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PHOTOCATALYTIC DECOMPOSITION OF GASEOUS TOLUENE BY TiO_2 NANOPARTICLES COATED ON ACTIVATED CARBON

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ABSTRACT

Volatile organic compounds are considered as a group of major environmental pollutants and toluene is recognized as one of the representatives. In this research, the photocatalytic activity for toluene removal was studied over TiO_2 nanoparticles embeded on activated carbon. Laboratory-scale experiments were conducted in a fixed-bed reactor equipped with 4 w and 8 w UV lamps (peak wavelength at 365 nm) to determine the oxidation rates of toluene. The photocatalyst was extensively characterized by means of X-ray diffraction and scan electronmicroscopy. Experiments were conducted under general laboratory temperature (25ºC±2) while the irradiation was provided by the UV lamps. The dependence of the reaction rate on light intensity as well as the deactivation of the catalyst were determined. The results indicated that the rate of the photocatalytic process increased with increasing the intensity of UV irradiation. Using the UV-A lamps, the decomposition rate of toluene was 98% The stabilized photocatalyst presented remarkable stability (no deactivation and excellent repeatability). The catalyst could be regenerated by UV irradiation in the absence of gas phase. The control experiments confirmed that the photocatalytic effects of toluene onto the TiO_2/activated carbon catalysts in the dark conditions were negligible. Reproducibility tests proved that the photocatalytic activity of the photocatalyst remains intact even after several experiments of new added toluene quantities. The study demonstrated that the TiO_2/activated carbon catalyst may be a practical and promising way to degrade the toluene under ultraviolet irradiation.

Key words: Toluene, TiO_2 nanoparticles, activated carbon,p hotocatalytic, coating

INTRODUCTION

The presence of atmospheric volatile organic compounds (VOCs), such as toluene, is of high concern as they impart adverse effects on human health and the environment (Beydoun *et al.,* 1999; Bernstein *et al.,* 2008). Inhalation studies have shown that toluene exposure can result in nervous system complications, such as reductions in thinking, memory and muscular abilities, as well as some level of loss in hearing and color vision (Peral *et al.,* 1997; Neubert *et al.,* 2001). Technologies for removing toluene include thermal and catalytic oxidation processes, which are intensive energy consuming (Tryba *et al.,* 2003*)*. Photocatalytic oxidation, whereby light, is used to activate a semiconductor material and is an alternative technology capable of treating VOCs under ambient conditions, particularly when they are present in low concentrations (Zoua *et al.,* 2006; Higashimoto *et al.,* 2007).

A heterogeneous photocatalytic system consists of semiconductor particles (photocatalyst) which are in close contact with a liquid or gaseous reaction medium. While exposing the catalyst to light excited states are generated which are able to initiate subsequent processes like redox reactions and molecular transformations. Due to their electronic structure, which is characterized by a filled valence band and an empty conduction band, semiconductor can act as sensitizers for light-induced redox processes. The energy difference between the lowest energy level of the conduction band and the highest energy level of the valence band is the so-called band gap energy. It corresponds to the minimum energy of light

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required to make the material electrically conductive. When a photon with an energy of hv exceeds the energy of the band gap, an electron (e^-) is promoted from the valence band to the conduction band, leaving a hole (h^+) behind.

In electrically conducting materials, i.e. metals, the produced charge carriers are immediately recombined. In semiconductors a portion of this photoexcited electron-hole pairs diffuse to the surface of the catalytic particle (electron hole pairs are trapped at the surface) and take part in the chemical reaction with the adsorbed donor (D) or acceptor (A) molecules. The holes can oxidize donor molecules ($D + h^+ \longrightarrow D^{\bullet +}$) whereas the conduction band electrons can reduce appropriate electron acceptor molecules ($A + e^- \longrightarrow A^{\bullet -}$). A characteristic feature of semiconducting metal oxides is the strong oxidation power of their holes (h^+).

They can react in an one-electron oxidation step with water ($H_2O + h^+ \longrightarrow {}^\bullet OH + H^+$) to produce the highly reactive hydroxyl radical ($OH^\bullet$). Both the holes and the hydroxyl radicals are very powerful oxidants, which can be used to oxidize most organic contaminants. In general, air oxygen acts as electron acceptor ($O_2 + e^- \longrightarrow O_2^{\bullet -}$) by forming the super-oxide ion $O_2^\bullet$–. Super-oxide ions are also highly reactive particles and are able to oxidize organic materials. TiO_2 mediated heterogeneous photocatalysis has become an innovative technology with attractive application potentials such as environmental pollution remediation, mainly due to degrade a wide range of inorganic and organic compounds in both aqueous and gaseous phase (Yu *et al*., 2007).

TiO_2 is an inexpensive non-toxic and biocompatible material and is one of the most important and widely investigated photocatalysts, because of its application potential in decomposition of various environmental pollutants in both gaseous and liquid phases (Carp *et al.,* 2007).

Photocatalytic degradation on TiO_2 of many substances was studied under various illumination conditions. The initial reaction step consists of electron-hole pairs production by irradiating the TiO_2 with light having energy content higher than the band gap (Uddin *et al.,* 2007). For anatase and rutile TiO_2, the band gap amounts 3.2 ev and 3.0 ev, respectively, corresponding with wavelengths of 388 nm and 410 nm (Mills *et al*., 1997). Ultraviolet light (UV) is thus needed for TiO_2 activation. With UV irradiation, electron hole pairs are excited in valence band of TiO_2 and then migrate to the surface to initiate redox reactions for adsorbed organic pollutants (Zhang *et al.,* 2007).

The design of TiO_2 photocatalyst embedded onto support materials with large surface areas, which could condense diluted polluted substances, would be of great significance, not only to avoid the filtration of small photocatalyst particles, but also to obtain higher efficiency. Many alternatives have been proposed in the last few years, which have tried a variety of supporting materials and coating methods in different arrangements for degradation of several organic compounds. One possible way was the use of materials such as glass beads, glass tubes, fiberglass, quartz, stainless steel, aluminum, activated carbon (AC) and silica (Hosseini *et al.,* 2007). AC is another type of co-adsorbent that has been used in photodegradation of organic pollutants in aqueous phase.

This effect has explained that the adsorption of organics on AC is followed by a transfer to the TiO_2 surface, where they are immediately degraded. It is based on the interaction between light and semiconductor particles, which produce the highly reactive oxygen species (ROS), such as $OH^\bullet$, $O2^{\bullet -}$ and $HO_2^\bullet$. In general, the key issues for practical photocatalytic applications are the specific surface area, the absorption range of UV light spectrum and the photoactivity or the efficiency of the photocatalysts (Ao *et al.,* 2003). In the present study, the TiO_2 was immobilized on AC and its photocatalytic activity was studied. Also, the influence of UV intensity on the efficiency of the process was investigated. AC was selected as a base for TiO_2 for its advantages including high porosity, low density, natural abundance, absence of toxicity and low price.

MATERIALS AND METHODS

Catalyst and chemicals

The photocatalyst was TiO_2, Degussa P-25, mainly anatase under the shape of nonporous polyhedral particles with a surface area of 50 m^2/g. Almond shell AC was obtained from Kimia Carbon company, Arak, Iran, with a particle size between 10 and 20 mesh sizes and 1mm effective size. The AC properties such as apparent (bulk) density, iodine adsorption test, pH, moisture and ash contents were analyzed according to ASTM (D2854; D46076; D3833; D2867; D2866) protocols.

Toluene was purchased from Merck Co. and was used without further purification. The water used was double-distilled water prepared in laboratory.

Preparation of coated AC

TiO_2 nanoparticles (P25 Degussa) were used as photocatalysts without any pretreatment. AC was washed with distilled water and was dried in an oven at 120°C for 60 min. The coated AC was prepared by mixing 5g of the TiO_2 nanoparticles in 100 mL distilled water and stirred for 3 min, after which 5 g of AC was added and then stirred for another 5 min. The mixture was poured into a petri dish and left to microwave at 180 W for 15 min. The amount of TiO_2 imposed was determined by the weight difference before and after the coating procedure (Lee *et al.,* 2004). The modified AC was stored until it was used in the photocatalytic tests.

Characterization of AC and TiO_2 photocatalysts

Surface morphology of AC and modified AC was studied by scanning microscopy (XL30 Philips model). X-ray diffraction (XRD) patterns were obtained with a Rigaku diffractometer (Tryba *et al.*,2003). The main grain size (L) can also be estimated from XRD data by applying the Scherrer's formula ($L=0.89\ \lambda/\beta \cos\theta$), i.e.:where L is the X-ray wavelength and θ is the full width at the half maximum of the diffraction peak (Carpio *et al.,* 2003). Specific surface areas and compositions of TiO_2 powders were evaluated using the Brunauer–Emmett–Teller (BET) method in a Quanta Sorb machine.

Photocatalytic experiments: reactor and set-up

The photocatalytic degradation of toluene was investigated in a rectangular plexiglass flat-plate photoreactor (length (*L*): 34 cm, width (*W*): 28 cm, height (*H*): 17 cm), operating in a flow-through mode (Fig. 1). Gas sampling points were provided at both the inlet and outlet of the reactor. Illumination was provided by UV-A lamps which emited a primary wavelength at 365 nm. The UV lamps were horizontally placed at the upper part of the reactor. The temperature in the reactor was controlled at 25.0±0.1°C. The inlet gas stream was contaminated with toluene. A zero air generator (Thermo Environmental Inc., Model 111) was used to supply the air stream. The gas streams were mixed by a gas blender and the desired flow was controlled by a mass flow controller inside the calibrator. After the inlet and the outlet concentration achieved equilibrium (1 h), the UV lamp was turned on and the reaction was initiated. After each experiment, at high toluene concentration levels, clean humidified air was flushed overnight through the reactor under

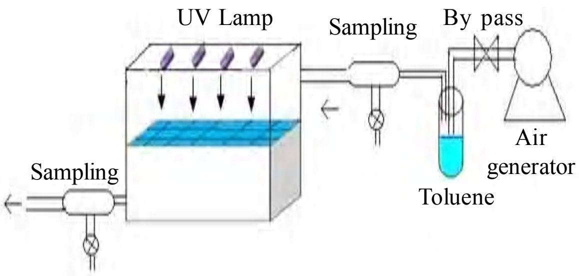

Fig. 1: A schematic diagram of the experimental set-up

UV-illumination

Toluene analysis

Toluene concentrations were determined using a Philips PU-4410 gas chromatograph (GC) equipped with a flame ionization detector. Gas samples of 1 mL each containing the target contaminants were obtained directly from the rubber septum sampling ports using 5 mL Hamilton gas-tight syringes and were injected immediately into the GC unit for concentration determination. The compounds were separated on a 10 % SE30 packed column (L=1.5 m, W=4 mm). The temperature of the injection port and detector were 220 and 250°C, respectively. Nitrogen gas (30 mL minÉ^{1}) was used as the carrier gas. The sample (100 µL) was injected into the GC, without further treatment.

RESULTS

Catalyst characterization

Physicochemical characteristics of almond shell AC is shown in Table 1. The SEM micrograph of the prepared TiO_2/AC is presented in Fig. 2. The micrograph of AC/TiO_2 surface confirm the high homoginisity of catalyst on AC as a good support for TiO_2.

The BET surface area of the support was around 680 m^2/g. For TiO_2 nanoparticle, the BET surface areas were in the range of 640–660 m^2/g. The XRD pattern of post-coated sample is shown in Fig. 3. It indicates that the coated sample mainly consists of anatase. The peaks of anatase TiO_2 are shown as well as some small peaks of rutile. Heating with microwave (180 w for 15 min) were regarded as optimal annealing temperature in our experiment. When the temperature exceeded, the gradual phase transformation from anatase to rutile occured.

Photocatalytic decomposition

Effect of initial concentration on toluene decomposition

The photochemical decomposition of toluene under UV irradiation in the absence and in the presence of TiO_2 has been studied. It can be claimed that the absence of TiO_2 almost could not bring about the photocatalytic decomposition of toluene. As TiO_2 was added into the reactor, the decomposition rate becames significant. Almost 98% toluene conversion was achieved at different toluene concentrations between 20-450 mg/m^3.

Effect of light intensity

The effect of UV intensity on the photocatalytic efficiency of prepared catalysts were investigated by changing the power of UV source lamps (4 w and 8 W). A series of experiments were carried out to examine the influence of irradiation intensity on decomposition rate of toluene and the results are shown in Fig. 4 and Fig. 5.

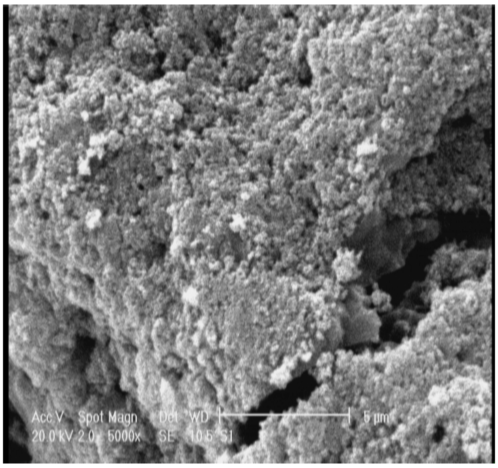

Fig. 2: SEM images of AC-coated TiO_2 nanoparticles

Table 1: Physicochemical characteristics of almond activated carbon

Parameters	Amounts
Apparent density (g/cm^3)	0.29
Bulk Density (g/cm^3)	0.25
Average pore diameter (nm)	41.26
Total cumulative volume(cc/g)	0.24
Total porosity (%)	12.25
Iodine adsorption test	375
Moisture content (%)	3.3

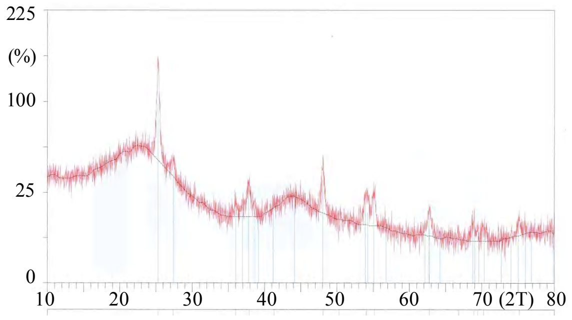

Fig. 3: XRD pattern of AC coated with TiO_2

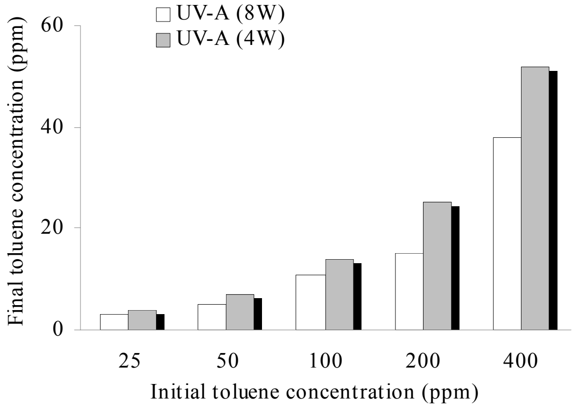

Fig. 4: The decomposition of toluene with different UV lamps

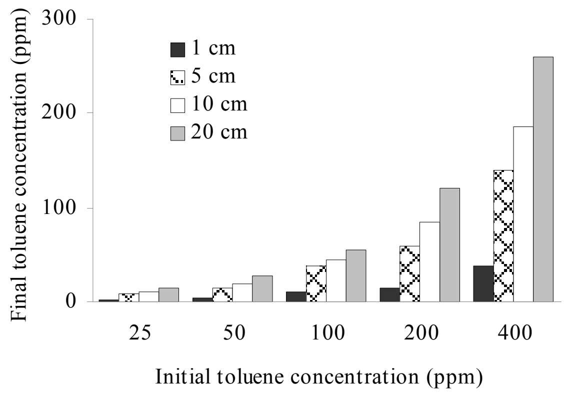

Fig. 5: The effect of UV-A lamp distance on toluene decomposition

DISCUSSION

The toluene in the gas phase was successfully decomposed by the photocatalytic reaction in a photoreactor under UV irradiation conditions. It was already observed a synergy effect when using TiO_2 and AC in the photocatalytic degradation of toluene. This synergistic effect was ascribed to the creation of a common contact interface between both solid phases and to a transfer of toluene adsorbed on AC to TiO_2 where it was immediately photocatalytically degraded. The chemical composition and crystalline properties of the investigated catalysts differed according to the preparation. XRD analysis suggests that the differences in the crystal size are not very important. But these differences exist and together with the different content of each crystalline phase lead to a different behavior of these photocatalysts. The efficiency of AC depends upon its surface area and porosity. The latter can be divided on the basis of diameter into micropore (d<2 nm), mesopore (2 nm<d<50 nm) and macropore (d>50 nm).

In the present investigation SEM and BET has been used to measure porosity of the AC. The slight decrease in BET area for nanospheres catalysts can be explained taking into account that contain a 5 wt% of TiO_2 that have a practically null contribution to the BET area value. So, there is not a plugging effect of pores by metal particles in the catalysts. The mesopore surface areas and the micropore surface areas of TiO_2/AC samples were all slightly smaller than those of the blank AC (within 10%), which could be attributed to the extra weight added from TiO_2 deposition.

With respect to toluene degradation, the decomposition rate was almost independent of the initial toluene concentration. This shows that coated of catalyst increases the transmission rate of UV light and promotes the contact between toluene and catalyst surface, so toluene can be more effectively decomposition in shorter residence time. At higher toluene inlet concentrations, the decomposition rate decreases with increasing initial toluene concentration because of the generation of more and more intermediate, outgrowth and terminating products. Some of the intermediate products are strong adsorptive species. According to adsorption equation, the products generated from the reaction could compete with toluene for the active sites on the catalyst surface, resulting in lower photocatalytic reaction efficiency. On the other hand, part of the products couldn't be removed from the catalyst surface in time and thus interfered with photo-catalytic reactions. Experimental result shows that the decomposition of toluene increases with the UV intensity irradiated, and the photocatalytic efficiency with 8 W lamp in all catalysts was more than the 4 W lamp. So more photons generated from higher UV light intensity, more photons participated in the photocatalytic reaction. As a result, more $OH^{\bullet}$ radicals with strong oxidizability were generated to decompose more toluene. With the increase in UV light intensity, toluene decomposition rate would also increase. Several proposals have already been made for the possible photocatalytic oxidation routes (Carp *et al.,* 2004; Zhang *et al., 2007;* Saquib *et al.,* 2008).

Surface oxidation could involve the transfer of photogenerated electrons to adsorbed O_2 and photogenerated holes to the organic molecule, and subsequent interaction between the ionic surface species (Amalric *et al.,*1994). It is generally accepted that the total degradation of organic molecules is favored by surface mechanisms in which the organic molecule reacts in the adsorbed phase (Aramendía *et al.,* 2008). Other oxidation pathways could require OH radicals attack. Generation of OH radicals via H_2O splitting or via O_2^- intermediates has been previously suggested by many authors (Saquib *et al.*, 2008).

TiO_2/AC samples, contain a high concentration of conduction electrons. The presence of these charge carriers could favor the surface O_2 reduction step to O_2^- without help from photogeneration. Maybe the adsorption of O_2 competes with the adsorption of other molecules. The dissociation of water on these samples is also possible. Homogeneous pathways through OH radical attack could also occur in such cases. Undoubtedly the nanoTiO_2/AC catalyst prepared in the laboratory showed good photocatalytic performance. On the other hand, the operating parameters including initial toluene concentration and ultraviolet light intensity have great effects on toluene decomposition rate. The results also showed that the degradation rate of toluene increased with increasing UV light intensity.

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