIR analysis in Figure 2b. The peaks at 2922 cm^{-1} and 3135 cm^{-1} in the FTIR spectrum of the ZIF-67 structure are due to the stretching vibration of the aliphatic C-H and O-H of MeIM, respectively. The peak at 1581 cm^{-1} results from the C=N ligand. The peak at 1422 cm^{-1} indicates the C-C group from MeIM. The peak of 424 cm^{-1} corresponds to the successful complexation of cobalt ions with imidazole (L. Qian et al., 2018; S. Duan et al., 2024). Briefly, the FTIR spectrum of the ZIF-67 structure synthesized in this study shows that MeIM and Co ions are successfully coordinated and coincide with the studies given in the literature for ZIF-67.

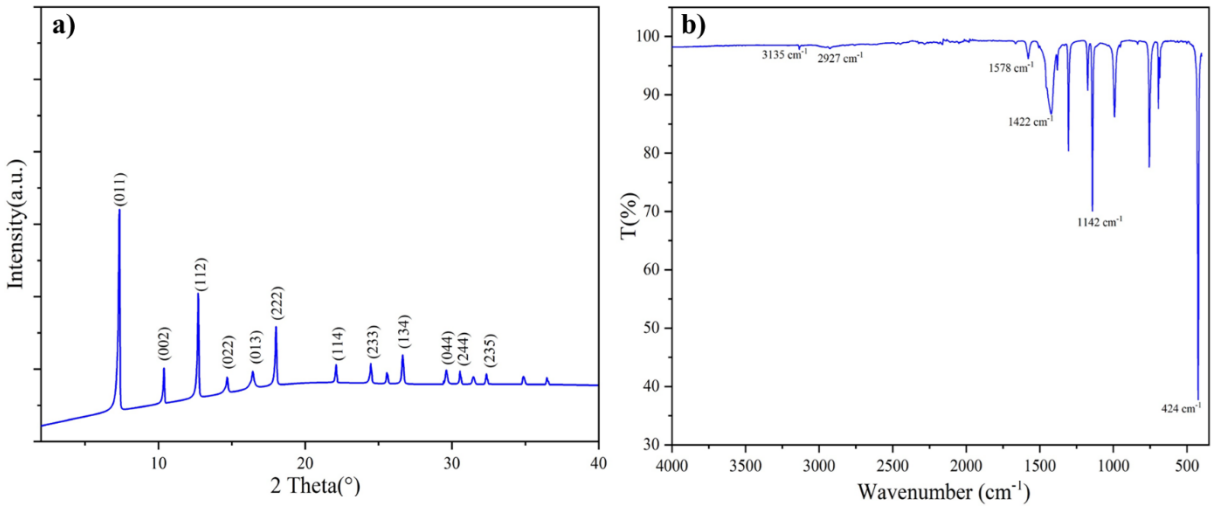

Figure 2. a. XRD Pattern and b. FTIR Spectrum of ZIF-67

The characterization of the surface properties of ZIFs is very important for adsorption and catalysis applications. The nitrogen adsorption isotherm created to determine the textural properties of the synthesized ZIF-67 structure, such as surface area and porosity, is shown in Figure 3. It can be seen from Figure 3 that the ZIF-67 adsorption isotherm is quite similar to the Type 1 isotherm type. This shows that the structure has microporosity. Moreover, the inset graph in Figure 3 shows that ZIF-67 has a narrow pore size distribution according to the nonlocal density functional theory (NLDFT) method.

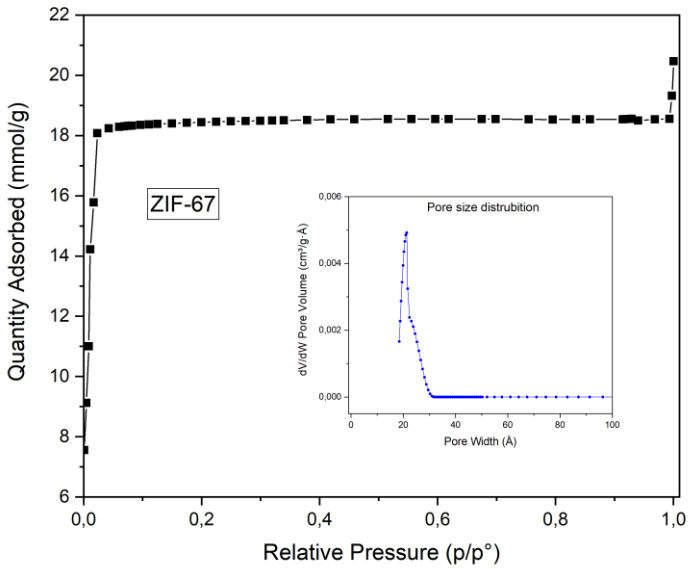

Figure 3. Nitrogen Adsorption Isotherm and Pore Size Distribution Plot (Inset) of ZIF-67

Table 2 displays the ZIF-67 structure's surface characteristics, such as specific surface area, micropore volume, pore size, and pore volume. BET and Langmuir models calculated ZIF-67's surface area to be 1656 m^2/g and 1813 m^2/g, respectively. The results showed that the maximum porous volume was 0.643 cm^3/g, and the microporous volume was 0.632 cm^3/g. The t-plot model's calculation of the micropore surface area is extremely close to the total surface area, indicating that microporosity is the predominant porosity. The pore size value of 1.08 nm calculated by BJH confirms the microporosity of the synthesized ZIF-67. The microporosity and specific surface area of ZIF-67 were consistent with other studies of ZIF-67 produced by different synthesis techniques (J. Qian et al., 2012; Pan et al., 2016; Nguyen Thi Thanh Tu et al., 2019).

Table 2. The Experimental Results of BET Surface Area, Average Pore Diameter, Maximum Pore Volume, and Particle Size of ZIF-67

	S_{BET} (m^2/g)	$S_{Langmuir}$ (m^2/g)	Average pore size[a] (nm)	Maximum Pore Volume[b] (cm^3/g)	t- plot micro pore volume (cm^3/g)	t-plot micro pore area m^2/g
ZIF-67	1656	1813	1.08	0.643	0.632	1643

[a]Barrett-Joyner-Halenda (BJH) adsorption model, [b] Horvath-Kawazoe model at P/P^0 = 0.929

Adsorption Experiments

Adsorption isotherms

The adsorption mechanism of phenol onto ZIF-67 can be analyzed with adsorption isotherms created using adsorption equilibrium data. The two most widely used sorption models, the Langmuir isotherm model and the Freundlich isotherm model were applied to investigate the phenol's adsorption onto the ZIF-67 structure. The assumption that adsorption is a monolayer is the foundation of the Langmuir isotherm. The saturated adsorption capacity can be computed in this manner. The following equation shows the Langmuir model in its linear form Equation 2:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (2)$$

where qe is the equilibrium adsorption capacity (mg/g), K_L is the Langmuir constant related to the sorption energy, Ce is the equilibrium phenol concentration (mg/L), and qmax is the maximum amount of phenol per unit weight of ZIF-67 (mg/g) to form a complete monolayer on the surface.

The concept, based on the Freundlich isotherm, assumes that adsorption on a heterogeneous surface is not uniform but is the result of a multilayer process. The linear form of the Freundlich isotherm model is a line equation with shift ln K_F and slope 1/n. Freundlich isotherm constants are found from the log C_e versus log q_e graph according to Equation 3:

$$\log q_e = log\ K_{F+} \frac{1}{n} log C_e \quad (3)$$

Adsorption isotherms were investigated at concentrations ranging from 20 to 100 mg phenol/L, a constant adsorbent concentration of 1 g/L, and 30 °C. Table 3 presents the linearized isotherm data for both models along with the calculated model constants (K_L, K_F, and n) and correlation coefficients (R^2). Many studies on phenol adsorption have suggested that adsorption data fit these two models, indicating a mixed adsorption behavior. When the correlation coefficients (R^2) are compared, the higher value of the Langmuir model results in it being more suitable than the Freundlich model. This indicated that the adsorption of phenol took place in a monolayer within the specified working range of phenol concentration. Stated differently, ZIF-67 exhibited a uniform phenol adsorption interface. The maximum phenol adsorption capacity value of 303.0 mg/g determined by the Langmuir isotherm for ZIF-67 was noteworthy.

Table 3. The Constants for the Langmuir and Freundlich Isotherms

Isotherms	Constans	Value
Langmuir	R^2	0.991
	K_L (L/g)	0.028
	q_{max} (mg/g)	303.0
Freundlich	R^2	0.985
	K_F(mg/g) $(L/mg)^{-n}$	193.5
	n	1.219

The phenol adsorption capacity for ZIF-67 was determined as 303.0 according to the Langmuir model at initial concentrations ranging from 20 to 100 mg/L. Phenol adsorption capacities of some adsorbents are summarized in Table 4. Table 4 shows that ultrasonic-assisted synthesized ZIF-67 was prominent in phenol adsorption.

Table 4. The Phenol Adsorption Capacity of Some Adsorbents

Adsorbents	q_{max} (mg/g)	References
Commercial AC	212.9	Xie et al., 2020
MIL-53(Cr)	398.0	Maes et al., 2011
Coconut magnetic AC	116.0	Gonçalves Júnior et al. 2022
Activated Clay	18.9	Djebbar et al. 2012
Functional chitosan	131.5	Li et al. 2009
Modified granular coconut AC	143.0	Desmiarti et al. 2019
Sugarcane bagasse AC	42.9	Mohtashami et al. 2018
Activated carbon fibers	110.2	Liu et al. 2010
Oily sludge AC	434.0	Mojoudi et al. 2019
Alkaline modified olive stone AC	500.0	Nouha et al. 2019
Ultrasonic assisted ZIF-67	303.0	This work

Effects of variables on the phenol adsorption

In this section, the effect of parameters such as temperature 20-40 °C (A), adsorbent concentration 0.5-1.5 g/L (B), initial phenol concentration 20-100 mg/L (C), and pH 4-9 (D) on the phenol adsorption process was investigated

using the face-centered central composite design (FCCD). The following Equation 4 was used to determine the number of experiments based on the k factor: where k and cp (6) represent the factor and the center point numbers, respectively.

$$N = 2^k + 2k + 6 \quad (4)$$

Phenol removal (%) was chosen as the answer, and the statistical model suggested 30 experiments, as seen in Table 5. The data provided suggests that the most effective removal efficiency achieved was 92.2% at a temperature of 30°C, an adsorbent concentration of 1 g/L, an initial phenol concentration of 20 mg/L, and a pH of 6.5.

Table 5. Experimental Design and Responses.

Run	A: Temperature	B: Adsorbent Concentration	C: Initial Phenol Concentration	D: pH	Removal phenol
	°C	g/L	mg/L		%
1	30	1	100	6.5	84.7
2	40	0.5	20	9	72.3
3	20	0.5	100	9	58.5
4	30	1	20	6.5	92.2
5	30	1	60	6.5	85.8
6	30	1	60	6.5	86.1
7	20	0.5	20	9	54.6
8	30	1	60	6.5	85.9
9	20	1.5	20	9	84.5
10	20	1.5	20	4	83.4
11	40	0.5	20	4	74.6
12	30	1	60	9	81.6
13	20	1.5	100	4	90.1
14	40	0.5	100	9	54.7
15	20	1.5	100	9	88.7
16	30	1	60	6.5	84.2
17	30	1	60	6.5	86.2
18	40	1	60	6.5	80.4
19	20	0.5	100	4	60.3
20	20	1	60	6.5	82.6
21	40	1.5	100	4	72.6
22	40	1.5	100	9	74.2
23	30	1	60	4	80.3
24	30	1	60	6.5	85.7
25	40	1.5	20	4	88.7
26	40	1.5	20	9	86.4
27	30	0.5	60	6.5	64.6
28	20	0.5	20	4	58.7
29	40	0.5	100	4	59.2
30	30	1.5	60	6.5	88.9

Statistical Model Fit Summary (used Design-Expert 11 software) suggested that phenol removal by ZIF-67 fit the quadratic model (Table 6). There is a reasonable agreement between the adjusted R^2 of 0.9892 and the predicted R^2 of 0.9700; there is a less than 0.2 difference.

Table 6. Statistical Fit Summary

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0.0001	< 0.0001	0.5217	0.3687	
2FI	0.1898	< 0.0001	0.5856	0.0448	
Quadratic	**< 0.0001**	**0.0799**	**0.9892**	**0.9700**	**Suggested**
Cubic	0.5535	0.0289	0.9886	0.5170	Aliased

A statistical technique called analysis of variance (ANOVA) is employed to assess how well independent variables influence the response. ANOVA was used to assess the quality of the resulting model; the results are shown in Table 7. For phenol removal, the model's F value was found to be 189.86, indicating its significance. Generally speaking, noise accounts for 0.01% of F values. P-values below 0.05 signify the significance of the model terms. Significant model terms in this instance are B, C, D, AB, AC, BD, A^2, B^2, C, and D^2. The model terms are not significant if the values are greater than 0.1000. Consequently, the ANOVA results for the removal of phenol by adsorption on ZIF-67 suggest that the model fit. Additionally, a comparison of the experimental and projected results for the removal of phenol is shown in Figure 4. It is evident that there is a straight line connecting the experimental and model results.

Table 7. ANOVA Results of the Models Obtained by FCCD

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4033.19	14	288.08	189.86	< 0.0001	significant
A-Temperature	0.1606	1	0.1606	0.1058	0.7495	
B-Adsorbent Concentration	2222.22	1	2222.22	1464.55	< 0.0001	
C-Phenol Concentration	152.54	1	152.54	100.53	< 0.0001	
D-pH	8.54	1	8.54	5.63	0.0315	
AB	178.89	1	178.89	117.90	< 0.0001	
AC	377.33	1	377.33	248.68	< 0.0001	
AD	0.1056	1	0.1056	0.0696	0.7955	
BC	6.38	1	6.38	4.20	0.0583	
BD	8.56	1	8.56	5.64	0.0313	
CD	0.1406	1	0.1406	0.0927	0.7650	
A^2	33.92	1	33.92	22.36	0.0003	
B^2	181.44	1	181.44	119.58	< 0.0001	
C^2	28.76	1	28.76	18.95	0.0006	
D^2	45.02	1	45.02	29.67	< 0.0001	
Residual	22.76	15	1.52			
Lack of Fit	20.07	10	2.01	3.72	0.0799	not significant
Pure Error	2.70	5	0.5390			
Cor Total	4055.95	29				

The obtained model-fit equation for phenol adsorption was shown in model Equation 5. Model Equation 5 shows that variables A and B have a positive effect on phenol elimination, but variables C and D have a negative effect. The magnitudes of the coefficients of the equation indicate that B (adsorbent concentration) for phenol removal is the most effective variable.

$$Y_{R(\%)}=0.094A+11.11B-2.91C-0.689D-3.34AB-4.86AC-0.081AD+0.631BC+0.731BD+ 0.094CD-3.62A^2-8.37B^2+3.33C^2-4.17D^2+85.38 \quad (5)$$

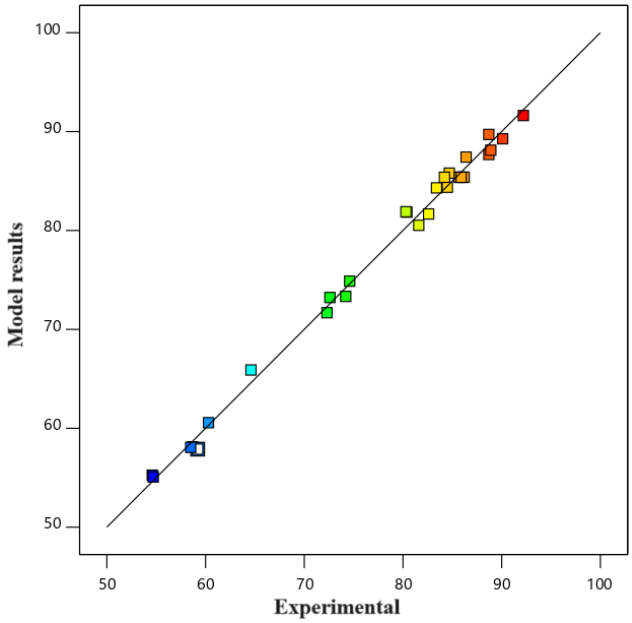

Figure 4. Comparison of Experiment and the FCCD Model Results for Phenol Adsorption Onto ZIF-67

Interactive effect of variables on phenol adsorption

The interactive effect of adsorbent concentration, which is the most important variable for phenol adsorption with ZIF-67, with other variables has been shown by the response surface 3D graphs (Figure 5-a-c) in the experimental range. These graphs allow for the prediction of the interactive influence of independent variables on the response to phenol removal. The interaction effect of temperature and adsorbent concentration on the percentage of phenol removed is shown in Figure 5a, with an initial phenol concentration of 60 mg/L and pH of 6.5. It can be seen from Figure 5a that phenol removal increases significantly as the adsorbent concentration changes from 0.5 g/L to 1.5 g/L at 20 °C. The highest phenol removal is achieved at 1.5 g/L adsorbent concentration and 20 °C temperature. On the contrary, at 40 °C, as the adsorbent concentration changed from 0.5 g/L to 1.5 g/L, phenol removal increased until 1.0 g/L and then decreased. The most likely reason for this result is that as the adsorbent concentration increases at this temperature, due to the agglomeration of the adsorbent, the active adsorption sites decrease, or the passage of phenol molecules to the active sites is prevented. The interaction effect of the initial phenol concentration and the adsorbent concentration on the phenol adsorption percentage is displayed in Fig. 5b at constant temperature (30 °C) and pH (6.5). It can be seen in Figure 5b that phenol adsorption percentage increases significantly with increasing adsorbent concentration at low (20 mg/L) and high (100 mg/L) initial phenol concentrations. According to the graph in Figure 5b, the highest phenol removal percentage occurred at the initial phenol concentration of 20 mg/L, and the phenol removal percentage decreased slightly in the 60 mg/L phenol initial concentration region. The interaction effect of the pH and the adsorbent concentration on the phenol adsorption percentage is displayed in Fig. 5c at constant temperature (30 °C) and initial phenol concentration (60 mg/L). It can be seen in Figure 5c that the most effective phenol adsorption percentage occurs at neutral pH. This result may have been caused by the occupation of the active sites of the adsorbent under alkaline and acidic conditions.

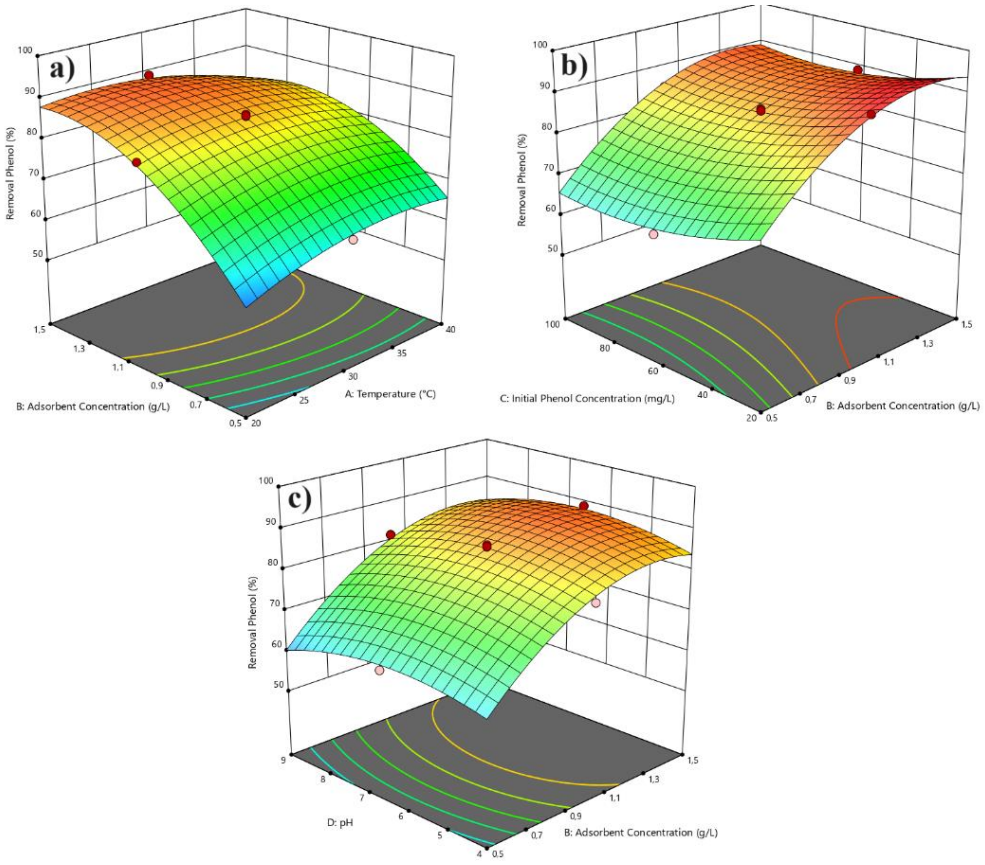

Figure 5. 3D Surface Graph of the Interaction Effects: **a** Temperature (°C) and Adsorbent Concentration(g/L), **b** Adsorbent Concentration(g/L) and Initial Phenol Concentration (mg/L), **c** Adsorbent Concentration (g/L) and pH

CONCLUSION

This study investigated the adsorptive removal of phenol, a dangerous pollutant in water, by ZIF-67, which was synthesized in a simple and environmentally friendly manner. ZIF-67 was synthesized time using the ultrasonically assisted hydrothermal method in a very short, and its characterization was accomplished. SEM images showed that the synthesized ZIF structure consisted of uniform polyhedral structures with a size of 1 µm. The XRD pattern of ZIF-67 was quite consistent with the literature. The adsorption isotherm showed that the ZIF-67 structure is microporous. The effects of variables such as temperature, adsorbent concentration, initial phenol concentration, and pH on the adsorption of phenol on ZIF-67 were investigated with the experimental program created with FCCD. ANOVA findings showed that the most effective variable was the adsorbent concentration. The adsorption mechanism of phenol on the ZIF-67 was investigated by Langmuir and Freundlich models. Experimental data revealed that the phenol adsorption on the ZIF-67 is compatible with the Langmuir model, and the maximum adsorption capacity of the ZIF-67 is 303.3 mg/g. As a result, it has been shown that the ZIF-67 structure synthesized in this study has notable potential for phenol adsorption. The data presented in this study may provide some preliminary information on the adsorption of phenol and similar organics by ZIF-67. Advanced environmental and economic studies are needed to evaluate this study for further application.

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