

Influence of pollution loading and flow rate on catalytic BTEX removal with a combined Cu_2O , Fe^0 /Zeolite bed

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ABSTRACT

Environmental impacts and health concerns of BTEX compounds have been pointed in many studies. The agencies responsible for health and environment have delivered standard and guideline for BTEX concentrations. Because of the extensive use in industries and the presence of these compounds in fossil fuels, their emission resources are very divers. Today's, Control of air pollution caused by these compounds is one of the air qualities controlling challenges. "Thermal catalyzed" process is one of the technologies to control this kind of air pollution and consistent with using nanoparticles as a catalyst, this process is further considered now. So, we conducted this study to survey elimination of the BTEX, from polluted air flow, by this process. In this study, removal of the BTEX from polluted air by a thermal catalyzed process in the presence of zero-valent iron and copper oxide nanoparticles was investigated and the effect of changes in pollution load and flow rate was surveyed on removal efficiency and the decomposition of the pollutants. Fe^0 and Cu_2O nanoparticles were coated on a bed of natural zeolite (Clinoptilolite) with a zeolite grains size of 1-2 mm. The thermal catalyst process was conducted at 350°C and different pollution loading and air flow rate. 96.18% and 78.42% of removal efficiency achieved with the retention times of 14.1s and 7.05s. Increasing the pollution load reduced removal efficiency and pollutants' mineralization. By doubling the pollution load, the removal efficiency declined as much as 14.5 %. According to the results, increasing of the flow rate has a greater effect than the pollution load on the complete decomposition. Also this process showed a good efficiency for BTEX removal under high pollution loading and flow rates.

Key words: Aromatic organics, Air pollution, Chemical process, Nanoparticles, Zeolite.

INTRODUCTION

The BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) are some of the volatile organic compounds (VOCs). Petroleum derivatives contain some concentration of these compounds. Furthermore, these are widely used in the industries as solvent. Harmful effects of the BTEX on the central nervous system are pointed in literatures and the BTEX known to cause of air, soil and ground water pollution around the petroleum and natural gas producing sites, gas stations, and petroleum reservoirs [1, 2]. The air flow containing VOCs might be treated by zeolite as a sorbent or oxidative catalyst. It is used as a sorbent that can be then cremated or recycled. If the recycling is not considered, the adsorption can be combined with an oxidative catalytic process. Advantage of zeolite application rather than carbon bases adsorbents such as activated carbon is its capability to be used

for the moist flow and low pollutant concentrations. In these cases, application of the zeolites with a high level of silica which are hydrophobic, are so effective [3].

The thermal catalytic process requires relatively high temperatures. In related studies, according to the type of catalyst and other conditions, different temperatures are obtained. In a study, catalytic incineration of benzene on metal oxide catalysts has been investigated. The results indicate a complete destruction of benzene in the temperature of 300°C and 5.5 wt% of copper nanoparticles on TiO_2 and when it increased to 7 wt%, the removal efficiency has dropped [4]. The results of a study to complete oxidation of naphthalene on metal oxide catalysts, showed the catalytic properties of metal oxides such as CuO in naphthalene removal [5]. Some other studies have shown destruction of the volatile organic compounds by iron nanoparticles

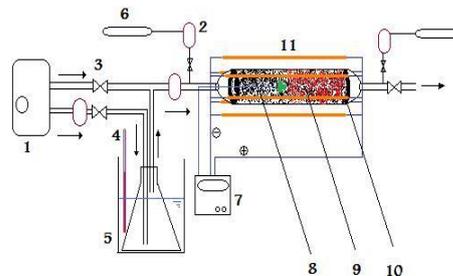
[6, 7]. Removal of VOCs is experimented with different sorbents and the absorbency of natural zeolites such as Clinoptilolite is declared [8]. Using a natural zeolite as a bed, zero-valent iron and copper oxide nanoparticles as catalysts in a thermal process showed high efficiency for BTEX removal and its mineralization at the temperatures around 350 °C [9]. However, just using Cu₂O nanoparticles on the zeolite bed has not been so efficient on BTEX removal [10]. The air flow rate and pollution loading are the inputs that can be varied widely and may have significant impact on pollutants' removal and complete distraction, in the catalytic processes. Thus, the purpose of this study was investigating the effect of changes in pollution loading and flow rate on the removal of BTEX compounds by a dual filter of zero-valent iron and copper oxide nanoparticles on a bed of modified Clinoptilolite.

MATERIAL AND METHODS

Crashed natural zeolite grains with 1-2 mm in diameter size were used as the bed. 1 and 2 mm sieves were used to gain the grains with that diameter size. This zeolite was containing about 85% Clinoptilolite and provided from Semnan region of Iran. It was a producing of Afraznd Inc. Two stages acidic modifications were done on the sieved zeolite using 1N hydrochloric acid at 50°C and each stage lasted six hours. After the second stage, it rinsed several times with distilled water and then dried at 180 °C for two hours [8].

We used copper oxide (Cu₂O) and zero-valent iron (Fe⁰) nanoparticles with the particle size of 30-60nm in this work. These nanoparticles were produced in the Plasma Chem Inc. of Germany. For the coating of particles on zeolite grains, the nanoparticles was poured in the Erlenmeyer flask containing distilled water and used ultrasonic devices to dispersing it. Then the zeolite grains added to the nanoparticles suspension in a flask and the flask was shaken for two hours. Finally, the flask containment was dried slowly at 80°C for ten hours. The added value of nanoparticles was so that it was 4.5wt% of zeolite [4, 11]. Required weight of the nanoparticles to gain this wt% was determined by preliminary tests. Coating of Fe⁰ and Cu₂O nanoparticles on the zeolite grains was done separately in this way. 200 grams of Fe⁰ coated zeolite and then 200 grams of 1:1 mixture of Fe⁰ coated zeolite and Cu₂O coated zeolite were placed in a stainless steel cylinder with a diameter of 4.5 cm and 30 cm of length. So, the first part of the cylinder was filled with Fe⁰ coated salt and the next part was filled with a mixture of Fe⁰ and Cu₂O coated zeolites. The containing of the cylinder is called "filter" in this study. Required temperature provided by 250W electric elements. Six numbers of the elements were arranged around the cylinder.

The synthetic polluted air flow was prepared by air flow passing over the BTEX compounds in a 500cc flask [12]. The pollution load was set with changing the air flow rate through the BTEX flask and also the flask temperature. For high pollution load, the flask temperature set at 55°C and for the low pollution load, the temperature was set 40°C. This polluted air was passed through the cylinder containing the filter. Figure 1 shows a scheme of the system described above.



| | | |
|-----------------------|-----------------------------------|---|
| 1- Pump | 5- Polluted air supply | 9- Cu ₂ O&Fe ⁰ coated zeolite |
| 2- Flow meter | 6- Sampler | 10- stainless steel cylinder |
| 3- Flow control valve | 7- Temperature controller | 11- Thermal electric element |
| 4- Thermometer | 8- Fe ⁰ coated zeolite | |

Fig 1: Scheme of the used pilot system

Removal of BTEX compounds at high and low pollution load with a constant flow rate of 1.5 l/min (56.62 m³/m² h) and, at a flow rate of 1 and 2 l/min (37.75 m³/m² h and 75.49 m³/m² h) with constant pollution loads were determined. During the experiments, the temperature of the filter was kept at 350 °C. The sampling flow rate for inlet and outlet air flow was set as much as 100 ml/min and the sample volume were 2 liters. Charcoal tubes applied for these samplings [13, 14] and BTEX compounds were extracted from the charcoal using 2 ml of Carbon disulfide (CS₂) in 5 ml vials. The samples were shaken for 10 minutes during the extraction [15]. The samples were analyzed using the GC-FID of Chrom Tech, Inc., with a 25 m in length and 0.32mm in diameter of silicone column and Helium was used as carrier gas. One micro liter of sample was injected to GC and the detection was performed during 10 minutes in the oven temperature of 40 °C, the detection temperature of 250 °C and the injection temperature of 180 °C. Because of overlapping curve for p-xylene and ethylbenzene, the ethylbenzene removal efficiency was evaluated separately.

The determination of CO₂ concentration in the inlet and outlet air flow of the filter was carried out using GAS-TEC CO₂ detector tubes [12]. The GAS-TECH manual pump was used for the air suction by volume of 100cc as instructions of the detector. The porosity of filter was determined to gain the net volume, the filter volume without its blank spaces, of the filter. The porosity tested by

measuring the amount of required water for saturation of a certain volume of filter [16, 17].

RESULTS AND DISCUSSIONS

The concentration of emission pollutants related to high and low loading rates tried to be significantly different. It was almost as much as two times higher in high loading rate rather than a low loading rate. The inflow concentrations are presented in Table 1. Increasing the concentrations of pollutants, cause an increase in the total pollution load on the filter and led to a reduction of all pollutant removal. In the both pollution loads, toluene removal was more than of the other once. The lowest removal allocated to benzene in the time which the pollution load was high. In low pollution load, the lowest removal of pollutants was related to the o-xylene. Figure 2, shows the removal of the pollutants in high and low pollution loading rates.

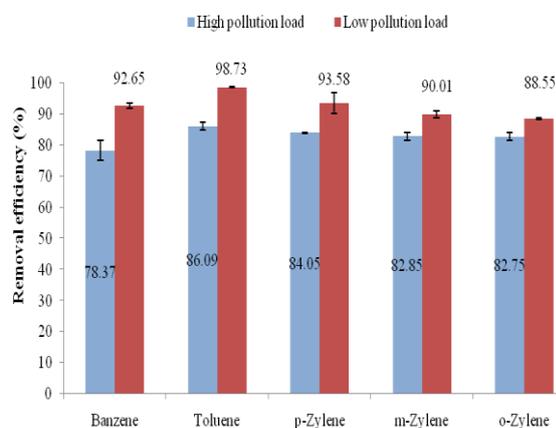


Fig 2: Removal efficiency of pollutants in high and low pollution loads.

The tests showed a porosity of 50.66 % for the filter. Considering this porosity the amount of the total volume, blank volume and net volume per 400 grams of the used filter are respectively 463.68, 234.9, 228.78 ml.

By having the concentration of pollutants, air flow rate through the filter and the reaction time, the mass of the imposed pollution over the filter and also removed the mass were calculated. Knowing the net volume of the filter, the amount of imposing pollution over the net volume unit of filter and removed pollution per net volume unit were obtained. These results are shown in Table 2.

These results indicate that the imposed and removed mass of pollution at high pollution load was much higher than low pollution load. Among the pollutants, the maximum imposed and removed mass on the filter was belonged to benzene.

The concentrations of CO₂ were constantly as much as 500 ppm in the inlet air flow. In high pollution load, the CO₂ concentration in the outlet was higher than the low pollution load. The

outflow concentrations of CO₂ for high pollution load, low pollution load, flow rate of 1 l/min and flow rate of 2 l/min respectively were 4800, 2800, 4000 and 2300ppm.

The pollutants removal in air flow rates of 1 and 2 l/min, are also presented in Table 1. The results showed further removal of pollution in the lower flow rate. The related removal efficiencies are illustrated in figure 3.

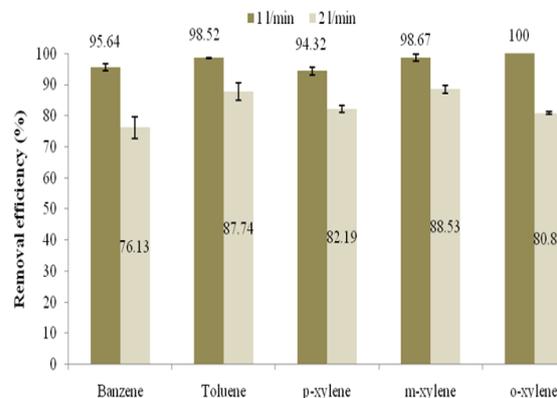


Fig 3: Removal efficiency in 1 and 2 l/min air flow rate

According to the mass balance principle, in a constant concentration, the changes of the air flow were effective on the pollution load on the filter. So, with having the concentration of pollutants and flow rate, the imposed pollution load on the filter and removed mass of the pollutions can be calculated. At higher flow rates, the retention time will be reduced. By having the total and net volume of the filter and flow rate, the retention times in the different flow rates were obtained. The related results are shown in Table 3.

Table 3: Imposed and removed mass of pollutants and Retention time in 1 and 2 l/min air flow rate.

| Flow rate (l/min) | Retention time (S) | Imposed mass per filter volume (µg/cm ³) | Removed mass per filter volume (µg/cm ³) |
|-------------------|--------------------|--|--|
| 1 | 14.1 | 124.53 | 119.78 |
| 2 | 7.05 | 256.48 | 201.12 |

Removal of ethylbenzene in the flow rate of 1 l/min was determined and compared with the other pollutants. The results showed that, ethylbenzene removal efficiency in these conditions was closer to the removal of p-xylene. With a 34.39ppm of inflow concentration, up to 92.73%±1.48 of removal efficiency was obtained for ethylbenzene and the CO₂ concentration of outflow was 600ppm. Equation 1 shows the mineralization of ethylbenzene.



Eq. 1, Stoichiometry decomposition of ethylbenzene

So, the mineralized portion of the pollutants was calculated by having the inflow and outflow concentration of the pollutants, flow rate, the

concentration of CO₂, and equation of the pollutants' mineralization. The results indicated that, just 64.61% of the removed ethylbenzene were completely decomposed and converted to

CO₂. In a similar manner for flow rate of 1 l/min the mineralization of pollutants was 65.2% and for the flow rate of 2 l/min it was 39.96%.

Table 1: Inlet concentration (ppm) of pollutants in different pollution loads and flow rates

| | Benzene | Toluene | p-Xylene | m-Xylene | o-Xylene |
|----------------------------|----------------|----------------|-----------------|-----------------|-----------------|
| High pollution load | 1818.92 | 486.16 | 42.01 | 35.74 | 7.21 |
| Low pollution load | 792.92 | 172.07 | 11.82 | 9.17 | 3.51 |
| 1 l/min flow rate | 910.01 | 200.99 | 5.62 | 9.61 | 4.32 |
| 2 l/min flow rate | 927.16 | 209.14 | 7.06 | 11.01 | 9.86 |

Table 2: Imposed and removed a mass of pollutants in high and low pollution loads

| | The net volume of the filter (cm³) | Pollutant | Imposed mass (µg) | Removed mass (µg) | Imposed mass per filter volume (µg/cm³) | Removed mass per filter volume (µg/cm³) |
|----------------------------|--|------------------|--------------------------|--------------------------|---|---|
| High pollution load | 228.78 | Benzene | 68755.29 | 53886.79 | 300.53 | 235.54 |
| | | Toluene | 18376.69 | 15820.09 | 80.33 | 69.15 |
| | | p-Xylene | 1588.01 | 1334.73 | 6.94 | 5.83 |
| | | m-Xylene | 1350.88 | 1119.25 | 5.91 | 4.89 |
| | | o-Xylene | 272.54 | 225.53 | 1.19 | 0.99 |
| | | Aggregate | 90343.42 | 72386.40 | 394.89 | 316.40 |
| Low pollution load | 228.78 | Benzene | 29972.27 | 27769.53 | 131.01 | 121.38 |
| | | Toluene | 6504.17 | 6421.68 | 28.43 | 28.07 |
| | | p-Xylene | 446.86 | 418.19 | 1.95 | 1.83 |
| | | m-Xylene | 346.63 | 311.98 | 1.52 | 1.36 |
| | | o-Xylene | 132.80 | 117.59 | 0.58 | 0.51 |
| | | Aggregate | 37402.72 | 35038.96 | 163.49 | 153.16 |

Also for the high and low pollution loadings, it was respectively 45.53% and 50.27%.

According to the results, in the experienced thermal catalyst process with Fe₀ and Cu₂O nanoparticle coated zeolite bed, increasing of the pollution load was led to declining of the BTEX removal. This decrease of the removal efficiency exhibits impact of the imposed pollution loading on the filter on pollutants' removal efficiency. Therefore, the large drop of benzene removal efficiency in the high pollution loading could also be due to its high concentration.

The results showed in table 2 indicated that, with increasing 2.42 times of the imposed pollution mass to the filter unit volume, the removal rate increased 2.07 fold. Thus, with a doubling of the imposed mass per filter unit volume, the removed pollution mass will increase 1.71 times. These results indicated that, doubling of the pollution load will cause a decline in the BTEX removal efficiency as much as 14.5 %. With this indication, the filter volume should be increased by 17% to obtain a removal efficiency as much as of the low

pollution loading of this study for the high pollution loading rate. Zou and *et al.* showed that, in a photocatalytic process using TiO₂-SiO₂, toluene has been removed by adsorption and catalysed mechanism. As the water and CO₂, which are the products of organic compounds' decomposition, and toluene were present in the exhaust air. They also found that, with increasing as the surface area the pollution removal has been increased [18]. Increasing of the filter volume will result in increasing of total surface area, which is in contact with the pollutants, and retention time. So, the higher surface area is a reason for the increased pollution removal by increasing filter volume, along with increased retention time.

Increased CO₂ concentration in the exhaust air stream is a confidence for mineralization of a greater amount of the pollutants. The results showed that, with doubling the pollution load the CO₂ concentration in outflow of filter just 1.41 folds increased. These results reveal that, with increasing pollution load the mineralization of pollutants has decreased.

When the air flow through the filter increased from 1 to 2 l/min, the retention time dropped from 14s to 7s. This drop in retention time has led to a reduction in pollutants removal. Removal of the imposed pollution mass on unit volume of the filter in the retention time of 14s was equal to 96.18%, while it was 78.42% at the retention time of 7s.

Hence, if the retention time is reduced in half, it causes a drop in pollution removal as much as 17.76%. So we can say that, when the pollution loading is doubled, the removal efficiency can be kept in the initial level by increasing the retention time by 82%. By the drop in retention time the concentration of CO₂ in outlet reduced 42.5%. These results indicate that, mineralization of the pollutants is more decreased than pollutants removal efficiency with a drop in retention time. Mineralization of BTEX compounds, for example benzene, may lead to production of the compounds such as Phenyl, Oxy phenyl, Dioxy phenyl and Hydroxy phenyl in the first stages of decomposition and with the subsequent decompositions, they are converted to other organic compounds and eventually when it completely oxidized turns into CO₂ and water [19, 20]. Previous researches declared that some factors such as temperature, concentration and presence of the free radicals are affecting the kind of by products and destruction pass-ways [21, 22]. In figure 4 some reaction pass-way for destruction of benzene are presented [19].

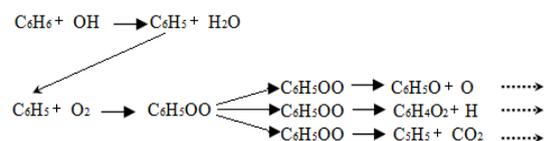


Fig 4: some reaction pass-ways of benzene destruction

Obtained with the results it can be stated that, the retention time and flow rate are more effectively than the pollution loading on the mineralization of the BTEX in this process.

The close removal efficiency of ethylbenzene and p-xylene could be due to their similar properties such as the boiling-point. It needs some more researches on the pollutants' removal efficiency in various removal processes to clear statement about the reason of difference or similarity in removal.

The results showed that, despite the minor imposed pollution mass on the filter unit volume at the flow rate of 2 l/min rather than the condition with a lower pollution load; the flow rate of 2 l/min has a lower mineralization of pollution. These results confirm the most impact of retention time versus the pollution loading on the pollutants complete decomposition.

Removal of BTEX by biofiltration using compost-activated carbon filter media showed a removal

efficiency of $\geq 90\%$ for inlet concentrations of ≥ 200 ppm of each of the BTEX compounds and a gas loading rate of $17.6 \text{ m}^3/\text{m}^2 \text{ h}$ [23]. The minimum gas loading rate in our work is 1 l/min, which is equal to $37.75 \text{ m}^3/\text{m}^2 \text{ h}$. According to the results in table 1, just xylene has lower concentration in comparison with Abumaizar's study. The air flow rate in our study is more than 2 fold higher than Abumaizar's and our results showed that, the flow rate has impacted the pollutants removal efficiency. However, the removal of each the BTEX is higher than 94% at the mentioned condition in our study and this is higher than the biofiltration process's removal efficiency for the BTEX.

Lu and *et al.* removed the BTEX using a trickle-bed air biofilter. In their study, in the flow range of 6.02–8.6 L/m³ h, removal efficiencies of each compound were greater than 80% with a loading of 143 g BTEX/m³ h [24]. Also it is very lower than the removal efficiency of this study with 490.5 g BTEX/m³ h and flow rate of $393.4 \text{ m}^3/\text{m}^3 \text{ h}$ in low pollution loading rate condition. The flow rates and loading rates are inferred from Table 1 and 2. These results indicate that, this process can be used for BTEX removal in the concentrations and flow rates very higher than for the biofilters.

Sleiman *et al.* were showed that in the removal of toluene by photocatalytic oxidation by using TiO₂ as photocatalyst [25], toluene conversion was up to 90–100% with a slight influence of inlet concentration under these conditions, and the mineralization was varied from 55 to 95%. The inlet concentration in their study was 20–400 ppbv and flow rate was 70–350 ml/min. They reported that the flow rate and inlet concentration exhibited a negligible effect on mineralization and has shown to be strongly inhibited by the increase of relative humidity. The inlet concentration has been much lower than the inlet concentrations for our study (see Table1). Also it has been same about the flow rate. However, the conversion of toluene in both studies is close together. The mineralization in our study was 39.96– 65.2% for all the BTEX compounds. This is some lower than the Sleiman's study. But, unlike the Sleiman's study, present results showed that the inlet concentration and especially flow rate strongly was influenced the mineralization. It seems that in the Sleiman's study, the flow rate variation was not adequate to reduce the retention time significantly and influence the mineralization. So, in all the flow rates, there was enough time for the process to mineralization of toluene. Toluene removal efficiencies up to $78 \pm 2\%$ were obtained under optimal conditions in a Heterogeneous photocatalytic process with TiO₂. These results obtained under the condition that, the toluene inlet concentration was 23–465 ppmv and gas residence time was 17–115 s [26]. Almost the same results obtained in other study [27], and in an

adsorptive photocatalytic process with combined nano-scale titania–montmorillonite–silica exhibited Almost 100% of degradation efficiency within 120 min with about 500 ppb initial concentration [28]. Degradation efficiencies of <2% for benzene, $11 \pm 2.4\%$ for toluene, $3 \pm 1\%$ for ethylbenzene, $1 \pm 1\%$ for o-xylene, and $3 \pm 0.4\%$ for m and p-xylene were obtained in a non-thermal plasma based air purifying system [29]. These results are very lower than present investigation. But the applied flow rate in the process was 320 l/min. This flow rate was so much than present study, and this may be a reason of the lower removal efficiency. In another study, Au was loaded (1.5 wt.%) on the supports (ZnO, Al₂O₃ and MgO) by a colloidal deposition method in a catalytic oxidation of benzene, toluene and p-xylene [30]. The results showed the benzene conversion exceeded 80% at 150 °C for the Au/ZnO catalyst. Loading rate in the process was 2.1 g/m³ for benzene, 0.6 g/m³ for toluene and 0.4 g/m³ for p-xylene. The flow rate in the process was 20 ml/min. The percent of used metal in the process and the temperature is lower for that and it is an advantage, but the flow rate and loading rate are much less in contrast to present research.

CONCLUSIONS

According to the results, the following conclusions can be derived.

With decreasing retention time, drop in the mineralization of the pollutants is greater than a drop in pollution removal. Increasing of the flow rate and decreasing retention time has a greater impact than pollution loading rate on the mineralization of BTEX compounds in this adsorption thermal catalyzed process. This shows the importance of contact time of the filter and pollutants to mineralization.

According to the results, this adsorption thermal-catalytic process by using Clinoptilolite as an adsorbent bed and combined Fe₀ and Cu₂O nanoparticles as catalysts is an efficient process under the condition of high flow rate and high pollution loading rate compared to other catalytic process and biofiltration for removal of BTEX from polluted air stream.

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