



Optimization of the Removal of Toluene in the Air by Activated Carbon / ZIF-8 Metal-Organic Framework

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ABSTRACT

In this research, the objective was to optimize the operating conditions for removing toluene from the air stream using a composite of activated carbon (AC) and ZIF-8 metal-organic framework (MOF). The experimental design involved defining the input variables (type of adsorbent, mass of adsorbent, air flow rate, temperature, and relative humidity) and response variables (adsorption capacity and breakthrough time). The study consisted of six steps: 1) synthesis of ZIF-8 MOF and AC@ZIF-8 composite, 2) creation of the experimental design using Central Composite Design (CCD), 3) structural analysis tests, 4) experimental runs, 5) statistical analysis, and 6) experimental verification tests. The 2FI model was determined to be the most suitable for predicting adsorption capacity and breakthrough time. The optimized run achieved a toluene inlet concentration of 300 ppm, AC@ZIF-8 as the adsorbent type, an air temperature of 27 °C, air relative humidity of 29%, adsorbent mass of 9 mg, and an airflow rate of 250 ml/min. The breakthrough time for 100% composite utilization was 18.6 hours. The results of toluene adsorption using AC@ZIF-8 showed a 50% higher breakthrough time and adsorption capacity compared to the other two adsorbents (AC and ZIF-8). In conclusion, the AC@ZIF-8 composite is well-suited for efficiently removing and adsorbing toluene from the air stream. Considering the high cost of MOF synthesis and the limitations of activated carbon in selectively removing volatile organic compounds, the AC@ZIF-8 composite can be a viable option for air adsorption and purification processes.

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INTRODUCTION

The process of industrialization has exacerbated the environmental crisis through pollution from industries, posing a serious threat to human health and survival. Volatile organic compounds (VOCs) are well-known carcinogenic pollutants that also contribute to environmental issues such as photochemical smog and particulate matter (Ma et al., 2021). Monocyclic aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylene (BTEX), are a group of volatile organic compounds produced by sources such as refineries, petrochemical industries, oil and gas extraction fields, and paint and adhesive industries. Even in low concentrations, these compounds can cause significant health and environmental issues (Wang et al., 2021). Toluene is a liquid compound containing a benzene ring and shares similar properties with benzene, but it is less volatile. It is used as a solvent in the creation of paints, polishes, adhesives, rubber, and plastics, as well as in the production of various chemical compounds across many industries

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(Alaei et al., 2022). Toluene is toxic and can cause harm to the liver and kidneys (Alaei et al., 2022). Due to toluene's wide use in various chemical industries, it is crucial to implement an effective method to control its concentration (Alaei et al., 2022). Various VOCs purification techniques, such as adsorption, photocatalysis, biodegradation, and catalytic combustion, have been explored and utilized to tackle this issue, but it remains challenging (Ma et al., 2021).

The adsorption method is a highly effective, simple, and low-cost technique that removes and recovers VOCs on a large scale (Ma et al., 2021). Different porous adsorbents, such as silica, zeolite, activated carbon, nanocomposites, and metal-organic frameworks (MOFs), are used to eliminate organic pollutants (Liu et al., 2023). Zeolitic imidazolate frameworks (ZIFs) are a type of MOF that is being considered as a replacement for adsorbent materials due to their superior porosity, thermal resistance, and larger surface area (Nazir et al., 2022). Activated carbon (AC) is a common and low-cost adsorbent with a high affinity for organic compounds. However, the lack of functional groups on its external surface can limit its practical application. Therefore, modifying its surface is crucial to improve its efficiency (Saqlain, Zhao, Kim, & Kim, 2021). Recent studies have shown that the synthesis of MOF@AC composites has a high ability to remove gaseous pollutants from the air (Vrtovec et al., 2020).

Improving a system involves either minimizing or maximizing a function that directly relates to the system's performance. This process ultimately leads to increased system efficiency. The goal of optimization is to identify the most suitable solution that meets the problem's limitations and requirements (Buragohain & Mahanta, 2008). The response surface method (RSM) is a technique used for both modeling and optimization purposes. Among the various optimization study design methods available, the Central Composite Design (CCD) is the preferred approach. RSM proves to be time and resource-saving when compared to the one agent/variable at a time (OFAT) approach. Moreover, RSM enables the efficient and interactive evaluation of the multivariate system interaction effect through the use of statistical methods (Norafizan et al., 2021).

The purpose of this study is to compare the effectiveness of different adsorbents, namely AC, ZIF-8, and AC@ZIF-8, in removing toluene from the airstream. While there have been recent studies on synthesizing composites for removing pollutants from both air and liquid environments, no research has been conducted on how experimental variables affect the adsorption capacity and breakthrough time for toluene adsorption in the AC@ZIF-8 composite. The objective of this study is to develop an optimized model for toluene adsorption. To achieve this, the response surface method was used to analyze the impact of five performance parameters (adsorbent type, adsorbent mass, air flowrate, air temperature, and air relative humidity) on the operational response of the adsorption process (adsorption capacity and breakthrough time).

MATERIALS AND METHODS

Materials

To synthesize ZIF-8 MOF, we used 2-methylimidazole (molar mass 82.11 g/mol, C₄H₆N₂) with the number 818964, zinc nitrate hexahydrate (molar mass 297.49 g/mol, Zn(NO₃)₂·6H₂O) with the number 10144, and 99.99% methanol (produced with the number 106009 from Merck Co.). For the synthesis of AC@ZIF-8 composite, we also purchased activated carbon (mass molar mass 12.01 g/mol) with Merck number 102186. Toluene (molar mass 92.14 g/mol, C₇H₈) prepared with Merck number 108325 was also used.

Synthesis of activated carbon/ZIF-8 composite

To synthesize AC@ZIF-8, 2 grams of zinc nitrate hexahydrate and 400 mg of activated carbon were stirred separately in 150 ml of methanol, while 4 g of 2-methylimidazole were stirred in another 150 ml of methanol. The stirring process for each solution lasted 180 minutes.

Subsequently, the mixture of zinc nitrate hexahydrate and activated carbon was sonicated for 30 minutes. After that, the two solutions were combined and stirred at 50°C for 140 minutes. The resulting solution was then centrifuged at a speed of 6000 rpm for 30 minutes, washed twice with methanol, and dried in an oven at 50°C for 24 hours (Parisa Mohammad-Gholikhan-Khalaj et al., 2023).

Structural characterization

To determine the type and structure of the adsorbents, as well as the crystallinity of the materials, X-ray diffraction (XRD) was utilized using a Philips/PW1730 instrument from the Netherlands. The radiation angle range of 5-80° served as the basis for analysis. The structure and type of the adsorbents were determined using Fourier Transform Infrared Spectroscopy (FTIR) with a ThermoAvatar instrument from the USA. The size and size distribution of the adsorbent particles were obtained by examining them under a field emission scanning electron microscope (FE-SEM) at a magnification of 200 nm. Furthermore, the BET analyzer (BELSORP/MINI II) from Japan was employed to determine the pore size (pore diameter) and surface area of the adsorbents.

Performance characterization

The test conditions were determined based on previous studies conducted by Liu et al. (2021), Khoshakhlaq et al. (2020), and the ISO standard No. BS EN ISO 10121-1:2014, as well as the available laboratory conditions. When conducting tests with low amounts, it takes more time for the filter to capture everything. Therefore, higher amounts were used to expedite the experiment. A level of 300 parts per million (ppm) was selected as the toluene input. The PhoCheck device from IONSCIENCE/Tiger in England was used to measure the amount of toluene in the input and output. Figure 1 illustrates the schematic diagram of the experimental setup used to evaluate the performance of the adsorbents in removing toluene. Equation 1 was employed to calculate the adsorption capacity (Khoshakhlagh et al., 2020).

$$q = \frac{Q}{M} \int_0^{t_e} (C_0 - C) dt \quad (1)$$

Where,

q: adsorption capacity (mg. g⁻¹)

C: output concentration (mg.m⁻³)

C₀: inlet concentration (mg.m⁻³)

Q: carrier gas flow rate (m³.h⁻¹)

t_e: adsorption equilibrium time (50% breakthrough time) (h).

Experimental design

Design Expert V.11 (Stat-Ease, Inc; USA) was utilized for designing experiments based on the central composite design (CCD) approach in response surface methodology (RSM) analysis. The input variables, namely adsorbent type (AC, ZIF-8, AC@ZIF-8), adsorbent mass (5-10 mg), air flowrate (100-500 ml/min), air temperature (25-36 °C), and air relative humidity (26-40%), were defined. The output variables considered were adsorption capacity and breakthrough time. The range of variables was selected based on previous studies and preliminary tests, while considering the operational conditions of the test setup. A total of 63 experimental runs were conducted according to the prepared experimental design (Table 1). The obtained data was subjected to statistical analysis using analysis of variance (ANOVA) through Design Expert.

RESULTS & DISCUSSION

Structural analysis of adsorbents

The X-ray diffraction results for analyzing the crystalline phases of the synthesized adsorbents indicate that the AC@ZIF-8 composite adsorbents and ZIF-8 possess a crystalline structure, matching the reference samples (Mohammadzadeh & Azadbe, 2013). The main diffraction peaks of ZIF-8 are evident in the AC@ZIF-8 composite, confirming that the crystalline properties and structure of ZIF-8 remained unaltered following the incorporation of AC. According to the Fourier transform infrared spectroscopy (FTIR) analysis, the characteristic peaks of ZIF-8 and AC in the FTIR spectrum are observed in the composite results, albeit with slight variations in peak intensity. Based on FESEM images of the adsorbents, the average particle size of the composite materials, ZIF-8 and AC, is approximately 78.89 nm, 81.39 nm, and 69.87 nm, respectively.

The results of the BET test shows the surface areas of AC, ZIF-8, and AC@ZIF-8 were 800.4 gm⁻², 1568 gm⁻², and 1146.4 gm⁻², respectively. The total pore volumes are 0.59 cm³g⁻¹, 1.26 cm³g⁻¹, and 0.68 cm³g⁻¹, respectively. The mean pore diameters of AC, ZIF-8, and AC@ZIF-8 are 2.98 nm, 3.25 nm, and 2.37 nm, respectively. The N₂ adsorption-desorption isotherms on AC, ZIF-8, and AC@ZIF-8 adsorbents at a temperature of 77 K closely resemble the original ZIF-8 adsorption-desorption isotherm, which exhibits a type IV isotherm (Mohammadzadeh & Azadbe, 2013). This type of isotherm is commonly observed in porous materials, indicating the presence of a significant mesoporous structure (Mohammadzadeh & Azadbe, 2013). Consequently, all three adsorbents investigated in this study possess a mesoporous structure.

Performance Characterization

Based on the experimental design developed using Design Expert software, a total of 63 experimental runs were conducted following the setup of the test. Table 1 presents the experimental design, along with the results of the output variables for each individual run. Among the 63 runs, the highest level of adsorption capacity (11830 mg/g) was achieved in run no. 22, utilizing the AC@ZIF-8 adsorbent type, an air temperature of approximately 34 °C, an air relative humidity of around 38%, an adsorbent mass of 6 mg, and an air flow rate of approximately 420 ml/min. Figure 7A illustrates the 3D response surface plots of the combined effects of input variables on the adsorption capacity of AC@ZIF-8. The simultaneous effect of all input variables on the response variables was examined using analysis of variance (ANOVA) and model fitting methods. This analysis involves conducting a null hypothesis test, using a P-value, under the assumption of normality of the error distribution, as well as independence and constant variance. The dispersion of the data points around the diagonal line indicates the normality of the remaining values or the error distribution. The P-value provides a statistical measure of the normality test. In the model fitting method, if the P-value of the model is less than 0.05, it indicates that the parameters of the model are statistically significant, with a 95% confidence level, and the lack of fit values are not statistically significant. This implies the validity of the created model. Conversely, if the P-value is greater than 0.05, the model is not valid. The non-significance of the F value for lack of fit also indicates a good fit of the models. Other indicators of model fitting include R², adjusted R², and predicted R² values. R² values close to 1 indicate a good fit of the regression models. When the values of R² are similar to the values of adjusted R², it suggests a low probability of non-significance of expressions in the models. Additionally, a difference of less than 0.2 between adjusted R² and predicted R² indicates that the models predict the response values accurately. Table 2 presents the proposed models and R² values for the investigated response variables. As an example, Table 3A displays the type I sequential sum of squares model, the lack of fit test, and summary statistics for the response variable "Adsorption capacity".

The analysis of variance (partial sum of squares, type III) presented by the software for both response variables is provided in Table 3. Upon conducting the experiments and modeling the

Table 1. Experimental design

Run No.	Air flow rate (ml/min)	Adsorbent mass (mg)	Air relative humidity (%)	Air temperature (°C)	Adsorbent type	Breakthrough time, 50% (s)	Adsorption capacity (mg/g)
1	300.00	7.50	33.00	30.50	AC@ZIF-8	9563	3606.33
2	418.92	6.01	28.84	33.77	AC	2022	1328.77
3	300.00	10.00	33.00	30.50	ZIF-8	10002	2828.91
4	300.00	7.50	33.00	30.50	AC	2150	275.293
5	181.08	6.01	37.16	27.23	ZIF-8	3092	878.284
6	181.08	6.01	28.84	27.23	AC@ZIF-8	7121	2022.78
7	418.92	8.99	37.16	27.23	AC@ZIF-8	9215	4048.35
8	181.08	6.01	37.16	27.23	AC@ZIF-8	9300	2641.74
9	300.00	7.50	33.00	25.00	ZIF-8	3023	1140.01
10	181.08	8.99	37.16	33.77	AC@ZIF-8	19800	3760
11	181.08	6.01	37.16	27.23	AC	2160	613.566
12	418.92	6.01	28.84	33.77	ZIF-8	4100	2694.34
13	300.00	7.50	33.00	30.50	ZIF-8	3353	1264.46
14	418.92	6.01	37.16	33.77	AC	1984	1303.8
15	300.00	7.50	33.00	30.50	ZIF-8	3500	1319.9
16	300.00	7.50	26.00	30.50	AC@ZIF-8	20259	7639.94
17	100.00	7.50	33.00	30.50	ZIF-8	11783.1	1480
18	418.92	8.99	37.16	27.23	ZIF-8	5767	2533.57
19	300.00	5.00	33.00	30.50	AC	1468.46	830
20	300.00	7.50	40.00	30.50	AC	2003	755.358
21	300.00	7.50	33.00	30.50	AC	2271	856.424
22	418.92	6.01	37.16	33.77	AC@ZIF-8	18003	11830
23	300.00	7.50	33.00	36.00	AC@ZIF-8	17006	6413.19
24	300.00	7.50	33.00	36.00	ZIF-8	3799	1432.65
25	300.00	5.00	33.00	30.50	AC@ZIF-8	5558.64	3141.84
26	100.00	7.50	33.00	30.50	AC@ZIF-8	30300.3	3805.84
27	300.00	7.50	33.00	30.50	ZIF-8	3240	1221.85
28	181.08	8.99	28.84	33.77	AC@ZIF-8	9410	1786.95
29	181.08	8.99	28.84	33.77	AC	3095	587.737
30	300.00	7.50	33.00	30.50	ZIF-8	3716	1401.35
31	181.08	6.01	28.84	27.23	AC	2328	661.288
32	300.00	7.50	40.00	30.50	ZIF-8	1620	610.923
33	418.92	6.01	37.16	33.77	ZIF-8	2577	1693.49
34	300.00	7.50	33.00	30.50	AC	2325	520.416
35	500.00	7.50	33.00	30.50	ZIF-8	1851.85	1163
36	300.00	7.50	26.00	30.50	AC	2788	1051.39
37	300.00	10.00	33.00	30.50	AC@ZIF-8	16045	4538.09
38	500.00	7.50	33.00	30.50	AC	1291.52	811.1
39	300.00	7.50	33.00	30.50	AC@ZIF-8	9340	3522.23
40	181.08	8.99	28.84	33.77	ZIF-8	3000	569.697
41	300.00	7.50	33.00	36.00	AC	4221	1591.79
42	181.08	8.99	37.16	33.77	AC	1448	274.974
43	300.00	7.50	40.00	30.50	AC@ZIF-8	8341	3145.5
44	300.00	7.50	33.00	30.50	ZIF-8	3317	1250.88
45	300.00	7.50	33.00	25.00	AC	4745	1789.4
46	418.92	8.99	37.16	27.23	AC	3895	1711.16
47	300.00	7.50	33.00	30.50	AC@ZIF-8	9803	3696.84
48	418.92	6.01	28.84	33.77	AC@ZIF-8	6897	4532.4
49	300.00	5.00	33.00	30.50	ZIF-8	2163.43	1222.81
50	100.00	7.50	33.00	30.50	AC	7569.23	950.725
51	300.00	7.50	33.00	30.50	AC@ZIF-8	9832	3707.78
52	418.92	8.99	28.84	27.23	AC	2865	1258.66

Continued Table 1. Experimental design

53	500.00	7.50	33.00	30.50	AC@ZIF-8	4711.51	2958.92
54	300.00	7.50	33.00	30.50	AC@ZIF-8	9427	3555.05
55	181.08	6.01	28.84	27.23	ZIF-8	3200	908.987
56	418.92	8.99	28.84	27.23	ZIF-8	3159	1380.35
57	300.00	7.50	33.00	30.50	AC	2210	833.42
58	418.92	8.99	28.84	27.23	AC@ZIF-8	9515	4180.15
59	181.08	8.99	37.16	33.77	ZIF-8	9900	1880
60	300.00	7.50	33.00	30.50	AC	2189	825.501
61	300.00	7.50	26.00	30.50	ZIF-8	3601	1357.98
62	300.00	10.00	33.00	30.50	AC	4521	1278.7
63	300.00	7.50	33.00	25.00	AC@ZIF-8	14020	5287.13

Table 2. Proposed model and R² for the investigated response variables

Parameter Response	The difference between the adjusted R ² and the predicted R ²	Predicted R ²	Adjusted R ²	R ²	Suggested model
Adsorption capacity (mg/g)	0.1807	0.5690	0.7497	0.8305	2FI
breakthrough time 50%) (s)	0.1936	0.6154	0.8090	0.8706	2FI

outcomes using the central composite design method, the associations between the variables and the adsorption capacity and breakthrough time were established. The results of these associations for the performance responses of adsorption capacity and breakthrough time are presented in the polynomial equation shown in Table 3. These equations depict the individual and combined impacts of the independent variables on the toluene adsorption capacity and breakthrough time. In terms of the individual effects, the adsorbent mass and air temperature exhibit a positive influence on both adsorption capacity and breakthrough time, whereas air relative humidity and flow rate have a negative impact on these variables.

Khoshakhlagh et al. (2020) conducted a synthesis of the microporous Cu-BDC@OAC composite. Their findings revealed a decrease in the level of adsorbed toluene as the air temperature increased from 21°C to 40°C. This decrease in toluene adsorption capacity implicates the significance of the physical adsorption mechanism between toluene and the composite. Baytar et al. (2020) also noted that the adsorption capacity decreased as expected with the rise in temperature, as gas adsorption is an exothermic process. Similar trends in temperature changes were observed in studies using different types of adsorbents. These consistent results suggest that physical adsorption is the primary mechanism governing the partitioning of vapor between the gas and adsorbed phases. This temperature-dependent effect on adsorption capacity is crucial in regulating vapor concentration, particularly for air quality applications. In this study, the increased temperature led to an increase in both adsorption capacity and breakthrough time. Consequently, the possibility of the presence of chemical bonds in the toluene adsorption process on the composite can be inferred. Alongside physical adsorption, chemical adsorption, an endothermic process, also takes place. Furthermore, the elevated air temperature weakens the bond between the toluene molecules and the composite, resulting in a longer breakthrough time of 100; consequently, the adsorption capacity is enhanced.

The air humidity has a detrimental impact on the adsorption capacity and breakthrough time of all three adsorbents. According to Khoshakhlagh et al. (2020), the relative humidity

Table 3. The existing mathematical model between the input variables in order to predict the response variables

Adsorbent	Response Variable	Equation	Model
Activated Carbon	Adsorption Capacity	$\ln(\text{adsorption capacity}) = -5.73398 - 0.017970A + 2.85088B - 0.149373C + 0.485953D - 0.000019A * B + 1.89404E - 0.06A * D + 0.000589A * D + 0.009609B * C - 0.100686B * D + 0.001880C * D$	Two-factor interaction (2FI)
	Breakthrough Time	$\ln(\text{breakthrough time}) = -7.15277 - 0.022324A + 3.36243B - 0.149468C + 0.573705D - 0.000017A * B + 1.44322E - 0.06A * C + 0.000600A * D + 0.009572B * C - 0.112893B * D + 0.001897C * D$	Two-factor interaction (2FI)
ZIF-8	Adsorption Capacity	$\ln(\text{adsorption capacity}) = -7.75781 - 0.018742A + 2.92055B - 0.130697C + 0.536982D - 0.000019A * B + 1.89404E - 0.06A * C + 0.000589A * D + 0.009609B * C - 0.100686B * D + 0.001880C * D$	Two-factor interaction (2FI)
	Breakthrough Time	$\ln(\text{breakthrough time}) = -9.24877 - 0.023092A + 3.43237B - 0.130887C + 0.624613D - 0.000017A * B + 1.44322E - 0.06A * C + 0.000600A * D + 0.009572B * C - 0.112893B * D + 0.001897C * D$	Two-factor interaction (2FI)
AC@ZIF-8	Adsorption Capacity	$\ln(\text{adsorption capacity}) = -6.89219 - 0.018566A + 2.83463B - 0.122136C + 0.554063D - 0.000019A * B + 1.89404E - 0.06A * C + 0.000589A * D + 0.009609BC - 0.100686B * D + 0.001880C * D$	Two-factor interaction (2FI)
	Breakthrough Time	$\ln(\text{breakthrough time}) = -8.38732 - 0.022920A + 3.34618B - 0.122229C + 0.641817D - 0.000017A * B + 1.44322E - 0.06A * C + 0.000600A * D + 0.009572B * C - 0.112893B * D + 0.001897C * D$	Two-factor interaction (2FI)

A: Air Flowrate B: Adsorbent Mass C: Air Relative Humidity D: Air Temperature

of the air in the gas stream entering the system affects both the adsorption parameters and the breaking point. Notably, when the relative humidity is 80%, the adsorption parameters are significantly lower compared to conditions with 30% and 50% relative humidity. In metal-organic frameworks, the metal clusters tend to be hydrophilic while the organic ligands are hydrophobic. The structures of the metal-organic framework compounds serve as adsorption sites, facilitating the adsorption of molecules into the benzene rings through the ligands or the organic components of the compounds. This adsorption process occurs due to the formation of relatively strong bonds. The presence of relative humidity has a notable negative impact on the adsorption of toluene on the adsorbent, indicating a competitive adsorption process between toluene and water vapor. The composite structure of the adsorbent can be distorted due to the interaction between the hydrogen in H₂O and the oxygen in the carboxylate, thus impeding the access of toluene to the active sites of the adsorbent.

In the present study, an increase in the mass of the adsorbent leads to an increase in adsorption. This can be attributed to the fact that a higher mass of the adsorbent provides a larger surface area available for adsorption. Consequently, it is expected that the adsorption capacity will

also increase. Khoshakhlagh et al. (2020) demonstrated that the adsorption capacity of toluene decreases with an increase in the amount of adsorbent. They suggested that increasing the amount of adsorbent would result in faster adsorption of the pollutant. This, in turn, reduces the number of available molecules for maximum surface coverage, leading to a decrease in the amount of pollutant adsorbed per unit weight of the adsorbent. However, it is important to note that due to the variation in the composite type and the interactive effect of other investigated parameters, the same results were not observed. He et al. (2013) indicated that toluene exhibits a preference for interacting with the phenyl groups of bIm in ZIF-11. Furthermore, the -CH₃ groups on toluene and -N Zn on phenyl rings are electron-donating and electron-accepting substitutes, respectively. These substitutions enhance the electrostatic interactions of toluene with aromatic rings.

Based on our findings, it was observed that the air flowrate had a negative impact on the adsorption capacity and breakthrough time of all three adsorbents. It has been demonstrated that as the flow rate increases, the breakthrough curve becomes steeper, indicating that the adsorbent reaches saturation in a shorter period of time. Consequently, an increase in flow rate can lead to a decrease in adsorption capacity due to the elevated velocity of air passing over the adsorbent surface. Consequently, toluene may be removed from the reactor before reaching adsorption equilibrium at that particular air flowrate, thereby reducing the adsorption capacity (Khoshakhlagh et al., 2020). The present study revealed that the AC@ZIF-8 composite exhibited a higher adsorption capacity compared to the other two adsorbents. This can be attributed to the incorporation of activated carbon into the ZIF-8 MOF, which enhances dispersion and hydrophobic interactions while increasing the number of active sites by reducing the accumulation of ZIF-8. Additionally, the composite's superior adsorption capacity can be attributed to its abundance of micropores and larger micropore diameter when compared to activated carbon and MOF.

The pore structure of the adsorbents plays a crucial role in the adsorption characteristics of toluene. Micropores have a positive impact on toluene adsorption (Khoshakhlagh et al., 2020). Consequently, our study highlights the influence of Zn-N bonds, hydrophobic phenyl groups, and functional groups containing AC on the increase of surface area and chemical affinity to toluene, resulting in the creation of more active adsorption sites. Bahri et al. (2017) compared the toluene adsorption capacities of MIL-101, MIL-53, and CPM-5. They found that MIL-101 exhibited a significantly longer breakthrough time and, consequently, a higher toluene capacity compared to MIL-53 and CPM-5. One explanation for this high adsorption capacity of the composite is the presence of π - π complexes, which enhance the adsorption of multiple layers of toluene molecules. The micro-mesoporous structure of AC@MOFs allows for greater toluene ingress, resulting in a higher adsorption capacity compared to MOFs (Khoshakhlagh et al., 2020).

In general, the metal-organic framework structure exhibits dual amphiphilic properties, with the metal component being hydrophilic and the organic bonds being lipophilic. Within the structure of organometallic frameworks, both the metal sites and the linkers serve as adsorption sites. In the case of the ZIF-8 structure, H₂O molecules are adsorbed by the hydrophilic zinc (Zn(II)) sites, while toluene molecules are adsorbed by the lipophilic 2-methylimidazole linkers. It is important to note that, despite being surrounded by imidazole, not all Zn(II) ions were completely enveloped by the imidazole linker during the synthesis of ZIF-8. These structural defects, characterized by open metal sites, can serve as water adsorption sites (Jafari et al., 2018).

Chu et al. (2018) conducted an investigation into the adsorption of toluene by a hybrid composite of graphene oxide (GO) and ZIF-8, with varying ratios of GO. The authors determined that the toluene adsorption capacity of the composite was 116 mg/g. In a separate study, Bahri et al. (2017) reported the adsorption capacities for toluene by three different

MOFs: MIL-101, MIL-53, and CPM-5, which were found to be 211.5 mg/g, 730.4 mg/g, and 388.5 mg/g, respectively. Another study by Hunterslar et al. (2021) reported an adsorption capacity of 321.8 mg/g for toluene on ZIF-8. The findings of the present study demonstrated an improvement in the toluene adsorption capacity of the AC@ZIF-8 adsorbent compared to previous research, highlighting the superior performance of the AC@ZIF-8 composite. The non-polar nature of both toluene and activated carbon contributes to the adsorption of toluene by the composite through the non-polar active carbon. Furthermore, the organic linkers in the MOF are also non-polar and capable of adsorbing toluene, leading to an increased number of toluene adsorption sites within the composite and consequently a higher adsorption capacity. The adsorption interaction of non-polar and weakly polar adsorbing gases is heavily influenced by the polarizability of the molecules (Yun et al. 1998). Additionally, the adsorption amount of organic compounds on AC is strongly dependent on both their structural characteristics and the presence of surface oxygen groups (Nahm et al., 2012). The results of the present study confirmed the significance of micropores in the removal of toluene, consistent with previous research. The micropore structure is considered a crucial characteristic that governs the surface adsorption behavior of volatile organic compounds on adsorbents (Khoshakhlagh et al., 2021).

The goodness of fit of the models was assessed using diagnostic charts such as the normal residual chart, the predicted vs. predicted residual chart, the predicted vs. actual chart, and the Box-Cox chart. The normal residual chart indicates the normality of the data when the points follow a straight line. The random distribution of residuals in the residual vs. predicted graph indicates that the changes in actual values are consistent for all responses. The proximity of points to the regression line in the predicted vs. actual graph indicates a good match between predicted and actual values. The closeness of the Lambda value (0 and 0 for adsorption capacity and breakthrough time, respectively) to the optimal Lambda value in the Box-Cox chart (-0.11 and -0.18 for adsorption capacity and breakthrough time, respectively) indicates the high accuracy of the models. Diagnostic plots of normalized residual, residual vs. predicted, and predicted vs. actual were examined to verify the accuracy of the models. Experimental validation was conducted using the proposed solution no.1 for the variables in the test setup with three repetitions of the experiments.

CONCLUSION

The aim of this research is to conduct a comparative analysis on the effectiveness of different adsorbents, namely AC, ZIF-8, and AC@ZIF-8, in the removal of toluene from the air. Additionally, the study seeks to develop an optimized model for toluene adsorption. To achieve this objective, the response surface methodology was employed to evaluate the impact of five performance parameters (adsorbent type, adsorbent mass, air flow rate, air temperature, and air relative humidity) on the operational response of the adsorption process (specifically, adsorption capacity and breakthrough time). The successful synthesis of a novel AC@ZIF-8 composite through in situ reactions of zinc nitrate hexahydrate and AC was achieved. The structural characteristics and toluene adsorption properties of the synthesized AC@ZIF-8 composite were then investigated. XRD analysis confirmed the successful synthesis of the AC@ZIF-8 composite. FESEM results indicated that the addition of AC did not result in any observable defects on the surface of ZIF-8. BET analysis demonstrated that the composite material exhibited a higher pore volume and specific surface area compared to AC alone. The adsorption-desorption isotherms of the adsorbents closely resembled those of the original ZIF-8, indicating a type IV isotherm characteristic of mesoporous materials. The proposed model for the response variables was 2FI. The RSM method successfully established the relationship between the input and output variables, and additional validation tests demonstrated good agreement between the predicted and experimental values. In conclusion, the selection of appropriate operating conditions for the adsorption process is vital in achieving the desired

conditions and adsorbent characteristics. The findings presented in these experimental models are expected to serve as a guide for optimizing the operational conditions for the effective utilization of the developed adsorbents. One of the strengths of this study is the synthesis of a novel composite by combining activated carbon and MOF, which was achieved for the first time. Another strength is the optimization of operational parameters in the toluene adsorption process. The study has some limitations. First, determining the failure time by checking the output concentration is a time-consuming process. Additionally, the use of a DC direct current source (battery) as the energy supply for the direct reading device sometimes caused monitoring problems, such as battery discharge during tests. Having an online GC analysis device would provide more accurate and convenient results. Furthermore, controlling the initial concentration and stability of toluene concentration was challenging due to its volatility, even though it was managed using a syringe pump. Regular checking and precise accuracy were necessary during the investigation of functional responses in the setup. It would be beneficial to have automatic adjustment systems to control temperature and humidity and maintain these variables constant. Lastly, due to time and financial constraints, the study focused on examining the 50% breakthrough time. The adsorbents, especially the composite, required a considerable amount of time for complete saturation, as evident from the 50% failure times observed in different runs.

ETHICS APPROVAL

Ethical approval for this study was obtained from School of Public Health and Neuroscience Research Center, Shahid Beheshti University of Medical Sciences IR.SBMU. PHNS.REC.1401.076.

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REFERENCES

- Alaei, Z., Ghasemi, R., Pourmand, M. R., Karimi, A., Masoorian, E., & Golbabaei, F. (2022). Comparative Survey of Virgin and Immobilized Activated Carbon With *Pseudomonas Putida* PTCC In Toluene Removal From Airflow. *Journal of Health and Safety at Work*, 12(2), 274-287.
- Bahri, M., Haghghat, F., Kazemian, H., & Rohani, S. (2017). A comparative study on metal organic frameworks for indoor environment application: Adsorption evaluation. *Chemical Engineering Journal*, 313, 711-723.
- Bahri, M., Haghghat, F., Rohani, S., & Kazemian, H. (2017). Metal organic frameworks for gas-phase VOCs removal in a NTP-catalytic reactor. *Chemical Engineering Journal*, 320, 308-318.
- Baytar, O., Şahin, Ö., Horoz, S., & Kutluay, S. (2020). High-performance gas-phase adsorption of benzene and toluene on activated carbon: response surface optimization, reusability, equilibrium, kinetic, and competitive adsorption studies. *Environmental Science and Pollution Research*, 27, 26191-26210.
- Buragohain, M., & Mahanta, C. (2008). A novel approach for ANFIS modelling based on full factorial design. *Applied soft computing*, 8(1), 609-625.
- Chu, F., Zheng, Y., Wen, B., Zhou, L., Yan, J., & Chen, Y. (2018). Adsorption of toluene with water on zeolitic imidazolate framework-8/graphene oxide hybrid nanocomposites in a humid atmosphere. *RSC advances*, 8(5), 2426-2432.
- He, M., Yao, J., Liu, Q., Zhong, Z., & Wang, H. (2013). Toluene-assisted synthesis of RHO-type zeolitic imidazolate frameworks: synthesis and formation mechanism of ZIF-11 and ZIF-12. *Dalton Transactions*, 42(47), 16608-16613.
- Hunter-Sellars, E., Saenz-Cavazos, P. A., Houghton, A. R., McIntyre, S. R., Parkin, I. P., & Williams, D. R. (2021). Sol-Gel Synthesis of High-Density Zeolitic Imidazolate Framework Monoliths via Ligand

- Assisted Methods: Exceptional Porosity, Hydrophobicity, and Applications in Vapor Adsorption. *Advanced Functional Materials*, 31(5), 2008357.
- ISO 10121-1:2014, Test method for assessing the performance of gas-phase air cleaning media and devices for general ventilation — Part 1: Gas-phase air cleaning media. (2014). In. Geneva, Switzerland. ISO: International Organization for Standardization.
- Jafari, S., Ghorbani-Shahna, F., Bahrami, A., & Kazemian, H. (2018). Effects of post-synthesis activation and relative humidity on adsorption performance of ZIF-8 for capturing toluene from a gas phase in a continuous mode. *Applied Sciences*, 8(2), 310.
- Khoshakhlagh, A. H., Golbabaie, F., Beygzadeh, M., Carrasco-Marín, F., & Shahtaheri, S. J. (2020). Toluene adsorption on porous Cu-BDC@OAC composite at various operating conditions: optimization by response surface methodology. *RSC advances*, 10(58), 35582-35596.
- Khoshakhlagh, A. H., Golbabaie, F., Beygzadeh, M., & Shahtaheri, S. J. (2021). Study of the dynamic adsorption process of toluene by a microporous copper metal-organic framework. *Journal of Health & Safety at Work*, 11(4), 556-576.
- Liu, B., Younis, S. A., & Kim, K.-H. (2021). The dynamic competition in adsorption between gaseous benzene and moisture on metal-organic frameworks across their varying concentration levels. *Chemical Engineering Journal*, 421, 127813.
- Liu, X., Li, Y., Chen, Z., Yang, H., Cai, Y., Wang, S., ... & Wang, X. (2023). Advanced porous nanomaterials as superior adsorbents for environmental pollutants removal from aqueous solutions. *Critical Reviews in Environmental Science and Technology*, 53(13), 1289-1309.
- Ma, X., Wang, W., Sun, C., Li, H., Sun, J., & Liu, X. (2021). Adsorption performance and kinetic study of hierarchical porous Fe-based MOFs for toluene removal. *Science of The Total Environment*, 793, 148622.
- Mohammadzadeh, A., & Azadbe, M. (2013). Modeling and Investigating the Effect of Supercalidium Liquid Phase Coupling Variables on the Physical and Mechanical Properties of Cu₂₈Zn Alloy *Journal of Modern Materials*, 3(3), 1-20.
- Naam, S. W., Shim, W. G., Park, Y.-K., & Kim, S. C. (2012). Thermal and chemical regeneration of spent activated carbon and its adsorption property for toluene. *Chemical Engineering Journal*, 210, 500-509.
- Nazir, M. A., Najam, T., Shahzad, K., Wattoo, M. A., Hussain, T., Tufail, M. K., ... & ur Rehman, A. (2022). Heterointerface engineering of water stable ZIF-8@ZIF-67: Adsorption of rhodamine B from water. *Surfaces and Interfaces*, 34, 102324.
- Norafizan, A. C. D., Aziz, F., Mohamed Amin, M. A., & Ismail, A. F. (2021). Copper adsorption on ZIF-8/alumina hollow fiber membrane: a response surface methodology analysis. *Arabian Journal for Science and Engineering*, 46(7), 6775-6786.
- Parisa Mohammad-Gholikhan-Khalaj, Mahdi Hasanzadeh, Davoud Panahi, Zahra Yazdankhah, & Dehghan, S. F. (2023). Feasibility study on the removal of toluene from the air stream by activated carbon/zeolite imidazolate framework composite material. *Journal of Environmental Chemical Engineering*, 11(5), 110885.
- Saqlain, S., Zhao, S., Kim, S. Y., & Kim, Y. D. (2021). Enhanced removal efficiency of toluene over activated carbon under visible light. *Journal of Hazardous Materials*, 418, 126317.
- Vrtovec, N., Mazaj, M., Buscarino, G., Terracina, A., Agnello, S., & Arčon, I. (2020). Structural and CO₂ Capture Properties of Ethylenediamine-Modified HKUST-1 Metal-Organic Framework. 20(8), 5455-5465.
- Wang, J., Muhammad, Y., Gao, Z., Shah, S. J., Nie, S., Kuang, L., ... & Zhao, Z. (2021). Implanting polyethylene glycol into MIL-101 (Cr) as hydrophobic barrier for enhancing toluene adsorption under highly humid environment. *Chemical Engineering Journal*, 404, 126562.
- Yun, J.-H., Hwang, K.-Y., & Choi, D.-K. (1998). Adsorption of benzene and toluene vapors on activated carbon fiber at 298, 323, and 348 K. *Journal of Chemical & Engineering Data*, 43(5), 843-845.