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Photocatalytic Removal of Methylbenzene Vapors by $MnO_2/Al_2O_3/Fe_2O_3$ Nano composite

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ABSTRACT

Methyl benzene, which has carcinogenic effects, is a volatile organic compound that is widely used in various industries. Nano composites of $Mno_2/Al_20_3/Fe_20_3$, which is a new photocatalyst, have not been applied to remove contaminants from air streams. Therefore, the aim of the present study was to investigate the photocatalytic removal of ethyl benzene by using this nano composite activated by visible light. Morphological characteristics of the synthesized Nano composite in a sol-gel method are determined through XRD, FTIR, and SEM. Through the photocatalyst process and by the use of visible light radiation, the synthesized Nano composite is used to degrade ethyl benzene in the gas phase. In order to estimate the main effects and interaction ones and to optimize the experiment numbers, the response surface method was used. Operational parameters investigated in the study are the initial concentration of contaminants, relative humidity, and the residence time, which were considered in three levels; further, the experiments were designed by Design Expert version 9 software. The results show the Nano composite particle sizes were less than 82 nanometers. The findings also indicate that relative humidity and residence time were effective parameters in removal efficiency of ethyl benzene. This Nano composite, at the optimal conditions, was capable of removing 98.72% of the pollutants, with an initial content of 300 ppm. $MnO_2/Al_2O_3/Fe_2O_3$ Nano composite is a suitable catalyst to remove ethyl benzene from air streams. Among the features of the Nano composite are reaction at room temperature and lower production dangerous byproducts, which are the main advantages of this Nano composite as compared with other nano composites.

Key word: Nano-Composite, Ethyl benzene, Photocatalyst, $MnO_2/Al_2O_3/Fe_2O_3$

INTRODUCTION

Air quality is directly related to health hazards, and volatile organic compounds (VOCs) play a role in many health problems [1]. VOCs are compounds that have high vapor pressure at room temperature. This high vapor pressure, due to the boiling point of this material, causes a significant amount of the molecules to evaporate or submerge in vapor and release in the air [2]. VOCs are important air pollutants, which are present in various industries, laboratories, and office buildings and are emitted into the environment [3]. Methylbenzene is one of the VOC compounds, due to the use in solvents, carpet adhesives, paint, and cigarettes as well as in the chemical and petrochemical industries [4, 5]. Some effects of exposure to ethylbenzene include skin irritation, respiratory problems, and cancer and effects on the central nervous and circulatory systems [6]; therefore, it is important to remove these contaminants. There are various methods to remove volatile organic compounds, including the oxidation method. Comparing the two methods of oxidation, the photocatalytic oxidation method is more common; in fact, the main advantage of photocatalytic oxidation is that the reaction takes place at lower temperatures [7]. Today, the photocatalyst oxidation method is a fast and cost-effective means for refining VOCs. The photocatalytic oxidation method typically uses a semiconductor as a catalyst and light for the oxidation of volatile organic compounds and changing it into water vapor and carbon dioxide [8]. A large variety of photocatalyst such as ZnO, GaP, TiO_2, SiC, CdS, Fe_2O_3, and for the degradation and removal of VOC compounds are used [8-10]. Including the oldest catalysts is titanium oxide, the catalyst is only able to absorb light in the range of UV wavelength and other types of catalysts are activated with UV light and visible light [9]. because of the dangers of UV radiation and that only 4 percent of the sunlight is containing UV[11] and because a larger percentage of the sun light is visible,and also accessible, safe and cheaper so the study of the catalyst with the ability of

being activated with visible light is more considered. [12, 13] To solve some photo-catalysts problems including the low absorption level or poor response to visible light, ways such as doping elements to the catalysts can be used [8, 11, 14, 15]. Several studies have suggested that metal doping TiO2 causing improve its photocatalytic activity. Therefore doping is commonly regarded as more effective and simpler than other methods for promotion efficiency[16]. Studies have shown that doping improved the photo-catalytic properties in the removal of the pollutants [8]. The studies on the use of catalysts that are known as noble and precious metals such as: Pt, Pd, Rh, Au because of their high catalytic activity is carried out as well [7, 11]. The main disadvantages of these catalysts are, the high cost compared to other metal catalysts and that are more catalytic poisoned with chlorine and sulfur, rather than the other metal catalysts [7]. Issues such as lower cost and more resistant to catalytic poisons cause study inclination to mediator metals with catalytic properties. Several studies of the appliance of catalysts such as iron, manganese oxides and magnetic nano composites in order to refining of the pollutants, removing color from wastewater and formaldehyde and benzene removal have been done [10, 15, 17-21]. Recent studies on the use of magnetic catalysts to remove pollutants from the air flow have been done [22, 23]. Removing some of VOC compounds such as ethylbenzene and dichloro-methane etc. including catalytic oxidation, a fusion system of plasma and catalysts as well as fusion bioreactor system as a way have been used in the studies [24-31]. MnO_2 / Al_2O_3 / Fe_2O_3 nano composite is a new photocatalyst that in the research for the removal of phenol and green malachite in wastewater refining has been studied [32, 33], while the volatile organic compounds are mostly in the form of gas and vapor in the environment, and inhalation exposure in work place is the most important type of exposure. Considering that no study of using the nano composite to remove contaminants from the air has been performed. The use of $MnO_2/Al_2O_3/Fe_2O_3$ nano composite in photocatalytic removal of ethyl benzene vapors and determining the factors affecting the performance of it have been the aim of this study.

MATERIALS AND METHODS

Experimental Design:

In order to assess main effects and interaction effects and to optimize number of experiments response surface method was used. Concentration, Residence time and relative humidity as the factors being studied, were considered at three levels. A total number of 17 experiments are estimated. Using Design Expert 9 software, the experiments are designed. Operating parameters which were examined in this study presented in Table 1.

Table 1: Factors and their levels

Code	Factor	Unite	level 1	level 2	level 3
A	Residence time	(S)	1	10	19
B	Concentration	(PPM)	100	200	300
C	Relative humidity	(%)	30	50	70

Nano composite Synthesis in Sol-Gel Method

$MnO_2/Al_2O_3/Fe_2O_3$ nano composite was synthesized by sol-gel method [32].in order to: $Fe(NO_3)_3.9H_2O$ (28.28gr),$Al(NO_3)_3.9H_2O$ (7.50gr), MnO_2 (0.87 gr) and butanol (20mL) were added into a separate200 mL beaker containing 28 mL, 8 mL, 4 mL and 0 mL distilled water, respectively, and stirred continuously by magnetic stirrer until dissolved. Each solution was mixed together into another 200 mL beaker containing 3mL of conc.HNO_3 and stirred by magnetic stirrer for 10 min to dissolve. Finally, the solution is left intact at room temperature for 5 days until gel is formed. After gelation, to more evaporation of the solution and drying the gel, it is heated in electric dryer at 100$^{\circ C}$ for 36 hours. Then the dried gel is transferred to a crucible for burning unnecessary organic materials and being calcinated is put in the electric furnace at 400$^{\circ C}$ for duration of 3 hours. The obtained material was in reddish-purple color. To avoid thermal shocks, the samples cooled down gradually to room temperature. The sample is milled with mortar and pestle to make fine powder and a powder in brown color is obtained. The produced nano composite is kept in separate polyethylene container and stayed in desiccators until further investigations.

Test of Nano composite

The experimental apparatus used is shown in Fig.1.

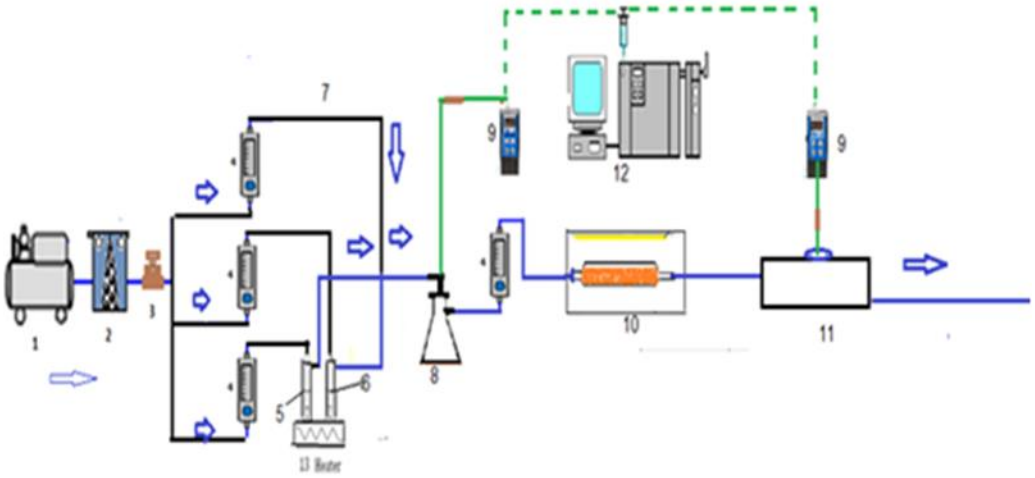

Fig. 1: test setup of nanocomposite

1-Air compressor, 2- silicagel adsorbent, 3- flow control valve, 4- rotameter, 5- impinge containing water, 6-impinger containing ethylbenzen 7- pathway of dilution air, 8- mixing chamber, 9 pump , 10-reactor, 11- sampling chamber, 12- gas chromatography, 13- heater

In the study a rectangular cube shape was used and in order to reflect the light to the all reactor surfaces, all the surfaces are made from the mirror. Inside the chamber, a Pyrex cylindrical reactor with a volume of 25ml has been included. 4 grams of the catalyst in the reactor have been put.

To activate the photo-catalyst, an LED lamp with the wavelength in the range of visible light, is used. In order to produce favorite concentration, the dilution method is used. This means that for vapor generation of Methylbenzene, an impinger containing ethyl-benzene and to supply required humidity an impinger containing water were used. By setting the air flow through the ethylbenzene and solution temperature, evaporation of the pollutant has been controlled and required concentration is produced. The Relative humidity was measured using a digital Thermohygrometers (model of TFA Dostmann/ wertheim). All tests were conducted at room temperature (25°C). To make sure to achieve the desired concentration after the circuit is working in specified concentration in period of about 15 minutes, using absorbent charcoal inside chambers embedded before and after the reactor, by the low flow rate pumps that of 100 ml/min were set for 15 minutes sampling of air was conducted. In this way, simultaneously the amount of pollutants generated in the experimental circuit and amount of removal of pollutants due to the reaction with nano composite is measured.

After sampling finished ,the pollutant is extracted with adding 1ml CS_2 , and analysis of prepared samples using GC (model of Shimadzu-2010) with FID detector and using capillary column RTX-1 with the characteristics of (30m 0.25mm ID ,0.25µm) was carried out. Using a direct reading of CO_2 (model KIMO -AQ 100) CO_2 concentrations measured before and after the reactor, thus the amount of photocatalytic activity of nano composite in the mineralization of contaminant have been investigated. To determine products resulting from the reaction of photocatalytic ethyl-benzene and the, samples after the reactor injected to the GC-MASS (Varian model) using capillary column RTX-624 with the characteristics of (30m 0.25mm ID, 1.4µm). By passing inert gas of nitrogen in condition of no humidity and LED lamp being turned off; the amounts of adsorption of the nano composite have been investigated. Using the formula 1, removal efficiency of ethyl-benzene is calculated.

1) $$X(\%) = \frac{C_{ETB\ in} - C_{ETB\ out}}{C_{ETB\ in}} \times 100$$

Morphological characteristics of $MnO_2/Al_2O_3/Fe_2O_3$ nano composite:

To determine the band structure of $MnO_2/Al_2O_3/Fe_2O_3$ nano composite the FTIR spectrum (PerkinElmer model) by a wavelength of about 1- cm 4000-500 is used. FTIR spectra of $MnO_2/Al_2O_3/Fe_2O_3$ nano composite through the sol-gel method and the calcination temperature of 400°C.

Images taken from the catalyst surface using electron images. To determine the crystal size and structure of $MnO_2/Al_2O_3/Fe_2O_3$ sample XRD pattern was prepared. crystal size (D) synthesized using XRD pattern is calculated according to the formula [33].

2) $$D = k\lambda \div \beta\cos\theta$$

K shape factor (0.94), and λ the wavelength of XRD (equal to 0.154 nm), β the full width at half maximum intensity of the radiation beam in radians, and θ the radiation angle in terms of radians.

RESULTS

FTIR Spectrum

FTIR spectrum Of $MnO_2/Al_2O_3/Fe_2O_3$ nano composite is presented in Figs. 2 and 3. The intense bands at 3376 cm^{-1} may be due to the stretching, in-plane bending and out-plane bending of hydroxide group (–OH) from adsorbed water in the sample. The sharp peak at 1384 cm-1 may be due to C-O stretching vibration of primary alcohol which was used to support the sol gel synthesis; while bands observed at 1627 cm^{-1} may be attributed to the –C–H, -CH_2 & -CH_3 functional groups bending vibrations. The peaks obtained at 826cm^{-1}, 675cm^{-1} indicates Fe-O bond presence in the sample and some interactions among iron (III), Al (III) & Mn (IV) though oxygen or hydroxide bridge. Thus, $MnO_2/Al_2O_3/Fe_2O_3$ has hydrous tri-metal composite. Additionally, results confirm adsorbed water presence on the sample surface at low temperature & short aging time [33].

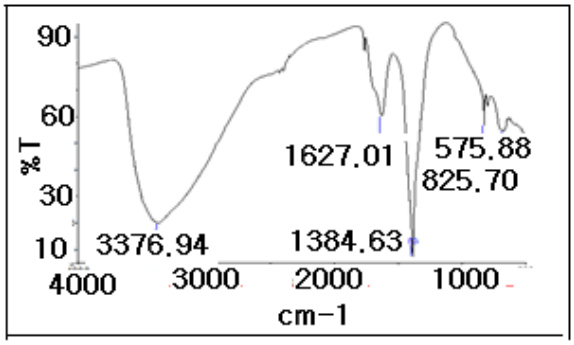

Fig 2: FTIR spectrum, $MnO_2/Al_2O_3/Fe_2O_3$ nanocomposite before calcination.

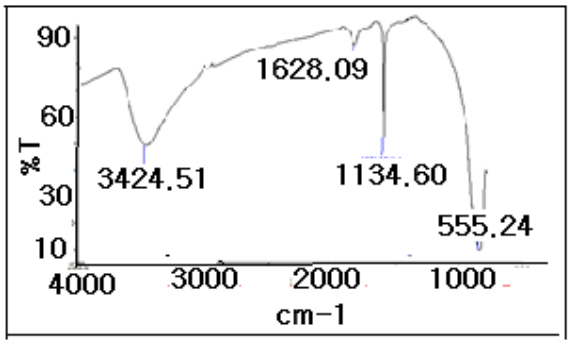

Fig 3: FTIR spectrum, $MnO_2/Al_2O_3/Fe_2O_3$ nano composite after calcination.

SEM images

electron images is presented in Fig. 4. As it can be seen the crystal size of $MnO_2/Al_2O_3/Fe_2O_3$ Nano composite is smaller in the range of 82 nm size.

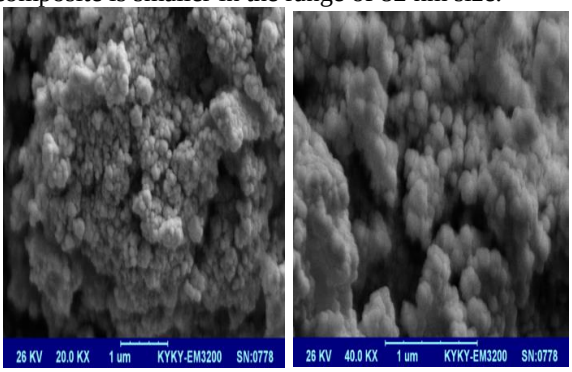

Fig 4: SEM images of $MnO_2/Al_2O_3/Fe_2O_3$ nano composite.

XRD Pattern

Fig. 5 shows XRD pattern of the example. Therefore, due to pattern, the largest of the synthesized particles size 83 nm are obtained.

Based on the description of the experimental design a list of 17 trials involving operating parameters and efficiency of contaminants removal is presented in Table 2.

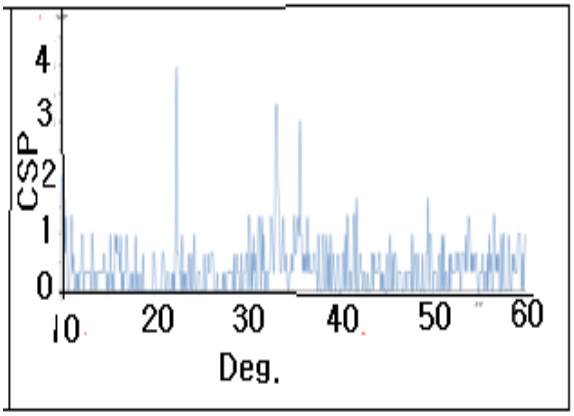

Fig 5: XRD pattern of $MnO_2/Al_2O_3/Fe_2O_3$ Nanocomposite

The optimal conditions in concentration of 300 ppm, relative humidity of 50% and Residence time of 19s is obtained under these conditions the highest efficiency of 98.72% is obtained.

Photocatalytic oxidation reaction products of Ethyl benzene by $MnO_2/Al_2O_3/Fe_2O_3$ nano composite include toluene, as well as CO_2 which in terms of the optimal conditions about 1200ppm CO_2 has been produced, Table 3.

The Effect of Relative Humidity on the Methylbenzene Removal Efficiency

The results of this study show that humidity has positive and meaningful impact on Methylbenzene removal so that by the increase of humidity from 30% to70% the CO_2 output concentration from the reactor

increases and this represents an increase in efficiency of photocatalytic activity of $MnO_2/Al_2O_3/ Fe_2O_3$ nano composite in oxidation of Ethyl benzene. The effect of relative humidity on the photocatalytic activity of the catalyst is shown in Fig. 6.

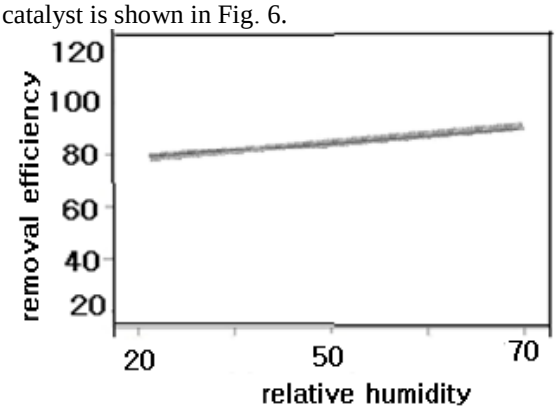

Fig 6: The effect of relative humidity on removal efficiency

The Effect of Residence Time on the Methylbenzene Removal Efficiency

The results of this study show that Residence time has positive and meaningful impact on the Methylbenzene removal efficiency so that by increasing of Residence time from 1 to19s the efficiency has increased. Fig. 7 shows the effect of Residence time on the removal efficiency.

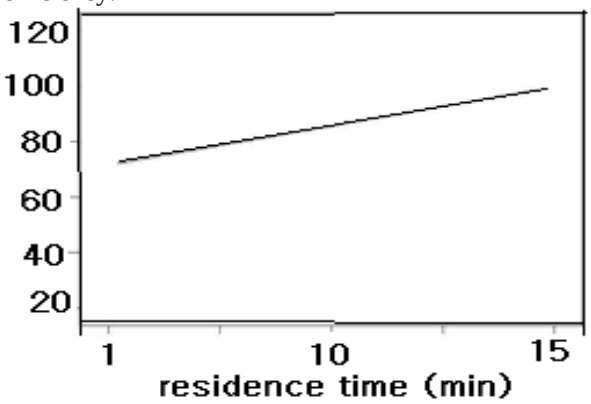

Fig 7: The effect of Residence time on the Ethylbenzene removal efficiency

Table 2: the designed experiments and the percentage of contaminants removal

Run	Residence time (s)	Concentration (ppm)	Humidity (%)	Efficiency (%)
1	10	100	50	94.31
2	19	200	50	96
3	1	200	30	25.07
4	1	200	70	65.18
5	10	300	50	98.72
6	10	200	30	94
7	19	100	70	97.34
8	19	200	50	96.1
9	1	300	50	86.61
10	19	200	50	95.95
11	19	100	30	97.18
12	19	200	50	95.68
13	19	300	70	97.81
14	1	100	50	79.55
15	19	300	30	96.75
16	19	200	50	95.82
17	10	200	70	97.59

Table 3: The conversion rate of ethyl benzene pollutant

Pollutant	Products resulting from Methylbenzene oxidation	Pollutant removal efficiency	Absorption Rate	The conversion rate of pollutant	
				Co_2	Toluene and other products
Methylbenzene	Toluene	%98.53	%70	%75	%25

The Effect of Concentration on the Methyl-benzene Removal Efficiency

In this study, concentration has a significant effect on the removal efficiency. So that by concentration increases in the studied range, there is little change was observed in the Methylbenzene removal efficiency, while at high residence times, by increasing the concentration up to 800 ppm, the removal efficiency from 93% to 64% is reduced. Fig. 8 shows the effect of Residence time on the removal efficiency.

In the chart of normal residuals, a comparison between experimental data of efficiency and predicted values of efficiency by the proposed model software has been shown. As stated in the Fig. 9 the data gathered from the experimental testing is close to the middle line, which means experimental results and predicted data

by the application matches and are being close which confirms high accuracy of the experiment.

Deactivation Catalyst

The nano composite efficiency was reduced to 35% after 31hr working in the condition of residence time of 1s, concentration 300 ppm and relative humidity 50%.

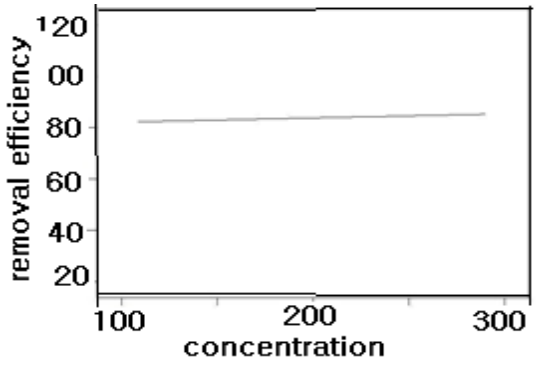

Fig 8: The effect of concentration on the Ethylbenzene removal efficiency

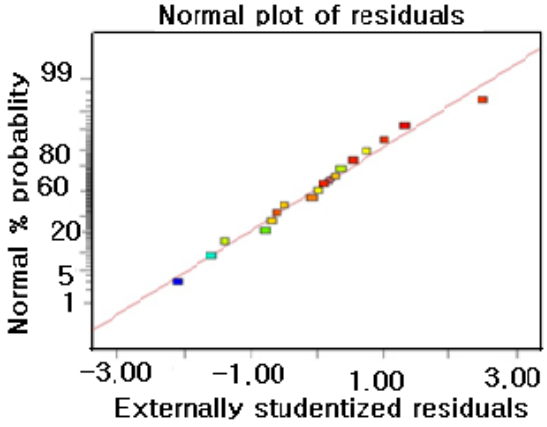

Fig 9: Chart of normalized cumulative residues

DISCUSSIONS

FTIR showed, the intense bands at 3376 cm^{-1} may be due to the stretching, in-plane bending and out-plane bending of hydroxide group (–OH) from adsorbed water in the sample. The sharp peak at 1384 cm^{-1} may be due to C-O stretching vibration of primary alcohol which was used to support the sol gel synthesis; while bands observed at 1627cm^{-1} may be attributed to the –C–H, -CH_2 & -CH_3 functional groups bending vibrations. The peaks obtained at 826 cm−1, 675 cm^{-1} indicates Fe-O bond presence in the sample and some interactions among iron (III), Al (III) & Mn (IV) though oxygen or hydroxide bridge. Thus, $MnO_2/Al_2O_3/Fe_2O_3$ has hydrous tri-metal composite. Additionally, results confirm adsorbed water presence on the sample surface at low temperature & short aging time [33].

XRD patterns and electron images obtained from the surface of the nano composite showed that particle sizes are less than 83 nanometers. A2014 study by Fufa *et al.* synthesized nano composites with particle size of 20 nm [33], demonstrated by comparing their FTIR spectra with spectra from a prior study[32]. In this study, photocatalytic efficiency was enhanced by increasing relative humidity because the water molecules are the source of OH radicals that oxidize contaminants. This finding is consistent with the results of Cheng's study on the removal of ethylbenzene using a titanium oxide catalyst doped with lanthanum [34]. In the removal of toluene gas using $ZnFe_2O_4$nanoparticles,humidity has also been shown to have a positive effect; in contrast, reduction in the availability of water molecules caused the formation of reducing hydroxyl radicals on the catalyst surface, leading to decreased performance [22]. Cheng *et al.* demonstrated that humidity levels of up to 40-50% cause an increase in efficiency, while humidity greater than 80%reducesefficiency[16]. However, in a study of the elimination of dichloromethane using UV light, Jiaming *et al.* found that 75-85% humidity increases efficiency and thus is more suitable for removal [35]. Similarly, a study by Regenhardt *et al.* on the catalytic oxidation of carbon tetrachloride on a zeolite matrix found the presence of water vapor is necessary to prevent degradation of the matrix and to maintain catalyst activity. Conversely, in studies on the removal of dichloromethane gas, carried out by Hong and Ma using the catalyst Pt/TiO_2 and by Hung *et al.* using TiO_2 and Fe-TiO_2 catalysts, increasing humidity reduced removal efficiency, and the no humidity condition was determined optimal for the removal of pollutants [30, 37].This is because dichloromethane oxidation produces chlorinated molecules; by increasing the amount of water, competition between water molecules and dichloromethane for active sites on the catalyst reduces removal efficiency.

This study showed that increasing residence time on the$MnO_2/Al_2O_3/Fe_2O_3$ nano composite causes an increase in ethylbenzene removal efficiency because contaminant exposure to the catalyst surface is increased, enabling the photocatalytic reaction to complete. These results match those of Cheng's study, which compared residence times ranging from12 to 36 seconds and determined the optimum to be 20 seconds [34]. Similarly, Abtahi *et al.* assessed the performance of a consolidated bioreactor liquid column-biofilter on the elimination of dichloromethane from an infected

gas flow and found that reducing the residence time from 200 to 150 seconds also reduced removal efficiency from79% to 71% [24]. In our study, increasing the concentration of ethylbenzen was observed to increase reaction efficiency, because ethylbenzene was a hyper-hydrogenated component and a facilitating agent for oxidation. By increasing the concentration up to800 ppm, the removal efficiency was decreased to 64% due to blocking active positions on the catalyst surface. Cheng carried out a study on the removal of ethylbenzene using a TiO_2catalyst doped with lanthanum, and also found that by increasing concentration, the removal efficiency of ethylbenzene dropped due to intermediate products occupying the active sites[35]. Another study by Mehrizadeh *et al.* on the removal of toluene gas using $ZnFe_2O_4$nanoparticles found that increasing the concentration from300 ppm to 900 ppm increased removal efficiency increased because more toluene molecules reached the catalyst surface [23]. They also found that above 900 ppm, photocatalytic activity decreased due to saturation of the active site; the production of hydroxyl radicals and active species declined. Similarly, Suwannahong *et al.* found that removal of dichloromethane at low concentrations is slower than at high concentrations[28]. This is because at low concentrations, the absorption of dichloro-methane on the catalyst surface is reduced. Abtahi *et al.* further demonstrated that the greatest efficiency for dichloromethane removal is obtained at the lowest rate of loading into the bioreactors [25].In contrast, a study by Fufa *et al.* using a $MnO_2/Al_2O_3/ Fe_2O_3$ nano composite on phenol with concentrations ranging from 50 to 90mg, they found that the reaction efficiency decreased from 93.1% to 62.3% [34]. Jiang *et al.* also showed that when removing polystyrene and ortho xylene using a DBD system, increasing the concentration from 115 ppm to 690 ppm decreases the removal efficiency from82.4% to 35.2% due to the occupation of active sites [37]. The observed byproducts resulting from ethylbenzene oxidation using a $MnO_2/Al_2O_3/Fe_2O_3$ nano composite included CO_2 and toluene. In contrast, Dhada *et al.* found that the products resulting from the photocatalysis of ethylbenzene by TiO_2 included hexane, benzene, toluene, benzoic acid, phenol, hydroquinone, steel benzene, acetic acid and other materials in small amounts [34, 38].The byproducts produced from the reaction of contaminants and photocatalyst thus depends on the type of catalyst [38].Some benefits of the nano composite, in addition to eliminating the contaminants with high efficiency, are that its by-products are either safe(CO_2)or less dangerous than ethylbenzene and produced in minor amounts.In this study, the absorption process has a larger share than the photocatalytic process, therefore fewer byproducts were produced.

CONCLUSION

$MnO_2/Al_2O_3/Fe_2O_3$ nano composite by particles size were less than 82 nm is a suitable catalyst to remove ethylbenzene from air streams .Some of the advantages of the catalyst is including: reaction at room temperature, high efficiency, production of lower dangerous by products are the main advantages of this nano composite as compared with other nano composites and also activation by the visible light.

ETHICAL ISSUES

Ethical issues have been observed by authors.

CONLICT OF INTERESTS

.The author(s) declare that they have no competing interests.

AUTHORS' CONTRIBUTIONS

Authors Contribute on this study as following items:
Maryam Feiz Arefi: study of design and execute the study,Farshid Ghorbani- Shahna: study Supervisor and reviewing manuscript.
Abdulrahman Bahrami: Study Advisor, Hossein Ebrahimi: Study Advisor, and Alireza Mahjub: statistical analysis.

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