

Removal of toluene vapors from the polluted air with modified natural zeolite and titanium dioxide nanoparticles

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Abstract

Toluene is a colorless and flammable liquid with the same solubilizing capacity as benzene that is in many cases used as an alternative to benzene, because of the uncertainty of being carcinogens. Workers can be exposed to toluene by breathing the chemical. To avoid inhalation and dermal effects caused by exposure to toluene, solutions such as adsorption, thermal oxidation, membrane separation and photocatalytic processes are applied. In this study, removal of toluene vapors with modified natural zeolite and titanium dioxide nanoparticles was discussed. The natural zeolite was modified using chemical and thermal methods. The samples characterized by Brunauer-Emmett-Teller, Barrett-Joyner-Halenda, X-ray diffraction and scanning electron microscopy tests. After stabilization of TiO₂ nanoparticles, the removal efficiency for the toluene vapors at a concentration of 50, 150 and 300 ppm were evaluated using a dynamic system. The results showed that the zeolite has a very porous surface and after modifying the context its specific surface area increased 2.54 times. The results of the adsorption capacity calculation and photocatalytic process showed that modified zeolite samples-TiO₂ bed has greater efficiency in the adsorption capacity and better photocatalytic activity than a Ze-TiO₂ bed. Ze-TiO₂ bed was able to remove 26% of toluene vapors at the concentration of 50 ppm and inlet flow rate of 1 L/m, which was 1.26 times more than a bed Ze-TiO₂. According to the results of this study, while modifying the natural zeolite increased desirable properties such as specific surface area and Si/Al ratio, but in comparison with similar studies with synthetic bed such as zeolite Y and ZSM-5, could not achieve desired results in a photocatalytic activity for its application in industry. However, because of its abundance in the world and Iran and therefore low cost of preparation and also due to its unique characteristics, it is recommended that more studies to be done about modifying and its application in photocatalytic processes.

Key words: natural zeolite; modified zeolite; toluene; titanium dioxide; reactor; adsorption capacity; photocatalytic removal

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INTRODUCTION

Volatile organic compounds (VOCs) are one of the greatest environmental and human society issues nowadays. Benzene, toluene and xylene are the main carbon compounds and considered as the major indoor and outdoor environment pollutants emitted by a wide range of transportation activities and chemical manufacturing industries, such as: organic chemicals, plastics, synthetic fibers, pesticides, and pharmaceuticals.¹ Many VOCs, such as benzene and chloroform, are known carcinogens to humans.² Toluene (C₆H₅CH₃) is a colorless, flammable liquid and due to the uncertainty of being carcinogenic, toluene is used as an alternative to benzene in many cases and as a solvent in the manufacture of chemicals such as paints, adhesives, rubber and leather.³ Inhalation of toluene vapors can cause the adverse effects on human such as effects on the nervous system, causing a decline in thinking, memory and ability of muscle.⁴ Therefore, the removal of toluene vapors from industrial workplace to prevent inhalation and skin effects is essential. Nowadays, many treatment procedures including

modifying equipment, process control, condensation, thermal oxidation, catalytic oxidation and adsorption have been applied to remove various pollutants such as toluene from air.⁵⁻⁷ Each method has its own advantages and disadvantages that must be considered. Disadvantages such as secondary pollution, high costs, high energy demand and commissioning problems that make the use of methods difficult and sometimes impossible. According to the techniques described and their advantages and disadvantages, photocatalytic method has become a promising one.⁸⁻¹⁰ In the photocatalytic process, a catalyst with the proper band gap such as zinc oxide or titanium dioxide and light source (usually ultraviolet (UV)) is used to convert organic compounds into benign and odorless constituents – water vapor (H₂O) and carbon dioxide (CO₂).¹⁰⁻¹² Titanium dioxide (with three crystalline phases: anatase, rutile and brookite), a white powder that has a photocatalytic and super-hydrophilic, is used in water and wastewater treatment, air pollution and buildings.^{12,13} Features such as low price, availability, chemical stability and lack of toxicity make the titanium dioxide as the



most appropriate photocatalyst.¹⁴ Photocatalytic oxidation by having advantages such as an activity at ambient temperature and low pressure, low cost and low power consumption in comparison with other methods, has introduced as one of the promising alternatives for treating a wide range of volatile organic compounds in the recent years.^{9,10,15} Perhaps the only limitation of photocatalytic processes is low residence time due to the catalyst low specific surface area. Today, foundations such as zeolites, activated carbon or diatomite with high surface area, provide more time for photocatalytic reactions of catalyst and UV by the absorption of volatile compounds on the surface and their pores, and thus increase the removal efficiency.¹⁶⁻¹⁸ The study of Fernanda et al.,¹⁹ evaluating photocatalytic activities of supported catalysts on NaX zeolite or activated charcoal, showed that the synergistic effect between ZnO and NaX support was higher than that with the activated charcoal, showing that these catalysts were more efficient. Today, zeolite is considered as a bed in refining processes. So far, more than 50 kinds of natural zeolite such as clinoptilolite, heulandite, laumontite, mordenite and phillipsite other than species synthesized in the laboratory are known.²⁰ Zeolite has the ability to absorb compounds such as SO₂, CO₂, NO₂, H₂S and polar or non-polar aromatic hydrocarbons²¹ and this ability depends on the histologic, surface and chemical properties.²² Modifying the zeolite by chemical or thermal methods or both, can improve features such as specific surface area, the functional groups and thus increase its efficiency in the refining processes.²³ According to the above-mentioned and the importance of the issue, in this study the removal of toluene vapors with photocatalytic process of titanium dioxide coated on natural zeolite were investigated before and after modification.

MATERIALS AND METHODS

Natural clinoptilolite zeolite from Garmsar, Semnan (Iran) mines was meshed by ASTM standard screen (size 20–40). The prepared samples were washed twice with distilled water in the ratio of 1 g/50 mL on a shaker under the temperature of 70°C in speed of 200 r/min for 6 hours. The sample was filtered with Whatman filter paper Grade 42 and Buchner funnel and that heated in the oven at a temperature of 105°C for 24 hours (shown with Ze). A solution containing 2 molar hydrochloric acid, trimethylchlorosilane and toluene (Merck, Germany, Supplier: Safirazma Company, Tehran) was used for Ze chemical treatment. Ze samples were subjected to chemical treatment twice with two molar solutions of hydrochloric acid on a shaker under the temperature of 70°C at 200 r/min for 6 hours. The sample was filtered with Whatman filter paper Grade 42 and Buchner funnel, and washed with hot and then cold distilled water and finally dried to reach pH7. A certain mass of the sample was weighted (with accuracy of hundred thousand) and poured in the two-necked flask in proportion of 0.56 mL trimethylchlorosilane and 500 mL toluene (buffer) for each gram and kept in the controlled temperature (10°C below the boiling point of the most volatile organic compound) for 24 hours under the reflux conditions and passage of nitrogen over the liquid surface to reform. Upon completion, the sample was washed with distilled water and acetone and finally, was dried under the conditions of the previous stage and placed in desiccator as modified zeolite samples (MZe).^{23,24}

To prepare zeolite bed containing 5% titanium dioxide (TiO₂-to-P25 Degussa Company, Germany), a certain amount of particles were weighed and poured into the flask before placing it in the ultrasonic device for 40 minutes to create a uniform suspension using deionized water. After adding a certain amount of Mze to the solution, it was placed on a shaker under the temperature of 35 ± 5°C and a speed of 200 r/min for 18 hours to load nanoparticles on the surface of bed appropriately and finally was filtered and dried. At the end, for calcination the solution was heated in the laboratory oven at a temperature of 450°C (temperature rate of 5°C/min) for 4 hours. Ze-TiO₂ bed was also prepared in the same way and finally placed in polyethylene containers named MZE-TiO₂ and Ze-TiO₂. Brunauer-Emmet-Teller (BET), Barrett-Joyner-Halenda (BJH), X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) technique were used in order to determine the characteristics of the samples. BET was used to determine the specific surface area and pore size. Total sample volume was determined by BJH using nitrogen gas adsorption-desorption. Evaluation of the morphological structure of samples was done by SEM technique. STOE-STADV device with 1.54 Å wavelength and 40 kV, 40 mA generator was used to record X-ray diffraction pattern. Zeolite samples were scanned at 1 < 2θ < 80.

In this study, as shown in **Figure 1**, a cylindrical glassy reactor made of quartz was used with a length of 22 cm, external diameter of 22 mm and internal diameter of 20 mm. Inlet and outlet of reactor were in the opposite direction the ends of the cylinder so that a lamp can be located inside of the reactor (center of it) and three other lamps on the exterior of the reactor. According to the result of studies, titanium dioxide nanoparticles show highest photocatalytic reactions in the of 365 nm UV_A wavelength. Therefore, in this study, three UV_A lamps and one UV_B lamp were used to radiate the wavelength in the range of 365 ± 5 nm. Two sides of reactor were sealed by polytetrafluoroethylene (PTFE) (surveys show this matter is resistant and not responding against chemicals (toluene)) in such a way that the ends of the middle lamp were out of the reactor. The bed was located between the central lamp and reactor so that both sides of it were irradiated with UVA. Saturated vapor, which is an inexpensive and convenient method, was applied to make different concentration since it was dynamical and with a flow rate of 1 L/m. Mofidi et al.²⁵ applied saturated steam for concentration and were able to control fluctuations in 50 and 300 ppm concentration for about 9% and 1.8% respectively. Conducted researches have been introduced the optimal moisture percentage for different photocatalytic processes. Masoud Rismanchian et al.²⁶ at the study of gaseous toluene removal by using of the photocatalytic activity of TiO₂ coated on foam nickel metal, reported 30% as the optimal moisture. Dezhi et al.²⁷ chose 25% moisture and Pham et al.² preferred 50% to carry out photocatalytic processes. In this study, the moisture and environmental volatile compounds is reduced to zero by passing the air through silica gel and activated charcoal. Then, inlet air moisture levels of the reactor were set at 40% using a humidifier and digital humidity meter. **Figure 2** shows the experimental setup used in this study.

Due to the long lead time to have multiple measurements

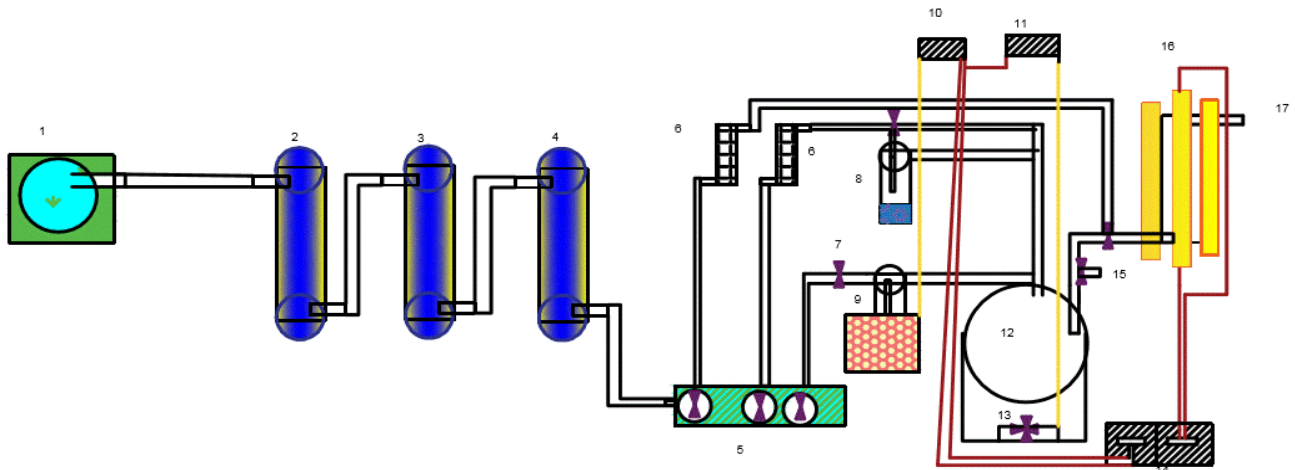


Figure 2: Schematic of laboratory setup.

Note: (1) Air Pump; (2) SILICAGEL; (3) Active carbon; (4) SILICAGE; (5) Branch wall boxes; (6) Rotameter; (7) Air adjustment valve; (8) Water container; (9) Styrene container; (10) Thermometer sensor; (11) Moisture Sensor; (12) Mixing tank; (13) Sockets; (14) Sampling port; (15) Pre-reactor output; (16) Photocatalytic reactor; (17) Reactor output.

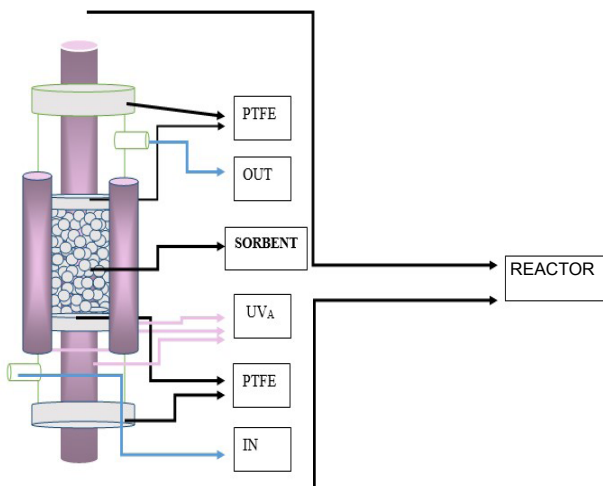


Figure 1: Placement of bed and ultraviolet A (UV_A) lamps in the reactor.

during operation, a direct reading device (Phocheck Tiger, England, UK. Based on Photo Ionization Detector) was employed for measuring the concentration. In order to ensure the accuracy and reliability of the device, after calibration, some of the samples were re-measured by gas chromatography (GC) which showed no significant difference in concentrations. Experiments were conducted at $27 \pm 2^\circ\text{C}$ ambient temperature. Finally 3 grams of each MZe-TiO₂ and Ze-TiO₂ bed was placed within the reactor in such a way that the two sides were irradiated with UVA to analyze photocatalytic activity. Photocatalytic removal process was evaluated in three concentrations of 50, 150 and 300 ppm. By entry of the polluted air stream into the reactor, UVA is turned on and the inlet and outlet concentrations were measured periodically. This action was done for both beds at all three concentrations. Finally performance indicators of each bed were measured using adsorptive capacity and photocatalytic removal efficiency of bed. In order to determine the adsorption capacity (C/C_0 ratio of 5%) and calculate the photocatalytic removal efficiency of bed equation 1 and 2 was used.²⁸

Table 1: The results of BET analysis of the removal toluene vapors with photocatalytic process of titanium dioxide coated on natural zeolite

	BET (m ² /g)	Average pore diameter(Å) (4V/A by BET)
RZe	56.4	38.43
MZe	143.8	61.4
MZe-TiO ₂	132.5	55.2

Note: RZe: Raw zeolite; Mze: Modified zeolite samples; BET: Brunauer-Emmet-Teller.

$$BC = \frac{Q \cdot C \cdot Tbk}{Madsorbent} \quad (1)$$

In which, BC : toluene mass adsorbed by the bed (mg/g); Q : flow rate entering the reactor (m³/min); C : toluene concentration (mg/m³); Tbk : breakthrough time (minutes).

$$\%R = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

In which, $\%R$: percentage of toluene photocatalytic conversion; C_0 : initial concentration (ppm); C : secondary concentration (ppm).

RESULTS

Characterization of the removal toluene vapors with photocatalytic process of titanium dioxide coated on natural zeolite

The results of the BET analysis of the zeolite samples are presented in **Table 1**. BJH analysis was also employed to determine the type of adsorption and desorption pattern of bed and the results are shown in **Figure 3**. As shown in **Table 1**, after chemical modification specific surface area of Ze (raw zeolite) increased from 56.4 m²/g to 143.8 m²/g, showing the removal of impurities and porosity enhancement which can be concluded by comparing the average pore diameter before and after the modification.

Structure and morphology of the bed (produced by SEM) are shown in **Figure 4** in three different states of before and

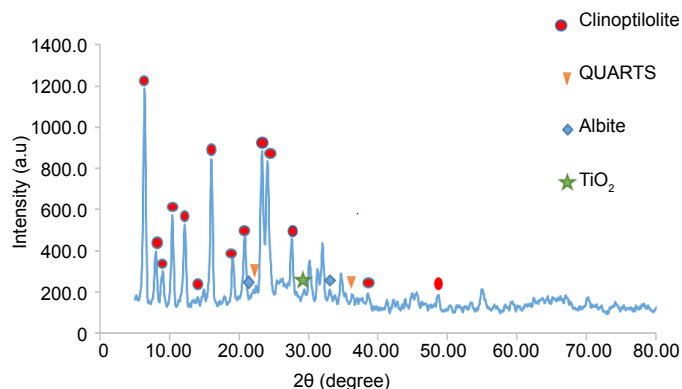
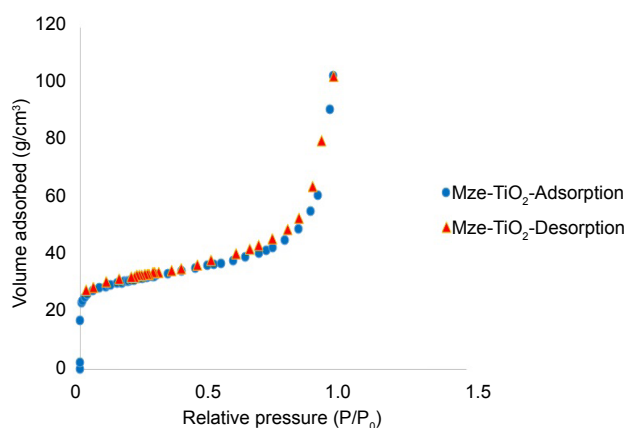


Figure 5: X-ray diffraction pattern of Mze-TiO₂ bed.

Figure 3: The adsorption-desorption pattern of nitrogen gas of the removal toluene vapors with photocatalytic process of titanium dioxide coated on natural zeolite.

Note: Mze: Modified zeolite samples.

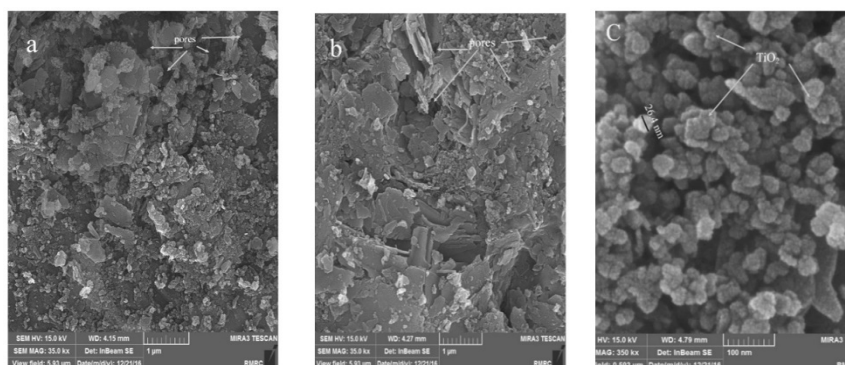


Figure 4: Scanning electron microscope images. Note: (A) Raw zeolite, (B) modified zeolite, (C) zeolite coated with TiO₂. Scale bars: 1 μm in A, B, 100 nm in C.

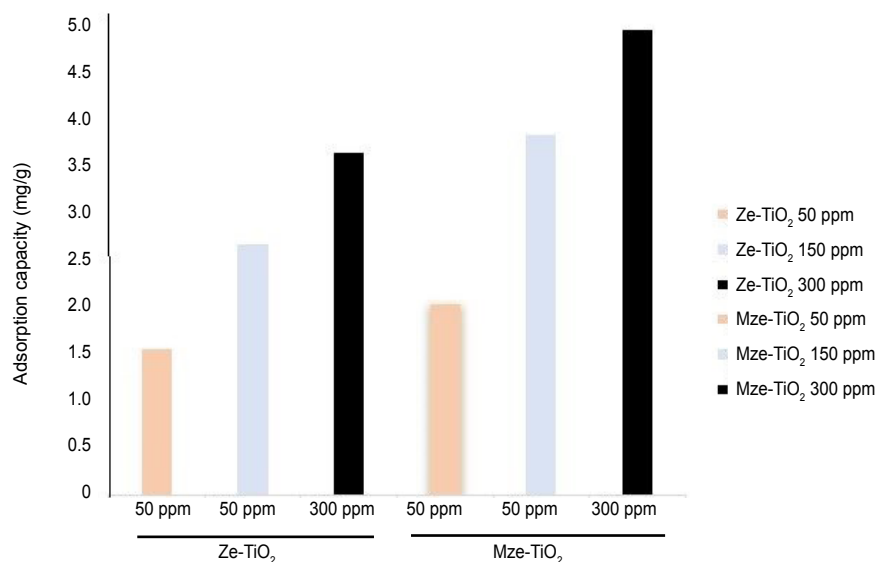


Figure 6: Comparison of adsorption capacity in 50, 150 and 300 ppm concentrations for Ze-TiO₂ and modified zeolite samples-TiO₂ bed.

after the modification and coated with TiO₂.

XRD patterns of Me-TiO₂ bed are given in **Figure 5** and confirms the presence of TiO₂ on the bed. The pattern also shows that the type of zeolite is clinoptilolite.

The results of adsorption capacity

Figure 6 shows the adsorption capacity of Ze-TiO₂ and Mze-TiO₂ bed. According to **Figure 6**, the adsorption capacity of

Mze-TiO₂ bed is higher than Ze-TiO₂ at the three levels of 50, 150 and 300 ppm.

To study the concentration effect on the adsorption capacity, the adsorption capacity of Ze-TiO₂ and Mze-TiO₂ bed calculated in 50, 150 and 300 ppm concentrations and presented in **Figure 6**. According to **Figure 6** the adsorption capacity of Ze-TiO₂ bed at a concentration of 50, 150 and 300 ppm calculated, 1.55, 2.65 and 3.62 mg/g, respectively.

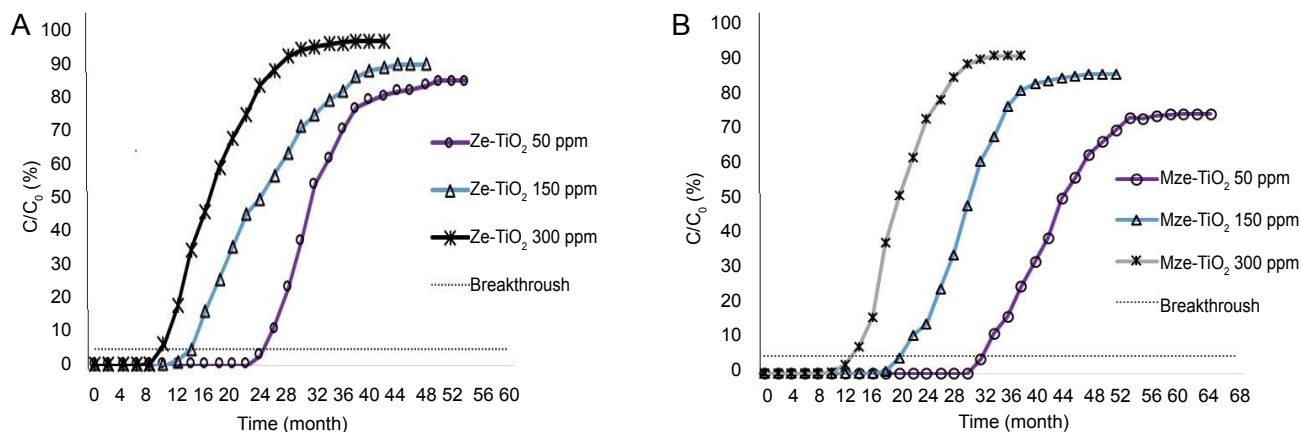


Figure 7: Photocatalytic conversion of toluene of Ze-TiO₂ (A) and MZe-TiO₂ (B) bed.

Note: Flow rate: 1 L/min, relative humidity: 40%, temperature: $27 \pm 2^\circ\text{C}$. C_0 : Initial concentration (ppm); C: secondary concentration (ppm).

And the adsorption capacity of the MZe-TiO₂ bed for 50, 150 and 300 ppm concentration obtained 2.02, 3.8 and 2.9 mg/g, respectively.

The results of the photocatalytic process

Comparison of two beds based on the photocatalytic activity

The results of the photocatalytic removal of Ze-TiO₂ and MZe-TiO₂ bed are presented in **Figures 7A** and **4**. According to **Figure 7A**, by placing the Ze-TiO₂ bed at the concentration of 50 ppm, the reactor output was zero within the first 24 minutes, but after toluene was observed in the reactor outlet, the bed performance decreased over time and finally the output level sustained after 54 minutes and was able to remove 16% of toluene vapors. This amount was 11.3% and 4.33% for 150 and 300 ppm concentration respectively. According to **Figure 7B**, of MZe-TiO₂ bed reactor outlet was zero at 50 ppm concentration in the first 32 minutes, and after being observed and stabilization of toluene concentration in the reactor outlet, the bed was able to remove 26% toluene vapors. 14.6% and 9.6% were recorded at concentration of 150 and 300 ppm, respectively.

Figure 7B shows the photocatalytic efficiency of MZe-TiO₂ bed in concentrations of 50, 150 and 300 ppm. According to this curves it was able to remove 26% of toluene vapors at the concentration of 50 ppm, which is the highest efficiency among other concentrations. The lowest efficiency were recorded 9.6% for 300 ppm. **Figure 7A** also demonstrates the decrement of photocatalytic efficiency in the Ze-TiO₂ bed by enhancement of the concentration.

DISCUSSION

Structural properties of the bed

The results of the BET analysis showed that specific surface area of RZe was 56.4 m²/g but chemical modification by hydrochloric acid and trimethylchlorosilane solution eliminated impurities and fossil carbon (calcite and aragonite) and increased the porosity and also its specific surface area for 2.54 times. Asilian et al.²³ modified zeolite with hydrochloric acid and trichlorosilane and stated that chemical modification increases the Si/A ratio and removal of fossil carbon (calcite and aragonite). Mortazavi et al.²⁹ by study modifying the natural

zeolite with surfactants found that specific surface area of bed after modification, decreased from 13.7 m²/g to 13.51 m²/g which can be due to closure of channels by anionic surfactant. According to the results of the BJH analysis (**Figure 3**) an increase of zeolite adsorption-desorption by nitrogen gas, before $P/P_0 = 0.8$ with increase of relative pressure, follows a certain pattern and after $P/P_0 = 0.8$ adsorption increases faster. According to International Union of Pure and Applied Chemistry (IUPAC) classification, this pattern is classified as Group IV, which is reserved for porous materials.³⁰ The results of electron microscope (**Figure 4**) and XRD pattern (**Figure 5**) showed that zeolite porosity that has increased with calcination, would reduce after chemical modification and stabilization of nanoparticles on it. It also confirms the successful stabilization of nanoparticles on the bed. Azimi Pirsraei et al.³¹ studied diatomite modification indicated that heat treatment of bed will reduce pore size and increase average pore radius, so that the specific surface area after calcination at temperature of 550°C, decreased from 43.3 m²/g to 16.8 m²/g.

Adsorption capacity

Effect of bed modification on adsorption capacity

According to **Figure 6** results, adsorption capacity increases by modifying the bed. BET and BJH analysis also confirm it. The adsorption capacity of MZe-TiO₂ at a concentration of 50 ppm increased 30.3% toward Ze-TiO₂. This amount was 43.4% at the concentration of 150 ppm and 35.3% for 300 ppm. The reason for this, can be enhancement of porosity, removal of impurities such as fossil carbon and specific surface area, as well as increased Si/Al ratio. Asilian et al.²³ at the study of styrene removal from air by natural zeolite, demonstrated that bed adsorption performance can significantly change with thermal and chemical modification. In their study, the adsorption of modified bed has increased 100%.

Effect of inlet concentration on the adsorption capacity

According to **Figure 6** and comparison of the adsorption capacity in different concentrations, increasing the concentration will decrease Leak time and breakthrough time, but have a positive effect on the adsorption capacity of the bed.



The reason for this direct relationship between increased concentration and adsorption capacity can be due to maximum adsorption capacity usage of bed and fast transfer of pollutants from the gas phase to solid in high concentrations. Because, by increasing the number of pollutant molecules, the number of active sites on the bed will increase. Mousavi et al.³² studied the efficacy of GAC/MgO composite for destructive adsorption of benzene from the waste air stream and indicated that increasing the concentration will reduce the breakthrough time and increase adsorption capacity. These findings comply with Chen et al.³³ study (removal of toluene using ZSM-5 and PSSF (paper-like sintered stainless steel fibers) composite) and also Rezai et al.³⁴ study about toluene adsorption from waste air stream using activated carbon impregnated with manganese and magnesium metal oxides.

Effect of bed modification on photocatalytic process

According to the results of **Figure 7**, the MZe-TiO₂ bed has better performance. It has removed 26% toluene vapors after stabilizing the output concentration level. While the Ze-TiO₂ bed was able to remove 16% toluene vapors, which confirmed the effectiveness of chemical and thermal modification process on increasing the photocatalytic efficiency of bed. Comparing **Figures 7A** and **4** indicates the enhancement of efficiency at a concentration of 150 and 300 ppm. Considering these results the maximum efficiency was obtained for MZe-TiO₂ bed at 50 ppm concentration. Masoud Rismanchian et al.²⁶ at the study of gaseous toluene removal by using of the photocatalytic activity of TiO₂ coated on foam nickel metal succeed to to remove 55% toluene vapors from waste air stream. In that study, a 7500 cm³ size static system was used at a concentration of 45 ppm which reduced to 20 ppm after 270 minutes. The increased efficiency of that study compared to present study can be due to lower volumes of pollutants and longer exposure time. In present study system was designed dynamically with a flow rate of 1 m/L. Pham et al.² were able to remove 80% toluene vapors. They employed visible light with a wavelength of 400–700 nm and TiO₂ nanoparticles to remove toluene vapors from the air with a flow rate of 0.2 L/m and concentration of 200 ppm. That is according to different conditions and variables such as flow rate, cannot be compared with the present study.

Effect of concentration on removal efficiency

According to **Figure 7**, the increase of concentration from 50 ppm to 300 ppm will reduce the Leak time and breakthrough time and also photocatalytic efficiency. By increasing the concentration from 50 ppm to 150 ppm and from 150 ppm to 300 ppm, the removal efficiency of MZe-TiO₂ bed (**Figure 7B**) declined 78% and 52% respectively. The same reduction in efficiency can be seen in Ze-TiO₂ bed in **Figure 7A**. As mentioned before, the reason of decrease in efficiency by increasing the concentration can be rapid saturation of TiO₂ active surfaces and the low retention time of toluene molecules on the surfaces of the catalyst which comply with Zou et al.³⁵ and Rezai³⁴ studies.

Conclusion

The results of the photocatalytic removal of Ze-TiO₂ and

MZe-TiO₂ bed at three defined concentrations (50,150 and 300 ppm) showed that chemical and thermal refining of bed can increase its efficiency in the photocatalytic processes. So that the bed performance increased 1.62, 1.28 and 2.23 times at concentrations of 50, 150 and 300 ppm respectively after modification. According to the great supply of the bed in the world and Iran and its low cost of preparation compared to commercial synthetic bed such as zeolite Y and ZSM-5, It can be used to control environmental pollutants such as VOCs.

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Author contributions

All the authors participated in the laboratory stages of the study.

Conflicts of interest

The authors declare that they have no conflict of interests.

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Data sharing statement

Datasets analyzed during the current study are available from the corresponding author on reasonable request.

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