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Original Article

Photocatalytic Removal of Toluene Vapour Pollutant from the Air Using Titanium Dioxide Nanoparticles Supported on the Natural Zeolite

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Abstract

Background: The emission of volatile organic compounds (VOCs) in industrial and urban areas has adverse effects on the environment and human health. Toluene, the main pollutant among the VOCs, has wide applications in different industries such as plastics, adhesives, silicone sealant, paint, etc. This study aimed to remove of toluene from the air by using TiO2 nanoparticles supported on the natural zeolite using the photocatalytic process.

Methods: This is an experimental study that was conducted in 2017 in the Chemical Agents Laboratory of the Occupational Health Engineering Department at Jundishapur University in Ahvaz. Toluene vapour decomposition was carried out using UV/ZE, UV/TiO2, and UV/TiO2-ZE under continuous flows conditions. The effects of toluene initial concentration, retention time, and nanocomposite surface weight on toluene vapour decomposition were also investigated.

Results: When UV/TiO2 and UV/TiO2-ZE systems are performed, increasing the initial toluene concentration reduces the efficiency of photocatalytic decomposition. The SEM images of TiO2-ZE catalyst show that zeolite pores were occupied by titanium dioxide nanoparticles. Moreover, the combination of titanium dioxide nanoparticles and zeolite has an incremental effect on toluene decomposition. Increasing retention time raises toluene decomposition, and the increased nanocomposite surface weight raises decomposition to the maximum level (70%) at 33.68 mg/cm2 weight and then decreases.

Conclusion: The increasing toluene decomposition rate by using the TiO2-ZE nanocomposite can be due to the incremental effect of absorption and photocatalytic decomposition.

Keywords: Toluene; Zeolite; Titanium dioxide nanoparticles; Photocatalytic decomposition

Introduction

Toluene ($C_6H_5CH_3$) is an aromatic hydrocarbon and has been used as a solvent in different industries such as paints, thinners, silicone sealant, chemical reagents, plastics, printing inks, adhesives, antiseptic, and disinfectant. It can also be used for the preparation of foam and TNT. Vehicles, aircraft, splurge petrol, and other processes in which toluene is used or produced are the other main toluene emission resources. Toluene is a deterrent agent of the central nervous system, and touching a small amount of this substance causes dizziness, euphoria, and confusion in the humans. However, touching high concentrations of toluene can cause ataxia, anaesthesia, and even death (1-5). The allowable concentration of toluene is 50 ppm for the workplace, as recommended by the ACGIH. Toluene usually enters the body via inhalation in the workplace (6). Regarding the harmful effects of toluene on the worker's health and also its wide application in different industries, it is essential to remove this pollutant and prevent its emission in the workplace.

The adsorption, burning, catalytic oxidation, absorption, condensation, biotechnology, and membrane processes are some methods of air pollution control in the VOCs removal (7, 8). Photocatalytic decomposition is one of the novel VOCs decomposition methods, and can easily be conducted at room temperature and room pressure. In this context, for the photocatalytic oxidation of organic compounds or breaking down into simpler components, these compounds were completely mineralized by using semiconductor metal oxides (9,10). Among the semiconductors, titanium dioxide (TiO_2) is the most effective photocatalyst, which has widely been applied in photocatalytic usage due to its physical and chemical stability, low-cost, inert and non-toxic, and corrosion-resistance properties (11-14). Titanium dioxide (TiO_2) excited with UV light can decompose various organic compounds in water and air into CO_2 and other minerals (15).

Researchers have considered the improvement and optimization of the TiO_2 surface in order to increase the contact surface of the photocatalyst with the pollutant. Much research has been carried out about the basic principles and the increase in photocatalytic activities under ultraviolet light (16, 17). On the other hand, the support of the photocatalyst on the supportive materials and stabilizers having a large surface area can condensate the diluted gas compounds or adsorb them, thereby increasing the decomposition yield (8,18,19).

Clinoptilolite is one of the most widely used and popular natural zeolites; it includes the most natural zeolite resources in Iran (20). Using this compound is economically affordable.

Therefore, in this research, the TiO_2 nanocatalyst was supported on the clinoptilolite natural zeolite as an adsorbent and supportive material in order to raise the toluene photocatalytic decomposition.

According to removal of pollutants from the inner places and also regarding the high efficiency, decreasing energy consumption, and other advantages of the photocatalytic process, a study has been carried out to determine the efficiency of toluene photocatalytic decomposition in the gas phase by using the dynamic flow state and UV/ZE, UV/TiO_2, and UV/TiO_2-ZE systems. Moreover, the effects of initial toluene concentration and retention time on the efficiency of toluene gas decomposition have been investigated.

Materials and Methods

Materials and the equipment

This is a experimental study that was conducted in 2017 in the Chemical Agents Laboratory of the Occupational Health Engineering Department at Jundishapur University in Ahvaz. Toluene with 99.8% purity was purchased from Merck Company. Double-distilled water, a 8 W UV-C lamp (Philips Model), an aquarium pump, a Phoceck direct reading instrument (Phoceck 5000), a flowmeter, and a 200 cc impinger were the main materials and equipment in this research.

Titanium dioxide made in the United States (US Nano America), has a diameter of 25-75 nm.

The zeolite with a diameter of 0-2 mm, on average, was used, produced by Afrazand Company in Garmsar, Semnan, and the granules were grained in 20-40 mesh by the ASTM standard sieves.

The TiO_2/ZE preparation

To prepare the TiO_2/ZE composite, the zeolite with 20-40 mesh and titanium dioxide nanoparticles in the 95:5 proportion were added together and converted into an aqueous suspension by using double-distilled water. Next, the mixture was stirred by using a magnet for 1 h. The prepared suspension was sonicated by using an ultrasonic bath device under 30 KHz frequency for 1 h in order to produce the uniform distribution of titanium dioxide. Then, the obtained TiO2/ZE was put into a shaker at 37 °C with 120 rpm speed for 2 h. After drying at room temperature, it was put into a furnace with 300 °C temperature for 1 h (8,17,21).

Catalysts characterization

Specific surface areas of the samples were determined by the nitrogen adsorption-desorption isotherms measured by gas sorption analyzer (VEGA-TESCAN).The solid structures were analyzed using scanning electronic microscopy (Belsorp mini- JAPEN).

The toluene vapour generation system

This system contains different parts such as a blow pump, a rotameter, the glassware and connections, and an impinger. Toluene vapour generated in the impinger along with the air blown by the pump entered the sampling glass. All tests were carried out at constant temperature under the laboratory hood, and laboratory atmospheric conditions such as the temperature and humidity were measured. The sampling glass was applied to measure the initial concentration of toluene steams and played a role as a levelling agent. Moreover, this glass can be used for more dilution by entering fresh air from a pump (8, 22, 23).

Measuring the toluene vapours concentration

To measure toluene vapours, a Phocheck direct reading device (Phocheck 5000) made by ION Science Company, England, was used. This device, equipped with a special lamp with 10.7 ev of energy, was simultaneously applied for sampling and measuring the vapours via the photo-ionization detection (PID) method. The toluene concentrations were regularly measured in the input and output system by using the Phocheck direct reading device. This device is really sensitive and exact, and analyses the condensation within the ppb range (8).

The photo-reactor system

The photo-reactor system includes a Pyrex cubic enclosure with a volume of 5.1 L (10 × 30 × 17 cm). An airflow input part was embedded at the top of it, and a gas flow output part exists at the bottom. Between the input and output parts and at the height of 5 cm from the bottom, a porous bed containing a thin uniform layer of the catalyst was embedded (8). In the upper part of the reactor and at a vertical distance from the surface of the catalyst bed, two UV-C (8 W) lamps with the 100-280 nm wavelength made by Philips Company were horizontally installed in such a manner that they have the maximum wavelength of 254 nm (Fig.1).

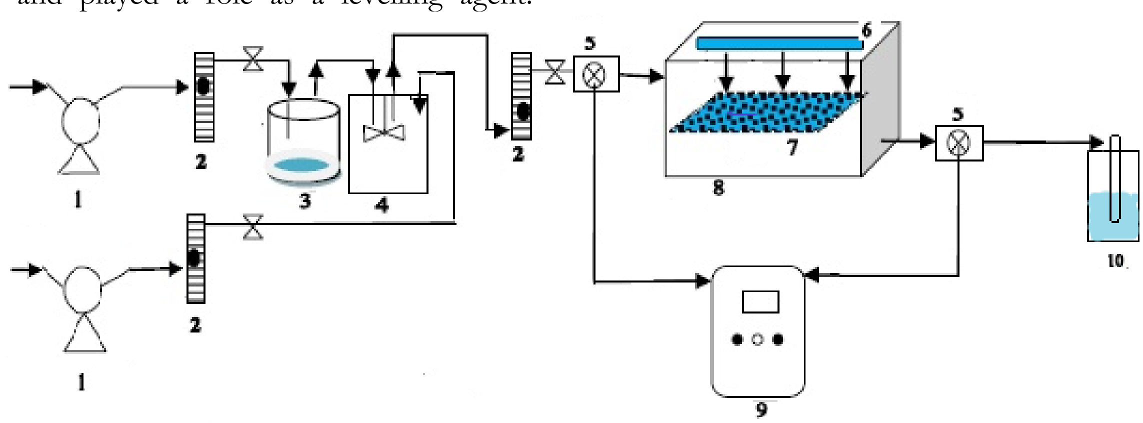


Fig. 1: A shematic diagram of continuous flow reactor.1air pump, 2 flow m, 3 Toluene saturator, 4 mixer, 5 Measurement port, 6 UV Lamp, 7 Catalysis film, 8 Photoreactor, 9 Detection apparatus, 10 Trap

The average amount of UV rays was measured about 1160 μw/cm^2 based on the radiant power density of the digital device made by Lutron Company (UV-C-254 model).

Ethics approval and consent to participate

No human samples were used in this study and all experiments were chemically and in laboratory scale.

Results

Catalysts characterization

Characteristics specific surface area (BET) TiO_2-nano, Zeolite, TiO_2- ZE was respectively 25.6, 138.755 and 53.637 m^2/g.

Fig. 2 and 3 show the scanning electron microscopy (SEM) images of the zeolite, TiO_2-ZE nanocomposite, and also their EDX diagrams.

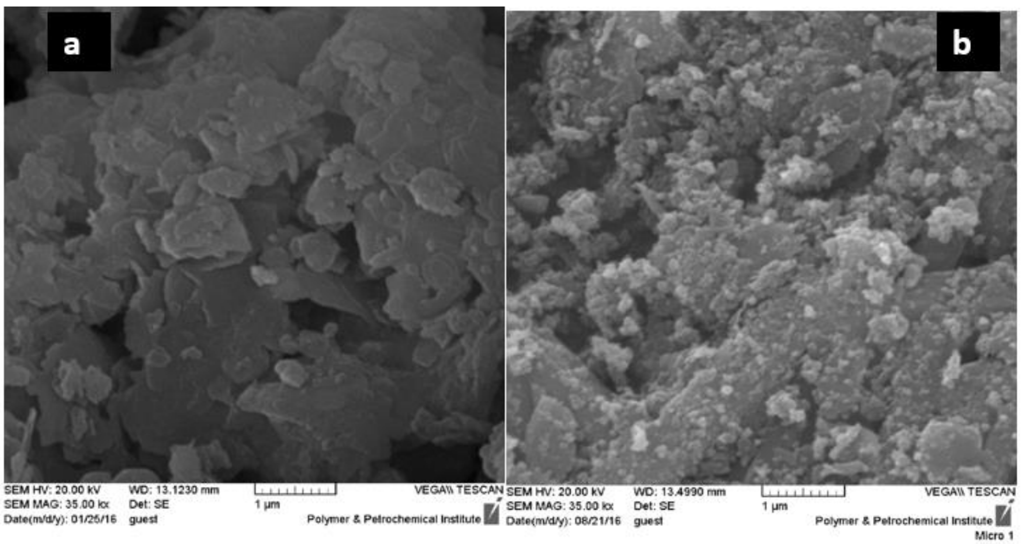
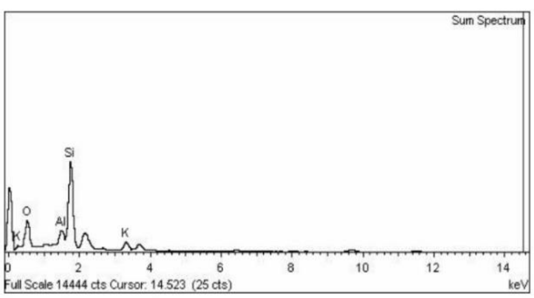
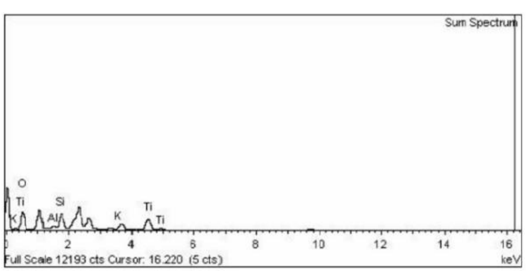


Fig. 2: Scanning electron micrographs of a ZE b TiO2 – ZE



Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
O K	51.84	0.5375	60.05	0.59	73.04
Al K	6.50	0.7817	5.18	0.21	3.73
Si K	39.66	0.8139	30.34	0.47	21.02
K K	6.35	0.8925	4.43	0.17	2.21
Totals			100.00		



Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
O K	58.54	0.4747	73.52	0.61	86.10
Al K	2.30	0.6759	2.03	0.19	1.41
Si K	13.00	0.7705	10.06	0.30	6.71
K K	2.70	0.9660	1.66	0.15	0.80
Ti K	16.85	0.7896	12.73	0.37	4.98
Totals			100.00		

Fig. 3: Energy Dispersive X-ray (EDX) analysis of a ZE b TiO_2- ZE

The effects of initial concentration on removal efficiency

The results of investigating toluene photocatalytic decomposition by using UV/ZE, UV/TiO_2, and UV/TiO_2-ZE process, considering the initial variable concentrations of toluene, have been shown in Fig. 4. The amounts of toluene decomposition efficiency were obtained in the initial concentrations of 25, 50, and 100 ppm with a relative humidity of 35% and the total volume flow rate of 1000 ml/min under constant conditions. Using UV/TiO_2 and UV/TiO_2-ZE systems, the efficiency of toluene photocatalytic decomposition decreases when the initial toluene concentration increases.

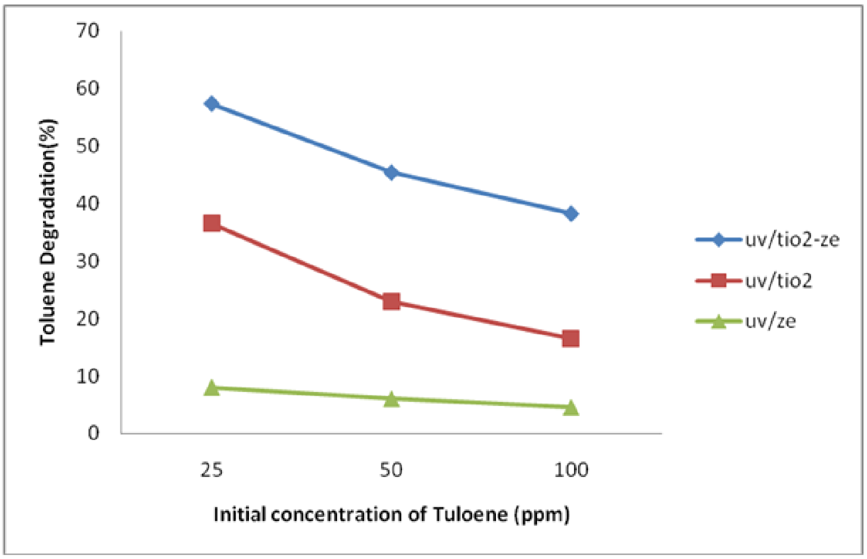


Fig. 4: Effect of initial Tuloene concentration on the potocatalytic removal; condition: humidity 35%;total flow rate 1000 ml/min; Surface weight loaded 16.84 mg/cm²

The effects of retention time on removal efficiency

Table 1 presents relation of flow rate and residence time in the photo-reactor system.

The effects of nanocomposite surface weight on removal efficiency

Fig. 6 illustrates the effects of nanocomposite surface weight on toluene removal efficiency by using the initial toluene concentration of 50 ppm, 35% relative humidity, and the input flow rate of 1000 ml/min.

Table 1: Relation of flow rate and residence time

Flow rate (ml/min)	*500*	*1000*	*1500*	*2000*
Residence time (s)	612	306	204	153

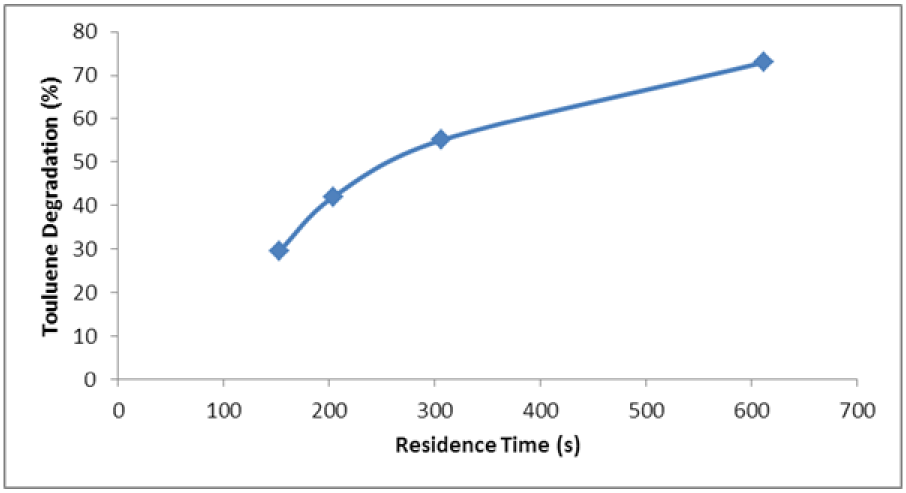


Fig. 5: Effect of residence time on decomposing Toluene; condition inlet Toluene concentration 50ppm; relative humidity 35%

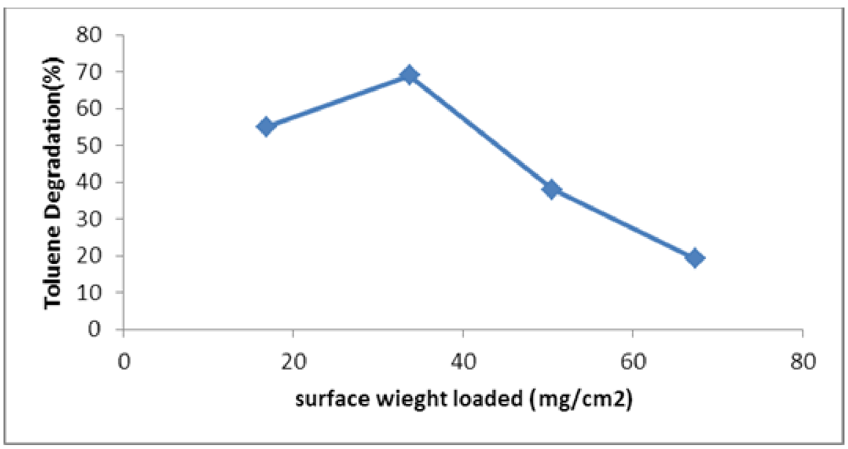


Fig. 6: Effect of surface wieght loaded on decomposing Toluene; condition: relative humidity 35%; total flow rate1000ml/min; intel Toluene concentration 50 ppm

Discussion

The SEM images of the TiO_2-ZE catalyst illustrates that the zeolite pores have been occupied by titanium dioxide nanoparticles.

The Energy Dispersive X-ray diagram (EDX) depicts that the structure of clinoptilolite zeolite includes elements such as oxygen (60.05%), aluminum (5.18%), silicon (30.34%), and potassium (4.43%) (Fig.3a). After doping the titanium dioxide nanoparticles on the zeolite, the percentage of oxygen increased from 60% to 73.52% while the aluminum and silicon percentages decreased from 5.18% to 2% and from 30.34% to 10%, respectively. Moreover, the percentage of potassium reduced to 1.66%, and although there was no Ti element in the zeolite structure, about 13% was added to this zeolite, which indicates that the doping process of titanium dioxide on the zeolite has been done (Fig.3b).

When the initial concentration increases from 25 to 100 ppm, the removal efficiency decreases from 36.6% to 16.5% and from 57.3 to 38.3% through the use UV/TiO_2 and UV/TiO_2-ZE systems, respectively (Fig. 4). Toluene decomposition efficiency is very low in each initial toluene concentration through the use of the UV/ZE process, and that increasing the concentration does not affect this efficiency, which can be due to the absence of semiconductor titanium dioxide nanoparticles in the UV/ZE structure. Moreover, zeolite has not been excited by UV ray and cannot decompose the toluene. This can be due to the effect of UV ray on the toluene photolysis. However, the presence of zeolite in the UV/TiO_2-ZE process can greatly increase toluene removal efficiency when compared with the UV/TiO_2 process. Titanium dioxide nanoparticles supported on the porous silicon dioxide (SiO_2) were applied to remove volatile organic compounds (toluene was considered as the main volatile organic compound), and the toluene is removed by the adsorption process by using the catalyst in such a manner that unpurified toluene, water, and carbon dioxide which are the products of organic compounds exist in outdoor air (24). This result is in agreement with the results of the other research (8, 17, 25 ,26), which is based on using nanoparticles supported on an adsorbent to improve pollutant removal efficiency. Increasing the retention time (Fig.5) (the decrease of input flow's speed Table 1) raises toluene decomposition efficiency by using the UV/TiO_2-ZE process. When the retention time is low (153 sec), this efficiency is 29.6%. When the retention time increases to 612 sec, toluene decomposition efficiency reaches 73%. Titanium dioxide was used to remove the volatile organic compounds, indicating that increasing the speed of input flow about two times decreases the removal amount about more than two times (27). In the photocatalytic system, the retention time for affecting the system on pollutants is vitally important (8, 22). Studying the effects of surface weight on the decomposition yield depicts that first of all, increasing the surface weight of nanocomposite (TiO_2-ZE) raises the decomposition efficiency to reach the highest amount (70%) in the 33.68 mg/cm2 weight. Then, the decomposition yield decreases. When the catalyst surface weight increases from 16.84 to 33.68 mg/cm^2, more toluene molecules are in the adsorption area of catalyst and the removal yield increases.

However, by raising the catalyst weight, the toluene decomposition yield to less than 20% decreases due to the increasing catalyst thickness in the filter, which creates pressure drop, and the lack of UV ray influence on the catalyst depth.

Conclusion

Doping titanium dioxide nanoparticles on natural zeolite under UV ray improves toluene removal efficiency from the air in such a manner that the UV/TiO2-ZE process can decompose the toluene with more efficiency when compared to the UV/TiO2 process. Toluene decomposition efficiency is affected by the initial concentration, retention time, and surface weight. Therefore, the combination of photocatalytic and adsorption processes can be an effective method for the removal of VOCs from the inner places.

Journalism Ethics considerations

Ethical issues (Including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc.) have been completely observed by the authors.

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Conflict of interest

The authors declare that they have no conflict of interests

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