The influence of ZnO-SnO_2 nanoparticles and activated carbon on the photocatalytic degradation of toluene using continuous flow mode

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Abstract

The present study examined the gas-phase photocatalytic degradation of toluene using ZnO-SnO_2 nanocomposite supported on activated carbon in a photocatalytic reactor. Toluene was selected as a model pollutant from volatile organic compounds to determine the pathway of photocatalytic degradation and the factors influencing this degradation. The ZnO-SnO_2 nanocomposite was synthesized through co-precipitation method in a ratio of 2:1 and then supported on activated carbon. The immobilization of ZnO-SnO_2 nanocomposite on activated carbon was determined by the surface area and scanning electron micrograph technique proposed by Brunauer, Emmett, and Teller. The laboratory findings showed that the highest efficiency was 40% for photocatalytic degradation of toluene. The results also indicated that ZnO-SnO_2 nano-oxides immobilization on activated carbon had a synergic effect on photocatalytic degradation of toluene. Use of a hybrid photocatalytic system (ZnO/SnO_2 nano coupled oxide) and application of absorbent (activated carbon) may be efficient and effective technique for refinement of toluene from air flow.

Key words: photocatalytic degradation; toluene; ZnO-SnO_2; activated carbon; volatile organic compounds; coupled oxide catalyst; ultraviolet; co-precipitation method

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Introduction

The most common pollutants that are identified both in urban and industrial areas are volatile organic compounds (VOCs).[1] VOCs are dangerous for human health and they are toxic, mutagenic and carcinogenic to all human beings, for instance they cause sick building syndrome (SBS).[2-4] One of these compounds is toluene, which is widely used as the starting material for production of benzaldehyde, benzyl alcohol, and its chlorinated derivatives.[4] Nevertheless, the focus of researches on VOCs have mostly been the toxicity of VOCs sources or the degradation conditions rather than the by-products that are generated during the treatment procedures.[5] The limitation of traditional methods like absorption, incineration and condensation used for removing VOCs from polluted air is that they are costly, have a short life spans, and lead to the production of secondary pollutants.[6] Many better techniques have been devised recently in order to solve the problem. Photocatalysis is a promising technology for purification of indoor air in which, under the illumination of ultraviolet (UV) light, TiO_2 is used as a photocatalyst, oxidizing the VOCs into CO_2 and H_2O at room temperature and atmospheric pressure.[7,8]

Common problems that are likely to happen include catalyst particles coagulation, reduction in the incidence of light, and complications in the filtration of fine photocatalyst particles, leading researchers to examine function of different support materials. For this purpose, Silica, alumina, zeolites, clay, bone char and activated carbon (AC) were investigated.[9,10] It has been proved that AC is an efficient absorbent which is widely used for the removal of all kinds of organic pollutants.[11] Photocatalytic activity of ZnO/AC was investigated by Sobana and Swaminathan[12] through degradation of Direct Blue 53. It was found that the use of AC, along with greater activity of ZnO/AC photocatalysts than ZnO, led to better ZnO distribution and less agglomeration.

The representative semiconductor metal oxides, namely ZnO and SnO_2, have been widely used in VOCs detection.[13] Recently introduced coupled photocatalysts produce increases in the efficacy of conventional photocatalysts by decreasing the degree of recombination and improving charge separation. They are TiO_2/ZnO,[14,15] TiO_2/WO[3,16] SnO_2/TiO_2,[17,18] ZnO/SnO_2,[19-26] and $ZnO/TiO_2/SnO_2$.[27] Some authors[23,25,28,29] have announced that on the photocatalytic removal, coupled semiconductor photocatalyst $ZnO\text{-}SnO_2$ is more efficacious than single semiconductor photocatalyst ZnO or SnO_2. In this study, the doping of ZnO nanoparticles with SnO_2 was used to increase the energy of the bands of the semiconductor zinc oxide material and as a result for promotion of its photocatalytic activity. This study aimed at determining the effect of the combination of $ZnO\text{-}SnO_2$ and AC on the photocatalytic removal of toluene gas.

Materials and Methods

Preparation of AC/ZnO-SnO_2 catalysts

Similar to our previous work,[30] $ZnO\text{-}SnO_2$ photocatalyst nanoparticles were obtained through co-precipitation method.[29] As starting materials, Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, 99%, Merck, Darmstadt, Germany) and tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, Aldrich, St. Louis, MO, USA), and as participant agent without purification, Ammonium hydroxide solution (NH_4OH, 25%, Merck) was used. $ZnSO_4 \cdot 7H_2O$ and $SnCl_4 \cdot 5H_2O$ in the molar ratio 2:1 were dissolved in the least required amount of deionized water. The 1:1 (v/v) NH_4OH solution was introduced in a drop wise manner to bring pH to about 7 under hard stirring. White precipitate was formed slowly during the reaction and it was filtered; while no SO_4^{2-} and Cl^- were found in filtrates the white precipitate continued to be washed.[4,25,29] Then the wet precipitate was dried at 100°C overnight and finally it was calcinated at 350°C for 2 hours.

Mixing $ZnO\text{-}SnO_2$ coupled oxide and granular AC (Vazin Carbon, Isfahan, Iran) with a particle size between 20–40-mesh sizes in an aqueous suspension with nonstop stir for 12 hours, led to creation of AC/$ZnO\text{-}SnO_2$ catalysts. The mixture was filtered and dried at room temperature. In order to create the composite catalysts of $ZnO\text{-}SnO_2$ coupled oxide immobilized on the AC, the solid materials were calcinated at 300°C for 2 hours. The catalysts have been shown as AC/$ZnO\text{-}SnO_2$ (a weight ratio of 13%).

Features of photocatalysts

The surface morphology of AC/$ZnO\text{-}SnO_2$, $ZnO\text{-}SnO_2$ and AC was observed by VEGA\\TESCAN-LMU scanning electron microscope and this was performed at a voltage of 15 kV. To characterize Crystal structure of $ZnO\text{-}SnO_2$ coupled oxide, X-ray diffraction (XRD) (EQuniox 3000, Inel, France) was undertaken, by employing graphite monochromatic copper radiation (Radiation: Cu-Ka; Wavelength: 1.541874 Å) 40 kV, 30 mA over the 2θ range 10°–110°. Specific surface area of AC, $ZnO\text{-}SnO_2$ and AC/$ZnO\text{-}SnO_2$ were evaluated using the Brunauer-Emmett-Teller (BET) method. Specific surface area (S_{BET}) were determined by the isotherms of N_2 gas absorption-desorption were gained at 77 K in a Micromeritics ASAP-2000 equipment. Before that, the sample was degassed at 300°C.

Setup of the photocatalytic system

Figure 1 shows the schematic diagram for experimental setup. The photocatalyst reactor (10 cm × 30 cm ×15 cm) and air mixer were made up of Pyrex glass. Three UV-A lamps (8 W) were located horizontally on top of the reactor to provide illumination; they emitted light at a primary wavelength of 365 nm. A fiberglass film supported the catalysts and it was put in place horizontally 1 cm higher than the UV lamp. The detection system involved the PhoCheck Tiger (Ion Science, Royston, UK), and it can analyze the Toluene concentration (the catalyst surface charge: 3.4 mg/cm^2).

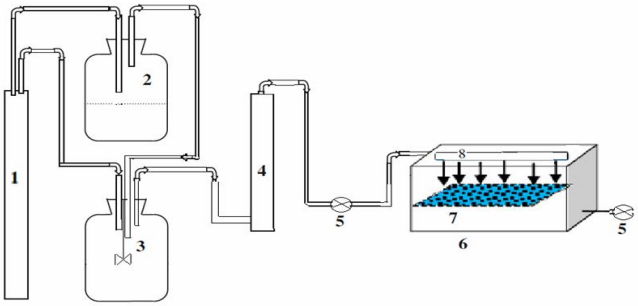

Figure 1: Photocatalytic decomposition reactor setup.
Note: 1: Air pump; 2: toluene liquid tank; 3: air mixing tank; 4: flow meters; 5: measurement port; 6: photocatalytic reactor; 7: catalysis film; 8: ultraviolet lamp.

Photocatalytic reaction

Pumping dry air through a reservoir of toluene liquid brought Toluene gas. After that, the gas was mixed and diluted in air mixer. Then, at a flow rate of 60 L/h and the inlet concentrations with a range from 75 to 1,500 mg/m^3,

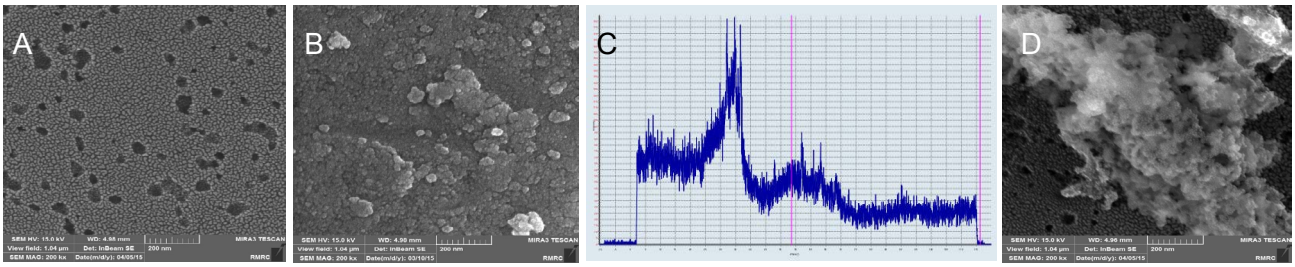

Figure 2: Characteristics of photocatalysts.
Note: Scanning electron microscopy (SEM) micrographs of pure activated carbon (AC) (A), pure SnO_2-ZnO (B) and ZnO/SnO_2-AC (C) photocatalysts calcined at 350°C for 2 hours. (D) X-ray diffraction (XRD) pattern of SnO_2-ZnO coupled oxide.

the mixed polluted air was pumped into the photocatalytic reactor until adsorption reached equivalence. Analyzing toluene concentrations was performed using the PhoCheck Tiger apparatus using a photoionization detector (PID). Removal efficiency of toluene is defined as:

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

where C_0 is the initial concentration of toluene and C is the concentration of toluene at time *t*.

The photocatalytic activity of photocatalysts was examined by assessment the rate of toluene removal, as the studied organic vapoure. All tests were conducted under identical conditions in order to properly compare performance of various catalysts.

Results

Characteristics of photocatalysts

The XRD pattern of the coupled oxide ZnO-SnO_2 is displayed in **Figure 2**. The pattern indicates the characteristic peak at 2θ of 29.9, 32.1, 33.7, 34.3, 34.7, 36.6, 47.9, 57.0 and 63.3 by their intensities (661, 936, 834, 829, 968, 994, 354, 465 and 402).

Images produced by scanning electron microscopy (SEM) indicated that pores on AC particles are occupied by ZnO/SnO_2 nano coupled oxide and the composite catalyst of ZnO/SnO_2-AC provides coverage in a homogeneous manner (**Figure 2**).

Measurement of S_{BET} indicated that specific surface area of AC was reduced after putting catalyst onto AC where this reduction was due to penetration of catalyst ZnO/SnO_2 into porosities of AC (**Table 1**).

Table 1: Surface area (m^2/g) of AC, ZnO/SnO_2 and AC-ZnO/SnO_2

Sample	S_{BET}
AC	605
ZnO/SnO_2	2.64
AC-ZnO/SnO_2	560

Note: S_{BET}: Specific surface area; AC: activated carbon.

Photocatalytic activity of ZnO/SnO_2-AC

The results related to the toluene's photocatalytic degradation efficiency by various photocatalysts are shown in **Figure 3A**. As it characterized, efficiency of photocatalytic removal of toluene by AC catalyst and ZnO/SnO_2 has been reported for 3 hours as 8.5% and 18% respectively while under the same conditions, the removal efficiency has been shown 40% using photocatalyst ZnO-SnO_2/AC for 3 hours.

The effects of initial toluene concentration

The results of analysis on efficiency of photocatalytic degradation of toluene under the influence of toluene primary concentrations with total volumetric flow 60 L/h are indicated in **Figure 3B**. The given results showed that the mean efficiency of photocatalytic degradation of toluene had significant difference ($P < 0.05$) at four different concentrations. The results of analysis on photocatalytic degradation of toluene by catalyst ZnO-SnO_2/AC under influence of variable of different concentrations in input toluene suggest that as concentration of input toluene is increased, rate of degradation efficiency of toluene shows reduction. When primary concentration of toluene is incased from 75 to 1,500 mg/m^3, degradation efficiency of toluene reduces from 38.5% to 4.5%.

The relationship between irradiation dosages and level of degradation

To perceive it better, effect of radiation intensity was examined on photocatalytic degradation in three different tests under the same laboratory conditions using 1, 2, and 3 UV-lamps. Efficiency of removal was measured 10%, 19.2%, and 25% in these three experiments and shown in **Figure 3C**. The results of this part indicated that photocatalytic efficiency of degradation of toluene increased as it was added to radiation intensity under the same laboratory conditions.

Discussion

Nowadays, photocatalysis is a promising technology for purification of indoor air. In this study, the gas-phase photocatalytic degradation of toluene is examined using ZnO-SnO_2 nanocomposite supported on AC in a photocatalytic

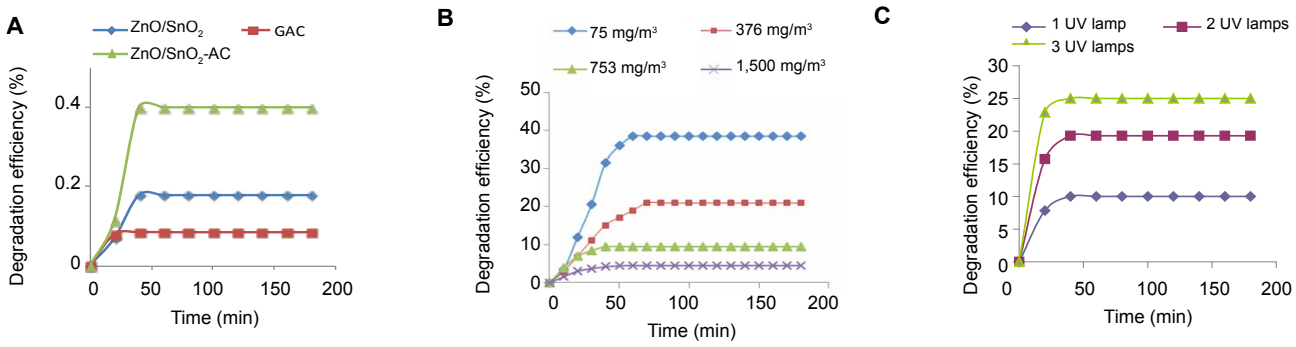

Figure 3: Photocatalytic degradation efficiency.
Note: (A) The comparison of the photocatalytic degradation reaction. (B) Initial concentrations of toluene and level of photocatalytic degradation. (C) Irradiation dosage and level of photocatalytic degradation. Min: Minute(s); AC: activated carbon; GAC: granular activated carbon; UV: ultraviolet.

reactor with regard to various photocatalysts, initial toluene concentration, irradiation dosages and time of encounter.

Characteristics of photocatalysts

The XRD pattern is showed in **Figure 2** similar to that reported in literature.[29] Findings obtained from SEM and BET indicated that specific surface area of AC was reduced after putting catalyst onto AC. Other studies have illustrated this reduction as a result of catalyst penetration into the adsorbent porosities.[11,12,30-32]

Photocatalytic activity of ZnO/SnO_2-AC

This study has been carried out dynamically and in a gas phase, in contrast to other studies that were conducted in statically or in aqueous phase. Our results showed that doping of ZnO nanoparticles with SnO_2 could increase the energy of the bands of the semiconductor zinc oxide material. Moreover, this process promoted the photocatalytic activity of ZnO-SnO_2. However, in current study, the photocatalytic degradation of toluene is carried out by three different catalysts (AC, ZnO/SnO_2, ZnO/SnO_2-AC). The maximum removal efficiency (40%) was found after action with photocatalyst ZnO-SnO_2/AC for 3 hours (**Figure 3A**). These findings are consistent with the results of other studies,[9,11,12,31,33] indicating that the stabilization of photocatalyst on absorbent substance noticeably increases removal efficiency.

The effects of initial toluene concentration

Rezaei et al.[7,34] reported that as primary concentration was increased from 2.5 to 25 mg/m^3, efficiency of synthesis showed reduction from 73% to 40%. These findings are consistent with studies done by Zeng et al.[4,31,33,34]

The relationship between irradiation dosages and degree of degradation

Intensity of radiation is a key factor in photocatalytic degradation. The results of this part of the study demonstrated that in the same experimental settings the photochemical removal efficiency of toluene improved as the irradiated light intensified. These findings may be justified in this way that photohole ray production has been increased due to increase in intensity of radiation of this ray and finally this may increase efficiency of photocatalytic removal of toluene. The results of this section are also complementary for other similar studies.[4,25]

Nevertheless, the main objective of this study is not to investigate the adsorption and desorption process in photocatalyst. This study focuses on the efficacy of photocatalytic degradation of toluene steam pollutants in the air and demonstrates the efficacy of ZnO-SnO_2 combination and AC on the photocatalytic removal of toluene gas. However, the saturation capacity of this ZnO-SnO_2 nanocomposite and hybrid photocatalytic system could be assess at future.

Conclusions

Based on above study, these findings may be inferred: use of nanocomposite ZnO/SnO_2 along with AC as absorbent increases removal efficiency of toluene from air. By analysis of effect of primary input concentration from 75–1,500 mg/m^3, rate of efficiency is reduced 38.5% to 4.5%. Similarly, the rate of optimal radiation intensity of ray was acquired 1.9 W/cm^2 in this study. Use of a hybrid photocatalytic system (ZnO/SnO_2 nano coupled oxide) and application of absorbent (AC) may be efficient and effective for refinement of toluene from air flow.

Author contributions
HAR: Contributions to the conception or design of the work; analysis and interpretation of data. FT: Contributions to the conception or design of the interpretation of data for the work. NJ: Contributions to the conception or design of the work. AM: Contributions to the conception or design of the work analysis, and interpretation of data for the work. All the authors approved the final version of the manuscript.

Conflicts of interest
There is no conflict of interest.

Data sharing statement
The datasets analyzed during the current study are available from the corresponding author on reasonable request.
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