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Original Article

Performance Catalytic Ozonation over the Carbosieve in the Removal of Toluene from Waste Air Stream

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ABSTRACT

Background: Toluene is a volatile organic compound, one of 189 hazardous air pollutants (HAPs) and the most important pollutant found in most industries and indoor environments; owing to its adverse health, toluene must be treated before being released into the environment.

Methods: In this research study, a continuous-flow system (including an air compressor, silica gel filters and activated charcoal, impinger, an ozone generation and a fixed bed reactor packed with the carbosieve in size 1.8-2.3 mm, specific surface: 972 m²/g,) was used. This glass reactor was 0.7 m in height; at a distance of 0.2 m from its bottom, a mesh plane was installed so as to hold the adsorbent. Moreover, 3 l/min oxygen passed through this system, 0.43 g/h ozone was prepared. The flow rate of waste airstream was 300 ml/min. The efficiency of this system for removal of toluene was compared under the same experimental conditions.

Results: Under similar conditions, performance of catalytic ozonation was better in toluene removal than that of ozonation and carbosieve alone. On average, increasing the removal efficiency was 45% at all concentrations. When carbosieve and ozone come together, their synergistic effects increased on toluene degradation.

Conclusions: Catalytic ozonation is a suitable, high-efficient and available method for removing toluene from various concentrations of waste air stream. This process due to the short contact time, low energy consuming and making use of cheap catalysts can be used as a novel process for removing various concentrations of volatile organic compounds.

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Introduction

Volatile Organic Compounds (VOCs) are a major group of air pollutants emitted from various sources and pollute the air. They contain more than 300 compounds such as oxygenated hydrocarbons, aromatic hydrocarbons and halogenated hydrocarbons¹⁻³. Benzene, toluene, ethyl benzene, xylene (BTEX) compounds are the most important and common chemical compounds of aromatic hydrocarbons and are considered as indices of VOCs. They are abundantly found in cities and industrial areas and have been classified as toxic priority pollutants. Their major problem in the atmosphere is the possibility of cancer and production of "Air Toxic"^{4,5}. Toluene or methyl benzene is one of volatile aromatic compounds which is very similar to benzene, but less volatile. This compound has a methyl branch on a benzene ring. Toluene is transparent, colorless and volatile liquid with obnoxious odor. As a solvent, toluene is highly used in oils, paints, resins, detergents and glues

and pastes. It is also used in gasoline, petrol and other aviation fuels to raise octane number.

According to ACGIH, toluene is one of 189 hazardous air pollutants and is a primacy and prioritized pollutant which has been classified in A₄ group of carcinogenic substances⁶⁻⁸. Due to various environmental and health effects of this compound, different methods (including adsorption, thermal and catalytic oxidation and advanced oxidation processes) have been examined to remove it from waste air stream^{9,10}. In comparison with conventional treatment methods, Advanced Oxidation Processes (AOPs) are suitable methods for degradation of toxic air pollutants. Degrading pollutants by AOPs is based on production of free active radicals that have high oxidative power and are capable of changing most organic compounds to minerals. The radicals by attaching molecules of organic substances and taking their hydrogen ion, convert these compounds to minerals, during one or some steps.

Catalytic ozonation process (COP) is a new method of single ozonation process (SOP) that has recently been taken into consideration in air pollution control industry. In this process, to improve SOP efficiency, various substances are used as catalysts to accelerate degradation process, increase reaction time and be sure of non-presence of ozone residues in exhaust air¹¹⁻¹⁵. So far some catalysts such as activated carbon, silica gel, metal oxides and various resins have been used in catalytic ozonation process to remove toluene from polluted air¹⁶⁻¹⁸.

According to capabilities of various carbon adsorbents in treating air pollutants, carbosieve, a kind of carbon-based adsorbent which is produced as a result of pyrolysis of synthetic polymers or some of petroleum compounds with high porosity and specific surface area (BET) and is mostly used to adsorb volatile hydrocarbons^{19,20}.

In this study, the carbosieve was used as a non-polar catalyst and adsorbent in catalytic ozonation process.

Methods

Experimental Pilot

This empirical laboratory study was carried out as a pilot scale from December 2012 to May 2013. A laboratory-scale pilot was designed and launched at Hamadan Environmental Chemistry Laboratory (Figure 1), western Iran. Toluene liquid with purity of 99.5% was prepared from German Merck Company. Air containing polluted gas and ozone gas entered bottom of a reactor with a continuous flow. Considering the aim of this study the reaction conditions were closer to the actual conditions thus a dynamic system with continuous flow was used. Contaminant gas in the first of the reactor enters into the bottom of the reactor and exits from the other side (Due to the absence of gas leaks in the system). To prevent condensation of contaminants in the reactor, all parts of the reactor was placed in isothermal chamber. Input air be-

fore entering to the bed enter to the converging chamber and after passing through reticulated plate and finally enter to the catalyst bed.

This glass reactor was 0.7 m in height; at a distance of 0.2 m from its bottom, a mesh plane was installed so as to hold the adsorbent. Required air was supplied by a compressor equipped with oil trap. After the pressure was adjusted, the air passed through a combined column of silica gel and activated charcoal in order to dry and remove any organic contamination. To prepare toluene-containing air in given concentrations, Standard Atmosphere Production method was used in a dynamic way with the aid of an impinger²¹. In this system, the air, produced by a compressor and dried as well as cleaned before, was divided into two branches; calibrated rotameter and needle valve were used to control carefully in the air stream in each branch so as to achieve certain concentrations. In one branch, toluene vapors entered air stream through impinger-bubbler (by keeping temperature of toluene constant) and in the other branch, there was pure stream of air. These two branches lead to a single branch in which a standard stream of air with the given concentration of toluene was created. The reactor was placed in the isothermal chamber for controlling temperature in the reactor. Our concept from constant pressure was atmospheric pressure in the laboratory environment. Dynamic method was used to create standard atmosphere. Inert and contaminant gas at determined concentration enter to the system with a regulated and specific ratio. This works was performed by maintain impinger temperature (Containing liquid toluene due to its vapor pressure) by a hot water bath. Besides for keeping a steady flow and to avoid concentration fluctuations a baffled mixing chamber was used before entering flow to the main reactor. However, in practice, only minor changes in concentration levels (a few ppm) was existed. Therefore, input and output load in the system was reported as removal efficiency.

- 1- Gas chromatography device
- 2- Sampling valve
- 3- Outlet and Ventilation
- 4- Carbosieve media
- 5- Processing reactor
- 6- Baffle mixing chamber
- 7- Ozone generator
- 8- Oxygen-making machine
- 9- Intercepted ozone injector
- 10- Sampling chamber
- 11- Connection pipes
- 12- Bubbler
- 13- Impinger and Toluene liquid
- 14- Rota meter
- 15- Needle valve for discharge control
- 16- Activated charcoal column
- 17- Silica gel column
- 18- Pressure adjustment valve and oil trap
- 19- Air production compressor

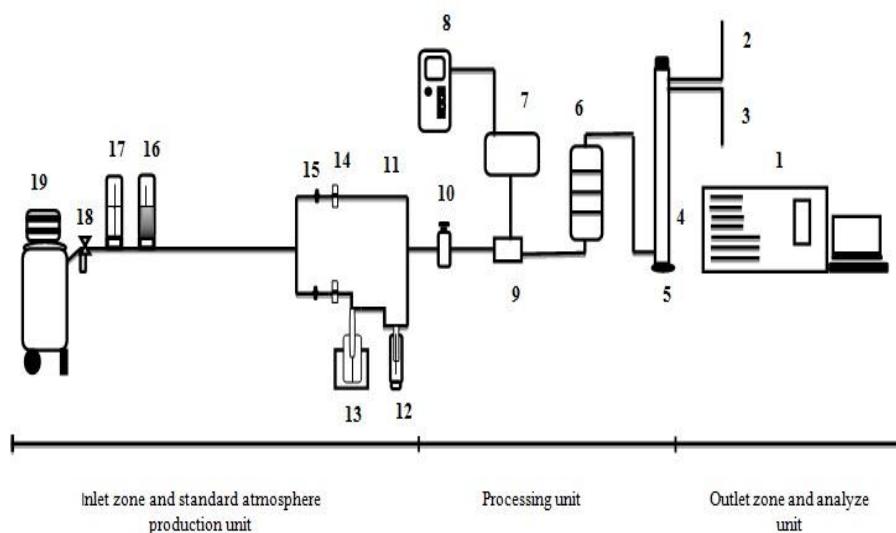


Figure 1: Schematic diagram of the experimental setup

Ozone was made using an ozone-making machine, AR-DA, model COG-OM. In this generator, ozone is produced through creating electrical discharge with alternating current in a sluice in presence of oxygen. Oxygen required for the ozone generator was supplied by an oxygen-making machine, model PORSA VF-3 with high purity level and the

ability to adjust oxygen injection level. The amount of ozone produced by an ozone generator was measured according to Iodometry method in the presence of 2% potassium iodide solution after 10 min of contact^{22,23}. As 3 l/min oxygen passed through this system, 0.43 g/h ozone was prepared. In ozonation unit, ozone gas entered toluene-containing waste

air stream; to prevent and reduce the probable fluctuations and to equalize and fix equilibrium, a baffled mixing chamber is used before the reactor which contains adsorbent bed. After current exits this mixing chamber, it enters carbosieve-containing reactor as a catalyst and non-polar adsorbent bed. Prior to experiments, carbosieve was placed in a in an oven for 2 h at 400 °C and was dried completely in order to remove all probable pollution. Carbosieve used in this study was purchased from Air Tools Co. in Tehran. Then the surface area was measured by BET method. Ten g of Carbosieve were used at each stage of the experiment. Although changes in pressure drop has not been measured before and after bed but the system was designed in such a way do not create the pressure drop in the input stream.

Sample Analysis

Toluene concentration was measured before and after experiments in an air stream using 1501 NMAM (NIOSH Manual Analytic Method) and gas-chromatography device, model SHIMADZU 2010, equipped with flame ionization detector (FID) with a column length of 60 m, column internal diameter of 0.25 mm, film thickness of 0.25 mm and temperature range of 50 to 180 °C according to temperature programming. Optimum analysis conditions of gas chromatography was prepared with injection site temperature of 200 °C, detector temperature of 250 °C, carrier gas flow of ap-

proximately 30 ml/min, hydrogen gas flow of 30 ml/min and air stream of about 300 ml/min^{24,25}. Toluene vapors collected with activated charcoal tube using sampling pump accordance with Method 1501²⁴. After extracting the samples in carbon disulfide 1 µL of extracted sample was injected into the GC in quick time. Experiments were performed in normal ambient temperature (27 ±2 °C) and desirable atmospheric pressure and ventilation. In order to assess the accuracy of the analysis method, was injected three times into the capillary column of gas chromatograph and their mean was reported as the amount of that parameter. The efficiency of carbosieve bed, single ozonation and catalytic ozonation were examined and compared separately.

Results

Efficiency of carbosieve bed

Parameters affecting system efficiency including air flow discharge entering the reactor, adsorbent bed size, ozone level and relative humidity were kept constant at 3 l/min, 15g, 0.43 g/h and 5% respectively; only system efficiency was examined on various concentrations of toluene in range of 20 to 200 ppm. As toluene concentration increased, bed saturation time and absorbent breakpoint decreased. Results of carbosieve efficiency of toluene removal are shown in Figure 2 (A).

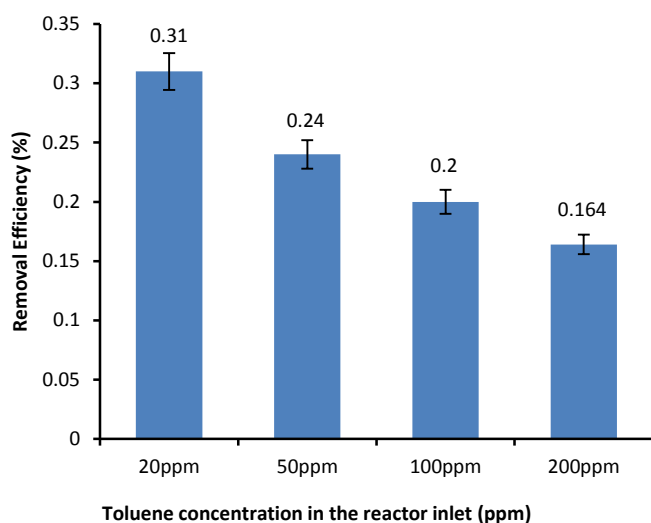
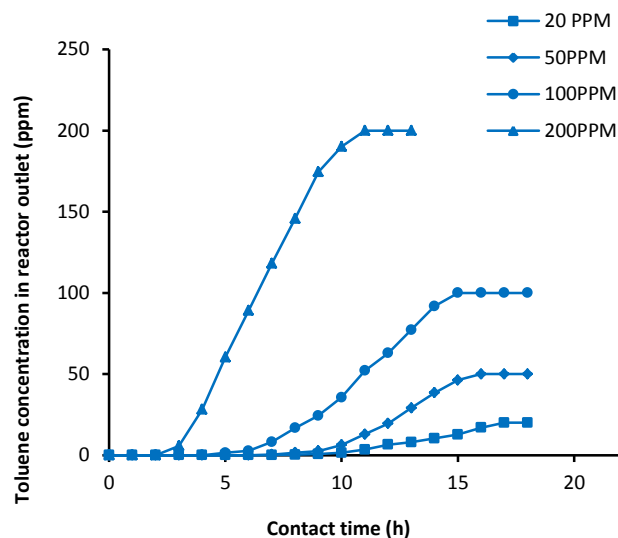


Figure 2: (A) Efficiency of carbosieve bed in removing toluene from waste air stream (B) Ozone efficiency (single ozonation) on removal of toluene from waste air stream

Ozone efficiency

Figure 2(B) shows the removal efficiency of toluene from waste air stream by the single ozonation process separately and without the presence of carbosieve. In this step, experiments conducted in various concentrations of toluene in range of 20-200 ppm and only ozone gas with 3 l/min input of pure oxygen to ozone-making machine and production of 0.43 g/h ozone was used, also other variables affecting system efficiency were kept constant as before. In this step, as concentration increased from 20 to 200 ppm, toluene removal efficiency decreased. In 20 ppm of toluene in the reactor inlet, the removal efficiency reached to 31%. On the other hand, in 200 ppm of toluene in the reactor inlet, ozone efficiency was about 16%. Therefore, the highest efficiency of process was observed in toluene concentration equal to 20 ppm and lowest removal efficiency was in toluene concentration equal to 200 ppm.



Efficiency of catalytic ozonation

Results of efficiency of catalytic ozonation are shown in Figure 3, 4. In this step, experiment was performed under the same conditions and efficiency of catalytic ozonation was examined in terms of toluene output concentration and adsorbent break point. In this step, efficiency of catalytic ozonation was examined on various concentrations of toluene in range of 20-200 ppm. In 20 ppm of toluene, the efficiency of catalytic ozonation in removal of this compound reached about 16 ppm (80%). On the other hand, in 200 ppm of toluene was observed 155 ppm (77.5%). Therefore, by increasing toluene concentration from 20 to 200 ppm, toluene removal efficiency decreased. Moreover, carbosieve saturation and break point were occurred significantly later than single carbosieve system.

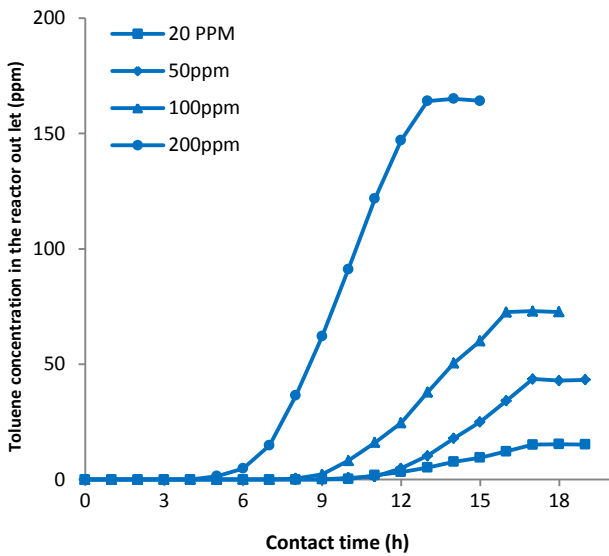


Figure 3: Efficiency of catalytic ozonation in removal of toluene from waste air stream

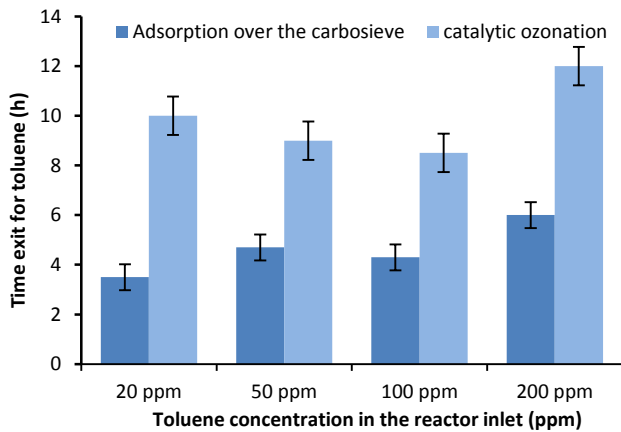


Figure 4: Comparison between times of toluene emergence in carbosieve system with COP process in the different concentrations

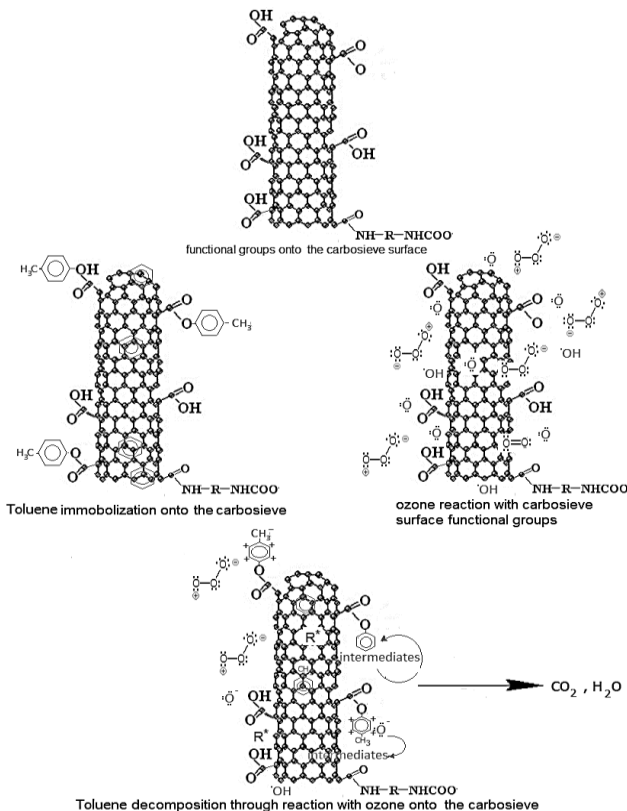


Figure 5: A schematic of toluene decomposition in the catalytic ozonation over the carbosieve

Discussion

This study investigated the efficiency of catalytic ozonation process in treating toluene-containing air as one of hazardous air pollutants. Toluene removal was examined separately on carbosieve bed, single ozonation and catalytic ozonation.

Results revealed that removal efficiency by SOP process was, on average, less than 23% at given concentrations; that is, as the concentration increased from 20 ppm at the beginning of the system to 200 ppm, removal efficiency by SOP process decreased from 31% to 16%. In a similar study by Mousavi et al. on removal of xylene from waste air stream, xylene removal efficiency by ozone gas was about 10%²⁶. On removal of volatile organic compounds (VOCs) using catalytic ozonation that removal efficiency of volatile organic compounds using only ozone was low and thus would result in production of harmful byproducts²⁷. Besides, obtained results are in accordance with the findings of Alvarez et al. on comparison between catalytic ozonation and activated carbon adsorption/ozone-regeneration processes for wastewater treatment²⁸.

Decreased efficiency by SOP process is due to ozone low ability to oxidize aromatic compounds and alkenes and low retention time necessary for complete reaction between ozone and toluene as a result of continuity of the system²⁹. According to obtained results while using carbosieve alone as concentration increased from 20 ppm to 200 ppm, adsorbent break point in the reactor outlet decreased from 10 h to 3 h (Figure 5). Accordingly, adsorbent beds including carbosieve remove the pollutants available in the air passing through adsorbent due to early saturation, especially at high concentrations, necessity to reclamation and most lack of change in the nature of pollutants that have been absorbed. Thus, when a pollutant is hazardous to the environment, making use of absorbents alone may be impractical.

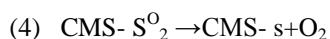
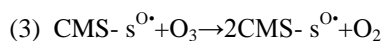
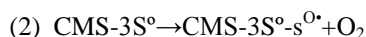
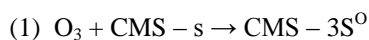
In the present study, to remove restrictions of SOP process and to adsorb over carbosieve, the combinations of these two methods were used. Results of this study indicate that catalytic ozonation has a significant efficiency compared with separate adsorption methods over carbosieve and SOP process. This advantage is shown in Figure 4. Accordingly, as concentration increased from 20 to 200 ppm, absorption break point and removal of toluene from hybrid reactor decreased from 12 to 6 h, while this time was between 3 and 10 h for carbosieve. Thus, it is observed that toluene creation time was higher in hybrid reactor output and COP process under similar laboratory conditions. For example, for concentration of 200 ppm, toluene discharge time increased by 50% compared to carbosieve bed; on average, efficiency in COP process increased by 45% at all concentrations compared with SOP. In carbosieve system, after the bed was saturated at reactor outlet, output toluene concentration was equal to input concentration, while in COP process concentration of output toluene was less than input concentration after saturation; it reflects that combining carbosieve and ozone systems strengthens the effect of them and thus results in more molecular degradation of toluene passing over bed. Xylene removal level increased 22% in COP process compared to activated charcoal and ozone²⁶. Similarly, Wung et al. revealed that toluene removal level increased 20% and 40% in COP process in comparison with zeolite adsorption and MCM-41

respectively. Furthermore, efficiency of ozonation alone in removal nitrobenzene from aqueous solution was about 25% and while was used of COP, the process efficiency reached to about 70%; these results are consistent with results of this section^{27,30}.

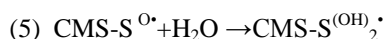
Since ozone is adsorbed over adsorbent, carbosieve adsorbs ozone which rapidly decomposes to activated oxygen atoms over adsorbent bed due to its instability. In other words, carbosieve acts as a catalyst and decomposes ozone into activated oxygen atoms. Having specific surface area and high porosity, carbosieve creates a surrounding bed; in addition to increasing contact surface and collision of toluene and ozone molecules, carbosieve increases retention time for reaction and thus improves removal efficiency.

In reaction between ozone and positions of acid Luis of adsorbent, ozone is decomposed into activated oxygen atoms which decompose toluene into CO₂ and H₂O through attacking single connective bonds between carbon atoms (C-C) or connective bonds between carbon-hydrogen atoms (C-H). Since, in practice, reaction between toluene and ozone is not done completely and may result in production of intermediate compounds, these compounds are again adsorbed by carbosieve (due to its high specific surface) and are decomposed by ozone or by the produced activated radicals (Figure 5).

No intermediate compound was observed in COP process output^{26,27}. In positions of acid Luis of adsorbents, toluene is decomposed into O₂ and O[•] according to the following reactions:

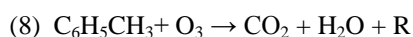
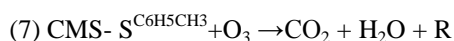


CMS-S and CMS-s[○]3, respectively, reflect positions of acid Luis and ozone molecules adsorbed over carbosieve. CMS-s[○]3 and CMS-s[○] show types of carbosieve surface oxides. CMS-s[○] can also react with water vapor available in the air entering the system and can produce activated hydroxyl radicals (OH[•]) which indirectly take part in decomposition and oxidation of toluene and thus improve removal efficiency.

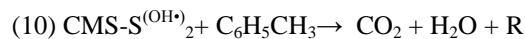


When toluene- and ozone-containing air passes over carbosieve, catalysed reactions of 1-5 occur and toluene is directly and indirectly removed from waste air stream by ozone and radicals resulted from ozone decomposition. In the following equations, R represents intermediate compounds produced during direct and indirect oxidation reactions.

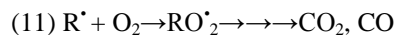
Direct oxidation:



Indirect oxidation:



Since the system used in this study was operated in dry mode, hydroxyl radicals are less likely to be formed so they cannot have an important and vital role in toluene decomposition. In COP process, in addition to ozone and radicals resulted from its decomposition, oxygen molecules play a significant role in toluene decomposition. In the presence of oxygen, ozone decomposition rate increases for more toluene oxidation. In autoxidation processes, this molecule oxidizes radical intermediate compounds (R^{*}) which are one of the reasons for deactivation of catalyst^{26,27,29,31,32}.



Conclusions

Removal of toluene from waste air stream, especially in higher concentrations, is more efficient by COP process than by adsorption system over carbosieve and SOP. This system can be one of promising alternatives for removing various concentrations of volatile organic compounds, especially toxic and hazardous volatile compounds, from waster air stream due to low energy consuming, making use of cheap catalysts and applying adsorbents proportional to pollutant. COP process adsorbs and destroys pollutant simultaneously; in addition to ozone O₃ (E[○] = 2.08 v), this process uses activated hydroxyl radicals (OH[•]) (E[○] = 2.80 v) and atomic oxygen O[•] (E[○] = 2.42 v) resulted from catalyzed reactions over bed. This phenomenon lead to bed chemical reclamation, increased system operating time and decreased the cost of bed reclamation. Therefore, the main benefit of catalytic ozonation is that reaction time is shortened, causing decomposition and purification of volatile organic compounds from air stream in high concentrations of ozone gas and pollutant without removal of excess ozone concentrations at the reactor outlet. However, additional studies are required to develop techniques to enhance the oxidation activity and industrial application in greater scales.

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Conflict of interest statement

This study did not have any conflict of interest statement.

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