Silica-coated magnetic Fe₃O₄ nanoparticles as efficient nano-adsorbents for the improvement of the vapor-phase adsorption of benzene

Mehmet Şakir ECE¹*, Sinan KUTLUAY², Ömer ŞAHİN²

¹Vocational High School of Health Services, Mardin Artuklu University, Mardin, 47100, Turkey
²Department of Chemical Engineering, Faculty of Engineering, Siirt University, Siirt, 56100, Turkey

Received: 21 June 2020; Revised: 13 April 2021; Accepted: 16 March 2021

Ece and co-workers

ABSTRACT

This study focused on the preparation of silica-coated Fe₃O₄ (Fe₃O₄@SiO₂) for the improvement of the vapor-phase adsorption of benzene. The Fe₃O₄@SiO₂ was prepared via the co-precipitation method, while its characterization was carried out using FT-IR, SEM and BET surface area analyses. The experimental parameters were evaluated for the vapor-phase adsorption of benzene using response surface methodology (RSM). The Fe₃O₄@SiO₂ adsorbed 197.50 mg g⁻¹ of the vapor-adsorption of benzene using response surface methodology (D-R), Freundlich and Langmuir, and the experimental data investigating the isotherms including Dubinin-Radushkevich experimental parameters were evaluated for the vapor-phase adsorption of benzene. The Fe₃O₄@SiO₂ was prepared via the co-precipitation method, while its characterization was carried out using FT-IR, SEM and BET surface area analyses. The experimental parameters were evaluated for the vapor-phase adsorption of benzene using response surface methodology (RSM). The Fe₃O₄@SiO₂ adsorbed 197.50 mg g⁻¹ of the vapor-phase benzene under the following optimum conditions: 39.93 min residence time, 13.57 mg l⁻¹ initial benzene concentration and 26.87°C temperature. The vapor-phase adsorption mechanism of benzene on the Fe₃O₄@SiO₂ was clarified by investigating the isotherms including Dubinin-Radushkevich (D-R), Freundlich and Langmuir, and the experimental data were well fitted to the D-R model. The vapor-phase adsorption kinetics of benzene on the Fe₃O₄@SiO₂ was clarified by investigating the kinetics such as pseudo first-order (PFO) model and pseudo second-order (PSO) model, and the experimental results obeyed the PSO model. This study demonstrated the application potential of magnetic Fe₃O₄@SiO₂ as promising low-cost nano-adsorbent.

Keywords: Fe₃O₄@SiO₂ magnetic nanoparticles, response surface methodology, vapor-phase adsorption of benzene.

Benzenin buhar-fazı adsorpsiyonunun iyileştirilmesi için etkili nano-adsorbentler olarak silika-kaplı manyetik Fe₃O₄ nanoparçacıkları

ÖZ

Bu çalışma, benzenin buhar-fazı adsorpsiyonunun iyileştirilmesi için silika-kaplı Fe₃O₄ (Fe₃O₄@SiO₂) hazırlanması odaklandı. Fe₃O₄@SiO₂ birlikte çözeltme yöntemi ile hazırlanırken karakterizasyonu FT-IR, SEM ve BET yüzey alanı analizleri yapılarak gerçekleştirilmiştir. Deneysel parametreler, yanıt yüzey metodolojisi (RSM) kullanılarak benzenin buhar-fazı adsorpsiyonunu için değerlendirildi. Fe₃O₄@SiO₂ ağırlıklı optimum koşullar altında 197,50 mg l⁻¹ buhar-fazı benzeni adsorb etti; 39,93 dakika kalma süresi, 13,57 mg l⁻¹ başlangıç benzen konsantrasyonuna ve 26,87°C sıcaklık. Benzenin Fe₃O₄@SiO₂ üzerindeki buhar fazı adsorpsiyonu mekanizması, Dubinin-Radushkevich (D-R), Freundlich ve Langmuir dahil izotermler incelenerek netleştirildi ve deneysel veriler D-R modeline iyi bir şekilde uyduruldu. Benzenin Fe₃O₄@SiO₂ üzerinden buhar-fazı adsorpsiyon kinetiği, sözde birinci-dereceden (SBD) model ve sözde ikinci dereceden (SID) model gibi kinetikler incelenerek netleştirildi, ve deneysel sonuçlar SID modele uydud. Bu çalışma, Fe₃O₄@SiO₂'nin umut verici düşük maliyetli nano-adsorbeni olarak uygulama potansiyeli gösterdi.

Anahtar Kelimeler: Benzenin buhar-fazı adsorpsiyonu, Fe₃O₄@SiO₂ manyetik nanoparçacıklar, yanıt yüzey metodu.

1. INTRODUCTION

Benzene, one of the important volatile organic compounds (VOCs), is an important material in chemical processing industries. VOCs are important air pollutants because of such detrimental effects as allergic reactions, nausea, throat irritation, nose, eye and headache. Besides, they cause dangerous environmental problems such as photochemical smog, suspended particulate matter, stratospheric ozone depletion and global warming.
Hence, VOCs with low concentrations have an important potential for environmental problem. This toxic product (benzene), which is extremely hazardous for human health and the environment, is emitted from automotive exhaust or fuels that evaporate from tanks, vehicle carburetors, and gas stations, particularly during oil refining operations, petrochemical production, and oil storage processes.\(^1\) In general, the quality and amount of air pollutant emissions from the exhaust pipes are closely related to the fuel composition. Emissions from consumer products, building materials, paints, and adhesives are also influential in this situation. Besides, tobacco smoke is a source of this pollutant.\(^5\) Industrial sectors considerably disrupt the gas rates in the air. The adverse effects on air quality create unfavorable conditions in terms of health. It is a necessity to decrease the entry of poisonous gases into the environmental atmosphere and to develop reduction strategies. To this end, pollutant removal methods have become essential. In this regard, nanotechnology presents effective solutions compared to traditional ones in adsorption technology as in all other fields.\(^6\) In adsorption technology, magnetic nanomaterials with unique properties such as paramagnetism or ferromagnetism have drawn much attention. Magnetite (Fe\(_3\)O\(_4\)) is a common material widely examined in nanotechnological research.\(^8\) It attracted considerable attention because of its magnetic properties such as biocompatibility, low-toxicity, low cost and high surface area.\(^9\) Functionalization of Fe\(_3\)O\(_4\) nanoparticles with functional groups both reduces agglomeration and provides new active sites for adsorption.\(^10\) Fe\(_3\)O\(_4\), which is one of many magnetic materials, facilitates recovery in the separation steps due to its magnetic feature. The pore volume of Fe\(_3\)O\(_4\) nanoparticles has a well-developed pore structure producing a large number of active sites. Pore volume declines in the active areas due to agglomeration. Coating with organic or inorganic surfactants is a method to prevent particle agglomeration.\(^13\) Silica (SiO\(_2\)) has extraordinary physical and chemical properties as an inorganic surfactant.\(^10\)

This study focused on the preparation of silica-coated Fe\(_3\)O\(_4\) (Fe\(_3\)O\(_4@\)SiO\(_2\)) magnetic nanoparticles and their application for the improvement of the vapor-phase adsorption of benzene. The Fe\(_3\)O\(_4@\)SiO\(_2\) was prepared via the co-precipitation method, while its characterization was carried out using FT-IR, SEM and BET surface area analyses. Experimental parameters were evaluated for the vapor-phase adsorption of benzene by using the Box-Behnken design (BBD) with the response surface method (RSM). The vapor-phase adsorption mechanism of benzene on the Fe\(_3\)O\(_4@\)SiO\(_2\) was clarified by investigating the isotherms including Dubinin-Radushkevich (D-R), Freundlich and Langmuir. The vapor-phase adsorption kinetics of benzene on the Fe\(_3\)O\(_4@\)SiO\(_2\) was clarified by investigating the kinetics such as pseudo first-order (PFO) model and pseudo second-order (PSO) model.

2. MATERIALS AND METHODS

2.1. Materials

The tetraethyl orthosilicate (TEOS, Si(OC\(_3\)H\(_3\))\(_4\)), benzene (C\(_6\)H\(_6\)), iron (II) chloride tetrahydrate (FeCl\(_2\).4H\(_2\)O), ethanol (CH\(_3\)CH\(_2\)OH), iron (III) chloride hexahydrate (FeCl\(_3\).6H\(_2\)O), and ammonia (NH\(_3\)) were purchased from MERCK, ALFA AESAR, SIGMA-ALDRICH, MERCK, SIGMA-ALDRICH and VWR Chemical Companies, respectively. All solvents and chemicals employed in the study have analytical purity.

2.2. Preparation of the Fe\(_3\)O\(_4@\)SiO\(_2\) magnetic nanoparticles

Fe\(_3\)O\(_4\) was prepared by co-precipitation of Fe (III) and Fe (II). The mixture of FeCl\(_2\).4H\(_2\)O and FeCl\(_3\).6H\(_2\)O salts, in which the ratio of Fe\(^{2+}/Fe^{3+}\) was stoichiometrically 1/2, was mixed for 30 min at 80°C under argon gas in 50 ml deionized water. The color of the homogenized solution immediately became orange. 10 ml NH\(_3\) solution was added drop-by-drop to obtain the co-precipitation. The color of the bulk solution instantly changed from orange to black. Amalgamation was continued under argon for 30 min. The Fe\(_3\)O\(_4\) obtained as a product was washed five times with ethanol and deionized water. Fe\(_3\)O\(_4\) was dried in a vacuum oven at 60°C for 24 h. 0.5 g of Fe\(_3\)O\(_4\) was dispersed in a flask in 20 ml of deionized water, 5 ml of ammonia and 100 ml of ethanol. The solution of mixture was homogenized by ultrasonication for 30 min to create an uniform distribution. Then 0.4 ml of TEOS was added drop-by-drop to the solution under a strong mixture. The amalgamation was continued under argon gas for 12 h at room temperature. The Fe\(_3\)O\(_4@\)SiO\(_2\) obtained as a product, was separated by a magnet, washed five times with deionized water and ethanol. The Fe\(_3\)O\(_4@\)SiO\(_2\) was dried in a vacuum oven at 60°C for 24 h.\(^13\) Schematic representation of the preparation of the Fe\(_3\)O\(_4@\)SiO\(_2\) was presented in Figure 1.
2.3. Removal of benzene vapor by adsorption process

The adsorption process practiced in the removal of benzene vapor by using Fe₃O₄@SiO₂ magnetic nanoparticles was defined with the previously published study. The nitrogen (N₂) flow rate for the removal of benzene vapor was chosen as 100 ml min⁻¹. The optimum dosage of Fe₃O₄@SiO₂ employed for the removal of benzene vapor was 0.09 g. The adsorption capacity, q (mg g⁻¹) for benzene vapor was defined with Eq. (1):15

\[
q = \frac{F}{m} \int_{0}^{t} (C_{in} - C_{eff}) \, dt
\]

Here m is the optimum dosage of Fe₃O₄@SiO₂ (g), F is the flow rate (l min⁻¹), Cᵢᵣ and Cₑₑₑₑₑ are the initial and output benzene vapor concentrations (mg 1⁻¹), respectively, and t is the residence time (min).

2.4. Characterization

Fourier Transform Infrared Spectroscopy (FT-IR) spectra were taken using a Bruker-Vertex 70v FT-IR spectrometer. Scanning Electron Microscopy (SEM) images were taken by a ZEISS-EVO 50 instrument. Brunauer–Emmett–Teller (BET) surface area was determined by means of a Quantachrome-Nova instrument. Mathematical modeling for experimental data were conducted by applying Design Expert 12.0.8.0 Software (Free Trial Version).

3. RESULTS AND DISCUSSION

3.1. Characterization of the Fe₃O₄@SiO₂ magnetic nanoparticles

Characterization of the Fe₃O₄@SiO₂ magnetic nanoparticles was conducted based on SEM, FTIR, and BET surface area. SEM images, FTIR spectra and N₂ gas adsorption/desorption isotherms of these nanoparticles were presented in Figure 2, Figure 3, and Figure 4, respectively.

3.1.1. SEM analysis

SEM analysis was used to observe the surface morphology of the Fe₃O₄ and Fe₃O₄@SiO₂ magnetic nanoparticles. Figure 2 presented SEM microphotographs (scale length = 500 nm) of Fe₃O₄ and Fe₃O₄@SiO₂. It was understood that Fe₃O₄, which had good dispersion, had a rough surface. It was observed that the pore structure was rough and spongy. Pores and voids were clearly noticeable on the surface of Fe₃O₄@SiO₂. It was understood that the intrusions, protrusions, and roughness increased the surface area in the microstructure of the Fe₃O₄@SiO₂. Considering the scale length, it is understood that the diameters of the magnetic nanoparticle spheres are approximately 70-110 nm.16

3.1.2. FTIR analysis

FTIR spectra of Fe₃O₄ and Fe₃O₄@SiO₂ magnetic nanoparticles were presented in Figure 3. The characteristic absorption peak at 552 cm⁻¹ observed in the FTIR spectrum of Fe₃O₄ belonged to the Fe-O bond, which verified the presence of Fe₃O₄. The peaks observed around 3446 cm⁻¹, 1654 cm⁻¹ and 1480 cm⁻¹ were peaks of stretching, bending, and deforming vibrations of the adsorbed water (-OH). The new peaks at 570 cm⁻¹ and 964 cm⁻¹ observed in the FTIR spectrum of the Fe₃O₄@SiO₂ were the peaks of the bending vibration of the Si-O bond and the stretching vibration of the Si-OH bond, respectively. The peak at 1082 cm⁻¹ belonged to the asymmetric stretching vibration of the Si-O-Si bond. This peak indicated that the surface of Fe₃O₄ was successfully coated with SiO₂. The FTIR spectra observed for Fe₃O₄ and Fe₃O₄@SiO₂ complied with the literature.17
3.1.3. BET analysis

The adsorption and desorption isotherms of Fe₃O₄@SiO₂ magnetic nanoparticles with BET surface area of 28.97 m² g⁻¹ were presented in Figure 4. When Figure 4 was analyzed, it was understood that Fe₃O₄@SiO₂ fitted the H3 type hysteresis cycle and IV type curve according to the IUPAC classification criteria. It was also estimated that there were homogeneous mesoporous layers. The low surface area of Fe₃O₄@SiO₂ indicated that the surface area was affected by the SiO₂ modification. It was because SiO₂ was a shell of magnetic nanoparticles, and SiO₂ infiltrated into the spaces on the surface.

3.2. Experimental design and optimization

In the present study, RSM, which is an experimental method for the development, improvement, and optimization of the design process, was applied to determine the importance of the potential interactions of the functioning parameters. The approach of RSM-based BBD was employed to perform statistical analyses and obtain the regression model. In the vapor-phase adsorption of benzene, all statistical analyzes for modeling and optimization of experimental studies were evaluated. Effective parameters and interactions were evaluated by the program through variance analysis (ANOVA) and three-dimensional graphics. The general quadratic model equation was obtained with ANOVA test and BBD approach to analyze the relationship between the obtained results and parameters. The predicted adsorption capacity values were defined depending on the parameter values selected by employing the obtained quadratic model equation. The significance of the model predicted by the program was evaluated with the R² obtained, and the p-value, adeq precision and F-value results achieved by the program were analyzed. In the study, a three-variable BBD was used to determine the effect of different parameters upon response. The residence time, initial benzene concentration, and temperature were chosen as the essential independent parameters affecting the vapor-phase adsorption. The adsorption capacity of the vapor-phase benzene was considered as the response. The parameters analyzed in the BBD were displayed in three coded values. Experimental design levels with independent factors and the results obtained by the BBD approach were presented in Table 1 and Table 2 respectively. The compatibility of the results was presented with ANOVA analysis in Table 3. According to ANOVA results, the p-value of the proposed model was calculated as 0.0001, which shows that 99.99% of the results obtained in the laboratory conditions of the experiments predicted by the program can be defined with the model obtained with the program. Besides, the high R² value, F-value (>4), and adeq precision (>4) results, which were determined as 99.89, 678.81 and 80.50% respectively, showed that the experimental data well defined with the predicted model. Besides, the fact that the actual and predicted adsorption capacities presented in Table 2 were close to each other indicated the suitability of the predicted model.

Table 1. Experimental design levels with independent factors

| Factors                  | Coded values |
|--------------------------|--------------|
| Residencetime (X₁) (min) | -1 0 +1      |
| Concentration (X₂) (mg l⁻¹) | 10 12.5 15  |
| Temperature (X₃) (°C)    | 25 30 35     |

Figure 5 presented three-dimensional (3D) plots achieved with the program, showing the influence of initial benzene concentration, adsorption temperature and residence time on the vapor-phase adsorption capacity of benzene. It could be observed in Figure 5a that the vapor-phase adsorption capacity of benzene increased with the increase in residence time.
Table 2. Experiment design results obtained for the vapor-phase adsorption of benzene by the Fe3O4@SiO2 magnetic nanoparticles.

| Run | Time (min) | Concentration (mg l⁻¹) | Temperature (°C) | Actual adsorption capacity (mg g⁻¹) | Predicted adsorption capacity (mg g⁻¹) |
|-----|------------|-------------------------|------------------|------------------------------------|--------------------------------------|
| 1   | 30         | 12.5                    | 30               | 80                                 | 83                                   |
| 2   | 20         | 15                      | 30               | 50                                 | 57                                   |
| 3   | 20         | 10                      | 30               | 41                                 | 40                                   |
| 4   | 30         | 15                      | 35               | 60                                 | 58                                   |
| 5   | 40         | 12.5                    | 35               | 150                                | 162                                  |
| 6   | 30         | 12.5                    | 30               | 80                                 | 86                                   |
| 7   | 20         | 12.5                    | 25               | 45                                 | 53                                   |
| 8   | 40         | 15                      | 30               | 185                                | 190                                  |
| 9   | 40         | 10                      | 30               | 160                                | 157                                  |
| 10  | 30         | 12.5                    | 30               | 82                                 | 85                                   |
| 11  | 30         | 15                      | 25               | 110                                | 116                                  |
| 12  | 40         | 12.5                    | 25               | 198                                | 201                                  |
| 13  | 30         | 10                      | 25               | 70                                 | 68                                   |
| 14  | 30         | 12.5                    | 30               | 80                                 | 89                                   |
| 15  | 30         | 10                      | 35               | 55                                 | 57                                   |
| 16  | 20         | 12.5                    | 35               | 36                                 | 28                                   |
| 17  | 30         | 12.5                    | 30               | 80                                 | 85                                   |

Table 3. ANOVA results created in accordance with the BBD approach

| Source                  | Sum of squares | df | F-value | p-value |
|-------------------------|----------------|----|---------|---------|
| Model (quadratic)       | 20627.11       | 9  | 678.81  | < 0.0001 Significant |
| X1                      | 8532.50        | 1  | 5005.50 | < 0.0001 |
| X2                      | 8247.96        | 1  | 115.09  | < 0.0001 |
| X3                      | 191.84         | 1  | 274.47  | < 0.0001 |
| X1X2                    | 1545.57        | 1  | 9.44    | 0.0180  |
| X1X3                    | 0.0071         | 1  | 56.10   | 0.0001  |
| X2X3                    | 3.64           | 1  | 45.18   | 0.0003  |
| X1²                     | 1242.51        | 1  | 598.85  | < 0.0001 |
| X2²                     | 1181.88        | 1  | 3.73    | 0.0948  |
| X3²                     | 472.13         | 1  | 10.96   | 0.0129  |

R² = 0.9989, Adeq precision = 80.50

The adsorption process reached equilibrium after a specific residence time because of the limited number of active areas on the surface of Fe3O4@SiO2. As observed in Figure 5b, the temperature had an adverse effect on vapor-phase adsorption. Adsorption capacity decreased as the temperature rose. Also, it could be said that the decrease in the amount adsorbed with the increased temperature might be caused by the destruction of the active bond sites on the adsorbent. When the surface plot for the initial benzene concentration versus temperature in Figure 5c was considered, it was evident that the initial benzene concentration did not have a meaningful effect on the vapor-phase adsorption capacity. The increase seen in the vapor-phase adsorption of benzene was caused by the less interest in Fe3O4@SiO2. Similar behaviors have been observed in previous studies. Process parameters were optimized to define the vapor-phase adsorption capacity of benzene by applying Fe3O4@SiO2. Based on the model equation for the actual values predicted by the quadratic model, the mathematically optimum conditions were defined. With the help of the predicted model equation, optimum values were determined to be 39.93 min for residence time, 13.57 mg l⁻¹ for initial benzene concentration, and 26.87°C for temperature. The vapor-phase adsorption capacity of benzene with Fe3O4@SiO2 was determined as 197.50 mg g⁻¹.
Figure 5. The influence of parameters on the vapor-phase adsorption capacity of benzene.

Figure 6. Optimum values for the vapor-phase adsorption of benzene.
3.3. Kinetic studies

Under optimum conditions defined by RSM, the vapor-phase adsorption kinetics of benzene on the Fe3O4@SiO2 was clarified by investigating the kinetics such as pseudo first-order (PFO) model and pseudo second-order (PSO) model. PFO model defines the adsorption rate proportional to the number of empty sites.23 PFO model was related to the change of concentration over time. The non-linear form of the PFO model kinetic equation was presented in Eq. (2). The PSO model equation, based on the capacity of the adsorption equilibrium, suggests that the rate of adsorption is related to the concentration of active sites on the surface of the adsorbent.23 The non-linear form of the PSO model was given with the Eq. (3). 24

\[ q_t = q_e \left(1 - e^{-k_f t} \right) \]  
(2)

\[ q_t = \frac{k_s q_e^2 t}{1+k_s q_e t} \]  
(3)

Where, \( q_e \) and \( q_t \) indicate the adsorption capacity at equilibrium and \( t \) time (mg g\(^{-1}\)), respectively, and \( k_f \) represents the PFO model rate constant (1 min\(^{-1}\)), \( k_s \) is the PSO model rate constant (g mg\(^{-1}\) min\(^{-1}\)).

In the vapor-phase adsorption process of benzene by the Fe3O4@SiO2, the experimental results obeyed the PSO model (Figure 7 and Table 4).

![Figure 7. Adsorption kinetic models of benzene by the Fe3O4@SiO2 magnetic nanoparticles](image)

**Table 4. Adsorption kinetic parameters of benzene by the Fe3O4@SiO2 magnetic nanoparticles**

| Kinetic models | Parameters | Values  |
|---------------|------------|---------|
| PFO model     | \( q_e \)  | 205.952 |
|               | \( k_f \)  | 0.0648  |
|               | R\(^2\)     | 0.967   |
| PSO model     | \( q_e \)  | 212.45  |
|               | \( k_s \)  | 0.0013  |
|               | R\(^2\)     | 0.990   |

3.4. Isotherm studies

Under optimum conditions defined by RSM, The vapor-phase adsorption mechanism of benzene on the Fe3O4@SiO2 was clarified by investigating the isotherms including Dubinin-Radushkevich (D-R), Freundlich and Langmuir. The Langmuir adsorption isotherm applies to single-layer surface adsorption, including a limited number of identical regions. The model assumes that the adsorption energies on the surface are the same and that there is no adsorbate migration at the surface plane. Based on these assumptions, the Langmuir model is formulated in Eq. (4). The Freundlich isotherm theory puts forward that the ratio of the amount of solute adsorbed on a particular sorbent mass to the concentration of the solute is not constant at different concentrations. The non-linear form of the Freundlich isotherm model was given in Eq. (5).25 The D-R isotherm model was developed to describe the effect of the porous structure of adsorbents. It is based on the theory of the adsorption potential and suggests that in contrast to the layered adsorption on pore walls, the adsorption process is associated with the filling of the microporous volume.26-27 The non-linear form of this model was presented in Eq. (6). 28 In Eq. (6), \( \beta \) gives \( E \) which represents the average free energy of adsorption per particle. \( E \) was presented in Eq. (8). 28

\[ q_e = \frac{q_{max} K_{L} C_e}{1 + K_{L} C_e} \]  
(4)

\[ q_e = K_F C_e^{1/n} \]  
(5)

\[ q_e = q_m \exp(-\beta \varepsilon^2) \]  
(6)

\[ \varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \]  
(7)

\[ E = \frac{1}{\sqrt{2\pi}} \]  
(8)

Where, \( C_e \) (mg l\(^{-1}\)) is the equilibrium concentration of the adsorbate, \( q_e \) (mg g\(^{-1}\)) is the adsorption capacity at equilibrium, \( q_{max} \) (mg g\(^{-1}\)) is the maximum monolayer adsorption capacity, \( K_L \) (l mg\(^{-1}\)) is Langmuir isotherm constant, \( K_F \) [(mg g\(^{-1}\)) (l mg\(^{-1}\))\(^{1/n}\)] is the Freundlich isotherm constant, \( n \) is the adsorption density, if \( n \) is between 1 and 10, this situation indicates a suitable adsorption process, \( q_m \) is the maximum adsorption capacity (mg g\(^{-1}\)), \( \beta \) is the activity coefficient constant (mol\(^2\) kJ\(^{-2}\)), \( \varepsilon \) is the polanyi potential (J mol\(^{-1}\)), \( R \) and \( T \) represent the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), absolute temperature (K), respectively, If \( E < 8 \) kJ mol\(^{-1}\), physical adsorption is dominant. However, in the situation indicating 8 kJ mol\(^{-1}\) < \( E < 16 \) kJ/mol and \( E > 16 \) kJ mol\(^{-1}\), adsorption occurs by ion exchange and diffusion, respectively.29

In the study, the estimated \( q_{max} \) from the Langmuir model was 237.192 mg g\(^{-1}\), \( K_L \) was 0.281 l mg\(^{-1}\). The R\(^2\) value
was 0.999, indicating the equilibrium isotherm data of benzene in the vapor-phase adsorption process by the Fe₃O₄@SiO₂ better fitted to the D-R model. The calculated E value in the study was determined as 0.463 kJ mol⁻¹, indicating that the vapor-phase adsorption process of benzene was physical (Figure 8 and Table 5). In addition, the n value of Freundlich model was calculated as 3.472, indicating that the vapor-phase adsorption process of benzene was suitable.

### Figure 8. Adsorption isotherm models of benzene by the Fe₃O₄@SiO₂ magnetic nanoparticles

### Table 5. Adsorption isotherm parameters of benzene by the Fe₃O₄@SiO₂ magnetic nanoparticles

| Isotherm models | Parameters | Values          |
|-----------------|------------|-----------------|
|                 | qmax       | 237.192         |
| Langmuir        | K_L        | 0.281           |
|                 | R²         | 0.997           |
|                 | K_F        | 86.056          |
| Freundlich      | n          | 3.472           |
|                 | R²         | 0.993           |
|                 | q_m        | 208.721         |
|                 | β          | 2.334*10⁻⁶      |
|                 | E          | 0.463           |
|                 | R²         | 0.999           |

### 4. CONCLUSIONS

The present study focused on the preparation of Fe₃O₄@SiO₂ for the improvement of the vapor-phase adsorption of benzene. The Fe₃O₄@SiO₂ was prepared via the co-precipitation method, while its characterization was carried out using FT-IR, SEM and BET surface area analyses. The experimental parameters were evaluated for the vapor-phase adsorption capacity of benzene using BBD under RSM. The Fe₃O₄@SiO₂ adsorbed 197.50 mg g⁻¹ of the vapor-phase benzene under the following optimum conditions: 39.93 min residence time, 13.57 mg l⁻¹ initial benzene concentration and 26.87°C temperature. The vapor-phase adsorption mechanism of benzene on the Fe₃O₄@SiO₂ was clarified by investigating the isotherm models such as Dubinin-Radushkevich (D-R), Freundlich and Langmuir, and the experimental data were well fitted to the D-R model. The vapor-phase adsorption kinetics of benzene on the Fe₃O₄@SiO₂ was clarified by investigating the kinetics such as PFO model and PSO model, and the experimental results obeyed the PSO model. This study demonstrated the application potential of magnetic Fe₃O₄@SiO₂ as promising low-cost nano-adsorbents for the vapor-phase adsorption of benzene.

### ACKNOWLEDGEMENTS

The authors are grateful to the Mardin Artuklu University Research Fund (MAUBAP, Project No. MAÜ.BAP.18.SHMYO.030) for their financial support.

### Conflict of interests

I declare that there is no a conflict of interest with any person, institute, company, etc.

### REFERENCES

1. Ece, M. Ş.; Kutluay, S.; Şahin, Ö.; Horoz, S. Ind. Eng. Chem. Res. 2020, 59 (48), 21106-21123.
2. Kutluay, S. Fuel 2021, 287, 119691.
3. Kutluay, S.; Temel, F. Colloid Surf. A-Physicochem. Eng. Asp. 2021, 609, 125848.
4. Şahin, Ö.; Kutluay, S.; Horoz, S.; Ece, M. Ş. Environ. Sci. Pollut. Res. 2021, 28 (5), 5231-5253.
5. Wallace, L. A. Environ. Health Perspect. 1989, 82, 165-169.
6. Yang, X.; Yi, H.; Tang, X.; Zhao, S.; Yang, Z.; Ma, Y.; Feng, T.; Cui, X. J. Environ. Sci. 2018, 67, 104-114.
7. Wibowo, N.; Setyadhi, L.; Wibowo, D.; Setiawan, J.; Ismadji, S. J. Hazard. Mater. 2007, 146 (1-2), 237-242.
8. de las Nieves Piña, M.; Rodríguez, P.; Gutiérrez, M. S.; Quiñonero, D.; Morey, J.; Frontera, A. Chem. Eur. J. 2018, 24 (49), 12820-12826.
9. Connie, Z. Y.; Ariya, P. A. J. Environ. Sci. 2015, 31, 164-174.
10. Roto, R.; Yusran, Y.; Kuncaka, A. Appl. Surf. Sci. 2016, 377, 30-36.
11. Mohamed, E. F. Environ. Dev. Sustain. 2017, 6 (2).
12. Duan, S.; Xu, X.; Liu, X.; Wang, Y.; Hayat, T.; Alsaeedi, A.; Meng, Y.; Li, J. J. Colloid Interface Sci. 2018, 513, 92-103.
13. Zandipak, R.; Sobhan Ardakani, S.; Shirzadi, A. Sep. Sci. Technol. 2020, 55 (3), 456-470.
14. Kutluay, S.; Baytar, O.; Şahin, O. J. Environ. Chem. Eng. 2019, 7 (2), 102947.
15. Zhao, Z.; Wang, S.; Yang, Y.; Li, X.; Li, J.; Li, Z. Chem. Eng. J. 2015, 259, 79-89.
16. Yousefi, V.; Tarhriz, V.; Eyvazi, S.; Dilmaghani, A. *J. Nanobiotechnology* **2020**, *18* (1), 155.

17. Ma, C.; Li, C.; He, N.; Wang, F.; Ma, N.; Zhang, L.; Lu, Z.; Ali, Z.; Xi, Z.; Li, X. *J. Biomed. Nanotechnol.* **2012**, *8* (6), 1000-1005.

18. Kutluay, S.; Ece, M. Ş.; Şahin, Ö. *Int. J. Chem. Technol.* **2020**, *4* (2), 146-155.

19. Temel, F.; Kutluay, S. *New J. Chem.* **2020**, *44* (30), 12949-12961.

20. Vohra, M. S. *Arab. J. Sci. Eng.* **2015**, *40* (11), 3007-3017.

21. Padmavathy, V. *Bioresour. Technol.* **2008**, *99* (8), 3100-3109.

22. Kutluay, S.; Baytar, O.; Şahin, Ö. *Res. Eng. Struct. Mater.* **2019**, *5* (3), 279-298.

23. Ali, R. M.; Hamad, H. A.; Hussein, M. M.; Malash, G. F. *Ecol. Eng.* **2016**, *91*, 317-332.

24. Vora, S.; Khimani, M.; De, C. *Ecol. Eng.* **2013**, *34* (7), 947-956.

25. Salih, W. M.; Gzar, H. A.; Hassan, N. F. *J. Eng.* **2012**, *18* (9), 1042-1054.

26. Laskar, I. I.; Hashisho, Z. *Sep. Purif. Technol.* **2020**, 116681.

27. Abbas, A.; Abussaud, B. A.; Al-Baghli, N. A.; Khraisheh, M.; Atieh, M. A. *J. Nanomater.* **2016**, *2016*.

28. Hu, Q.; Zhang, Z. *J. Mol. Liq.* **2019**, *277*, 646-648.

29. Sadeghalvad, B.; Azadmehr, A.; Hezarkhani, A. *RSC Adv.* **2016**, *6* (72), 67630-67642.

30. Wang, C.; Zhong, H.; Wu, W.; Pan, C.; Wei, X.; Zhou, G.; Yang, F. *ACS Omega* **2019**, *4* (1), 1652-1661.