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Photocatalytic Decomposition of Ethylbenzene in Air using TiO_2 Nano-catalysts in an Annular Photoreactor

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Abstract

The contaminated environment by various pollutants in the last decades is a serious concern for the governments and human societies all over the world. Volatile Organic Compounds (VOCs), emitted from a wide range of industries, are among such pollutants which can easily move in the air due to their volatile nature and are toxic and harmful to the environment and human health. Removal of gaseous ethylbenzene as an aromatic VOC using photocatalytic oxidation in an annular photoreactor packed with TiO_2 nanoparticle-coated glass beads has been investigated in this research. The TiO_2 nano-catalysts were characterized by XRD and FE-SEM. The removal efficiencies of about 75-100% could be yielded for the initial ethylbenzene concentrations up to 0.6 g/m^3 in the UV irradiated reactor at a relatively low residence time. The inlet flow rate and initial ethylbenzene concentration were effective parameters on the removal efficiency and their increase caused reduction of removal efficiency. CO_2 production in the photoreactor showed the mineralization of the pollutant during photocatalytic decomposition of ethylbenzene.

Keywords: VOCs, Ethylbenzene, Air Pollution, Photocatalysis, Annular Photoreactor.

Introduction

Environmental pollution increase during the last decades by growth of the industry has been a critical issue for the governments all over the world. In this regard, indoor and outdoor air pollution is a major problem for the public health which is becoming a much more challenging issue in both developing and developed countries (Amini et al. 2017; Matsumoto et al. 2015; Yousefi et al. 2017). Aromatic compounds among the Volatile Organic Compounds (VOCs) which are volatile at relatively low temperatures have been considered as main dangerous pollutants and can adversely affect both the human health and the ecological environment (Borhani and Noorpoor, 2017; Dai et al. 2017). Monocyclic aromatic compounds such as ethylbenzene are widespread in the environment since they are emitted to

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the atmosphere from various sources such as paint, chemical and petrochemical plants, storage tanks, waste incinerators, composting facilities and almost all combustion processes utilizing fossil fuels (El-Naas et al. 2014). Ethylbenzene is also a toxic contaminant of indoor air emitted from various sources including certain consumer products, office equipment, solvents, paintings, varnishes, glues and tobacco smoke leading to a poor indoor air quality which may be even a more important issue due to the fact that people spend most of their time in indoor environments (Masih et al. 2017; Hazrati et al. 2016).

Heterogeneous photocatalysis as an advanced oxidation process is a promising technology among various methods to improve the air quality contaminated by such pollutants (Ren et al. 2017). Gas-phase photocatalytic oxidation using semiconductor catalysts has a great potential in mineralization of pollutants and converting them to the harmless compounds such as water and carbon dioxide at room temperature and it is highly efficient at low concentration levels, despite the conventional treatment methods including adsorption, absorption and condensation which practically do not eliminate them and the treated compound is just transferred from one phase to another one or consume a large amount of energy like thermal oxidation (Cheng et al. 2013; Huang et al. 2017).

Titanium dioxide (TiO_2), a popular and effective semiconductor, has been extensively applied in photocatalytic oxidation processes as the photocatalyst due to its distinguished features such as low cost availability, non-toxicity, long-time photo-stability, as well as potent oxidizing power (Petronella et al. 2017; Tasbihi et al. 2017). Degussa P-25, the commercial available form of TiO_2 as nanoparticles, has been identified as the superior standard catalyst considering its high activity in heterogeneous photocatalysis for environmental applications due to having mixed phases of anatase and rutile and also its nano-sized structure (Hwang et al. 2017; Rengiffo-Herrera et al. 2016).

There are several types of gas-phase laboratory scale photocatalytic reactors, but basically an effective photoreactor should have a large specific surface area, small pass-through channels and direct irradiation to the reaction surface in order to provide appropriate contact among the reactants, catalysts and photons (Ibhadon and Fitzpatrick, 2014; Jafarikojour et al. 2015; Ochiai and Fujishima, 2012). Therefore, the photocatalytic reaction in this study has been accomplished in an annular packed bed photoreactor providing high surface area as well as efficient irradiation by installation of the light source at the center of the reactor (Ida et al. 2014).

Hence, due to the above descriptions, the photocatalytic decomposition of gaseous ethylbenzene in the air has been evaluated in an annular packed-bed photoreactor using Degussa-P25 nanoparticles coated on glass beads and the removal efficiency of ethylbenzne under UV irradiation was calculated in this study.

Materials and Methods

Preparation of catalyst coated glass beads

Degussa (Evonik) P25 nano-powder was used as the starting material to prepare the catalyst coated glass beads. The surface of purchased glass beads with 5.5- 6 mm diameter were physically roughened in a mixture of water, sandblasting sand and Carborundum powder using a mechanical mixer. They were also etched in 1M NaOH solution and then thoroughly washed with detergents and deionized water. Then the slurry of TiO_2 powder in methanol/water mixture (95%/5%) was prepared having a 10 g/l concentration and completely dispersed by sonicating for 15 min. The coating of photocatalysts on the treated beads was performed by adsorption of the slurry on the heated glass beads (100 °C) and they

were dried in an oven at 100 °C. Finally, the coated glass beads were stabilized at 350 °C for 30 min (Khalilian et al. 2015; Korologos et al. 2012).

The XRD analysis on TiO_2 nano-catalyst was carried out by a Philips PW 1729 X-ray diffractometer at room temperature using a Cu Kα radiation operating at 40 kV and 30 mA to identify and confirm the crystalline phases. The size and morphology of catalysts were investigated using a TESCAN MIRA3 field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 15 kV.

Photocatalytic experiments

Photoctalytic decomposition of ethylbenzene in the air using Degussa-P25 catalysts was evaluated at room temperature in an experimental annular reactor packed with glass beads on which the catalysts had been coated. The continuous gas flow photoreactor with the length of 40 cm was consisted of two coaxial tubes. The inner tube was made of quartz glass housing the light source and the outer one was a Pyrex tube packed with catalyst coated glass beads to a height of 27 cm which provided an effective volume of 230 ml in the reactor. The light source was a Philips TUV T8 15W SLV/25 germicidal lamp to evaluate activity under UV radiation.

The reactor feed was prepared by mixing of ethylbenzene vapors and humid/dry air which were generated via passing the air (by an air pump, HAILEA, ACO-9620) through two glass impingers containing pure liquid ethylbenzne and distilled water. Ethylbenzne concentration and humidity were adjusted by rotameters controlling the air flow into the impingers and also the dry air entering the mixing tank. The concentration of ethylbenzene in the inlet and outlet streams of the photoreactor was measured by a TVOC fixed PID Detector (Ion Science, UK) and also the humidity and CO_2 content were measured by a SAMWON ENG SU-503B device and a KIMO AQ-100 CO_2 meter, respectively. The relative humidity was maintained around 50% in all experiments. The reactor inlet flow rate was adjusted by a rotameter just before entering the photoreactor. The removal efficiency of etyhlbenzene is given by:

$$Removal\ Efficiency\ (RE\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Where C_0 is the inlet concentration of ethylbenzene and C is the outlet concentration.

Results

Photocatalysts characterization

X-ray diffraction (XRD) pattern of Degussa-P25 nanoparticles is shown in Figure 1. It contains both anatase and rutile phases with a domination of anatase just like the pristine Degussa P25 attributable to the reports of Joint Committee on Powder Difrraction Standards (JCPDS) card No. 21-1272 for anatase and JCPDS card No. 21-1276 for rutile (Le et al. 2015; Wang et al. 2017). The crystallite average size calculated using the Scherrer equation was found to be about 35 nm well comparable to the particles size obtained from FE-SEM images.

The FE-SEM image of TiO_2 catalysts is shown in Figure 2a. It can be seen that the prepared nanoparticles have a spherical morphology. The obtained sizes are in the range of about 26-40 nm, which is well comparable to the average crystallite size obtained by the Scherrer equation. The image of the surface of glass beads coated by the mentioned catalysts is shown in Figure 2b.

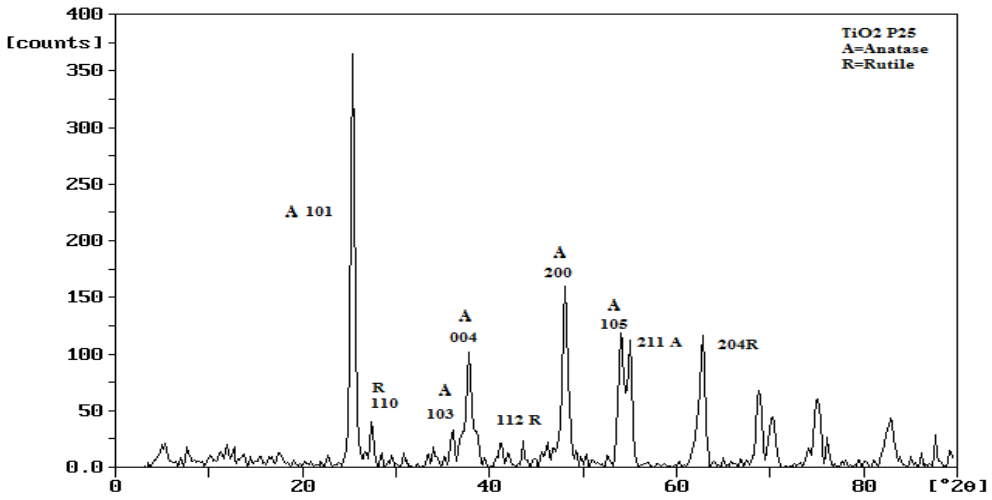
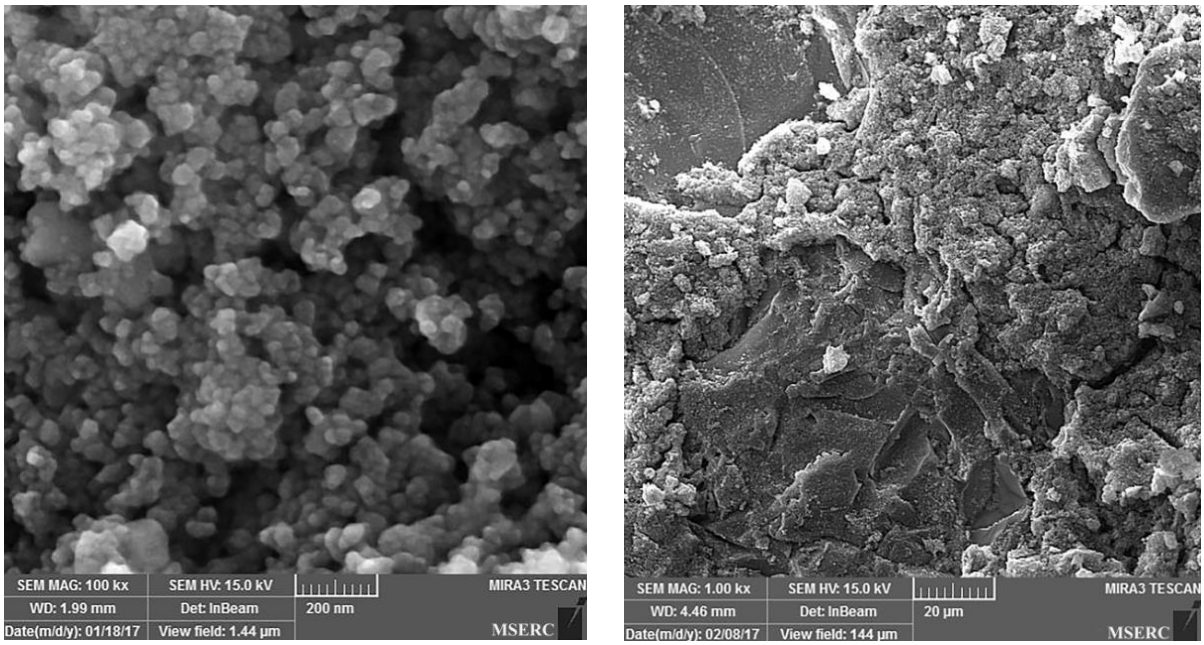


Figure 1. XRD pattern of Degussa P25 catalyst



(a) (b)

Figure 2. FE-SEM images of (a) TiO_2 catalyst, and (b) the surface of coated glass bead

Photocatalytic decomposition tests

The photocatayltic degradation of ethylbenzene in the air was evaluated in the mentioned photoreactor using the as-prepared commercial TiO_2 under UV irradiation. Figure 3 shows the removal efficiency of ethylbenzene using P25-TiO_2 photocatalysts under UV irradiation in different inlet concentrations (about 0.2- 1 g/m^3) and the desired residence time of 1 min. The removal efficiency at the residence time of 1 min was not affected by increase in the inlet concentration up to the concentration of about 0.4 g/m^3 (about 100 ppmv) and showed an efficiency of 100% in ethylbenzene degradation, but for greater inlet concentrations the removal efficiency decreased continuously and reached to the value of 34% at inlet concentration equal to 1.085 g/m^3 (250 ppmv) which could be because of blocking more active sites by the extra pollutant molecules entering the reactor (Cheng et al. 2013; Mehrizadeh et al. 2017).

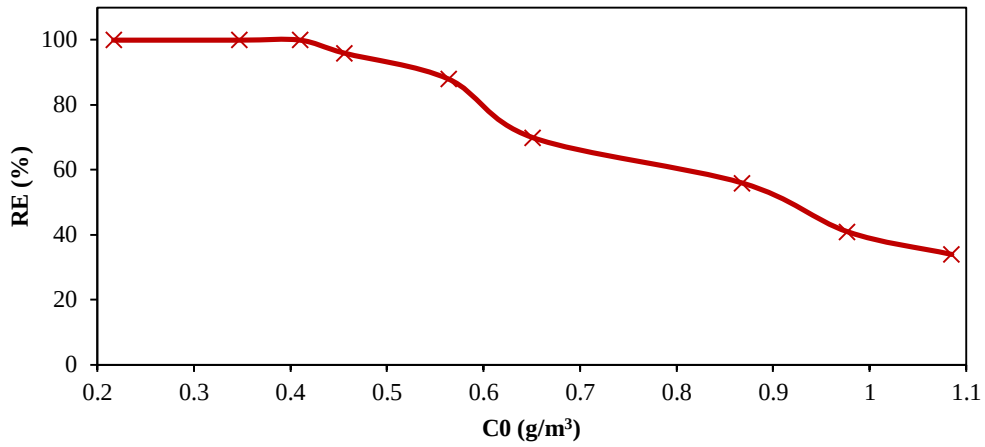


Figure 3. Effect of inlet concentration on removal efficiency at 1 min residence time.

Figure 4 shows the removal efficiency of ethylbenzene at three different residence times while the initial concentration of ethylbenzene is fixed. Increasing the residence time in the reactor or in other words decreasing the feed flow rate resulted in enhancement of photocatalytic decomposition. At the fixed inlet concentration of 0.564 g/m^3 (about 130 ppmv), the removal efficiency of 36% for residence time of 30 s increased to the value of 100% at the residence time of 30 s.

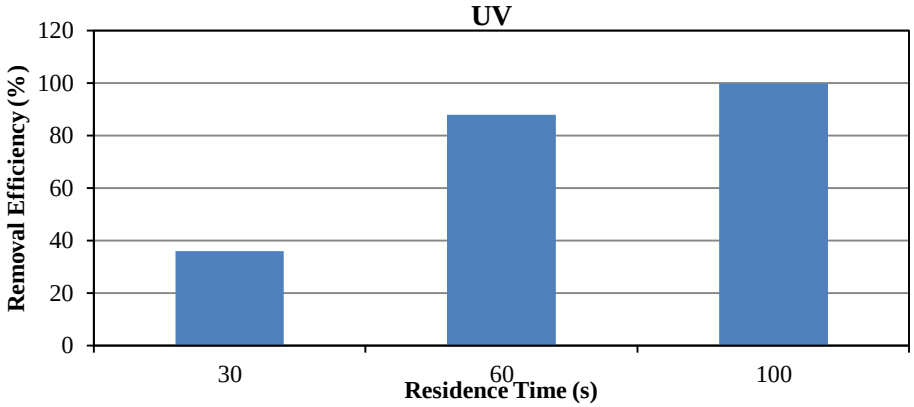


Figure 4. Removal efficiency at different residence times

The carbon dioxide as a final product of VOCs photocatalytic reactions was measured in the photoreactor (Pham and Lee, 2017; Zhang et al. 2016). Figure 5 shows the CO_2 production by photocatalysis against the ethylbenzene inlet load entering the reactor. Increasing the ethylbenzene inlet load leaded to a continuous enhancement of CO_2 production to a maximum value, but further addition of ethylbenzene inlet load did not lead to CO_2 increase anymore and slightly reduced the CO_2 production in photoreactor which is in correspondence with the obtained removal efficiencies at low and high inlet concentrations shown in Figure 3. The maximum value of CO_2 production was about 1.6 g/m^{3}min in the investigated range of ethylbenzene inlet load (about 0.2-1 g/m^{3}min).

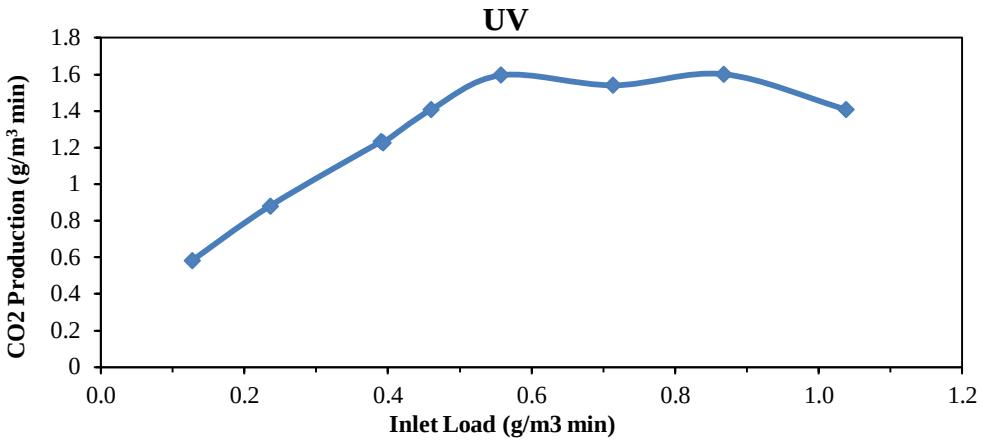


Figure 5. CO_2 production against the ethlylbenzene inlet load in photocatalytic reaction

Conclusions

Using commercial TiO_2 nano-catalysts for photocatalytic decomposition of gaseous ethylbenzene by a packed-bed annular photoreactor in this study demonstrated that the designed photocatalytic system is capable to degrade the model pollutant within a pertinent residence time. For instance, complete decomposition of ethylbenzene (100% removal efficiency) could be yielded using this system for the initial concentrations up to 0.41 g/m^3 (about 100 ppmv) at 1 min residence time which shows a suitable performance in an appropriate residence time. The removal efficiency at this residence time was still above 80% for inlet concentrations up to 0.586 g/m^3 (135 ppmv). Also, characterization of the catalysts by FE-SEM indicated their nano-size structure and the XRD analysis confirmed the presence of both crystalline phases of anatase and rutile which are the characteristic features of Degussa-P25 compound.

Moreover, investigating the impact of inlet flow rate and initial ethylbenzene concentration parameters on the removal efficiency showed their importance in photocatlytic performance of the designed system. They were effective parameters on the removal efficiency so that increasing each one resulted in reduction of the removal efficiency. When the inlet flow rate to the reactor was doubled at a fixed initial concentration, the removal efficiency of the photocatalytic system was reduced from 88% to the value of 36%. Also, increasing the initial concentration of ethylbenzene at the fixed residence time of 1 min and for concentrations above 0.4 g/m^3could reduce the removal efficiency slightly from 100% to the value of 34%. Measurement of CO_2 production in the photoreactor indicated mineralization of the pollutant which is a favorable response in photocatalytic reactions. Considering the obtained results, the photocatalytic reaction system in this research could be well applied for the conditions where the pollutant concentration is relatively low in order to improve the air quality.

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