



Enhancing ethylbenzene vapors degradation in a hybrid system based on photocatalytic oxidation UV/TiO₂–In and a biofiltration process

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ARTICLE INFO

Article history:

Received 21 September 2011

Received in revised form 8 December 2011

Accepted 10 January 2012

Available online 18 January 2012

Keywords:

Ethylbenzene

Photocatalytic

Biofilter

Hybrid processes

UV black light irradiation

TiO₂–In catalyst

ABSTRACT

The use of hybrid processes for the continuous degradation of ethylbenzene (EB) vapors has been evaluated. The hybrid system consists of an UV/TiO₂–In photooxidation coupled with a biofiltration process. Both the photocatalytic system using P25-Degussa or indium-doped TiO₂ catalysts and the photolytic process were performed at UV-wavelengths of 254 nm and 365 nm. The experiments were carried out in an annular plug flow photoreactor packed with granular perlite previously impregnated with the catalysts, and in a glass biofilter packed with perlite and inoculated with a microbial consortium. Both reactors were operated at an inlet loading rate of 127 g m⁻³ h⁻¹. The greatest degradation rate of EB (0.414 ng m⁻² min⁻¹) was obtained with the TiO₂–In 1%/365 nm photocatalytic system. The elimination capacity (EC) obtained in the control biofilter had values ~60 g m⁻³ h⁻¹. Consequently, the coupled system was operated for 15 days, and a maximal EC of 275 g m⁻³ h⁻¹. Thus, the results indicate that the use of hybrid processes enhanced the EB vapor degradation and that this could be a promising technology for the abatement of recalcitrant volatile organic compounds.

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1. Introduction

Air pollution represents a serious health and environmental problem that requires effective control. In particular, many volatile organic compounds (VOCs) can cause odor nuisances and have toxic effects, and must be removed from contaminated streams [1]. Currently, there are major efforts under way to develop better treatment and prevention technologies to reduce the health and economic impacts of air pollutants. Biological gas cleaning and advanced oxidation processes (AOP) are among the promising technologies capable of eliminating a wide range of organic compounds. Biological gas cleaning offers cost-effective removal of hydrophilic and highly biodegradable VOCs. AOP are also effective to mineralize or partially oxidizing a wide range of VOCs, including non-biodegradable and recalcitrant VOCs. Each technology, however, suffers from significant technical limitations. Slow biological oxidation of less biodegradable VOCs (i.e. recalcitrant or hydrophobic VOCs) makes biofilters very large and uncompetitive [2]. Also, biofiltration processes may not run consistently and are slow to adapt to fluctuating concentrations (high concentration of VOCs) in waste gas streams, thus decreasing VOCs elimination capacities.

UV photooxidation are limited in their applications owing to their tendency to produce byproducts that might be as toxic as the parent compounds [3,4]. Thus, coupling AOP and biofiltration has the potential to provide more effective elimination of recalcitrant and slowly biodegradable VOCs (hydrophobic or recalcitrant VOCs). Byproducts of AOP photooxidation are often more biodegradable and have a higher water solubility than their parent compounds. Pretreatment of a contaminated gas stream with AOP helps degrade recalcitrant pollutants completely or transform them into more biodegradable compounds (more soluble compounds), which are then readily treated by biofiltration, operating downstream of the AOP processes.

TiO₂-assisted photodegradation of VOCs has already been proposed as an alternative AOP for decontamination of water and air. This process is initiated from the generation of hole–electron pairs in the semiconductor upon absorbing UV light with energy equal to or higher than the band gap energy of the semiconductor. The electrons and holes can recombine on the surface or in the bulk of the semiconductor within a few nanoseconds or be trapped in a surface state where they can react with donor or acceptor species adsorbed on the surface of the semiconductor, thereby initiating subsequent oxidation–reduction reactions [5]. Furthermore, since the recombination of the electrons and holes is obviously detrimental to the efficiency of semiconductor as a photocatalyst, modifications to semiconductor surfaces, such as the addition of metals or

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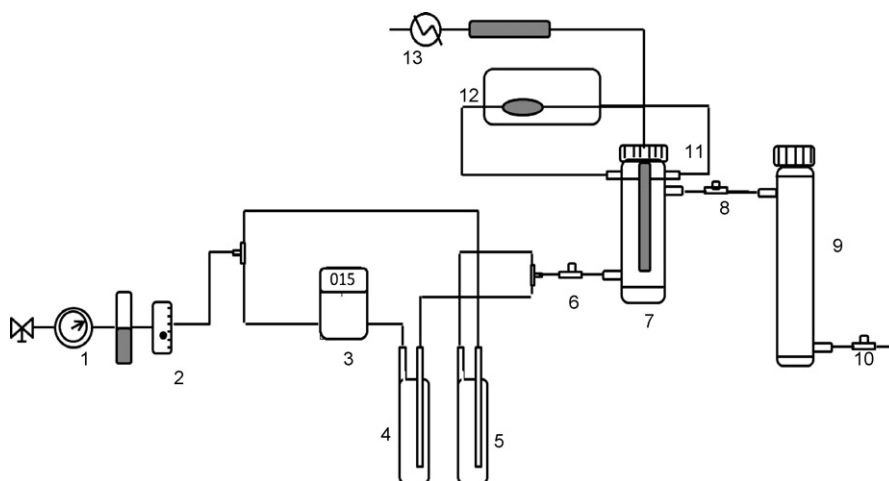


Fig. 1. Experimental device for the hybrid UV-vis/TiO₂-In and biofiltration system. (1) Air compressor, (2) rotameter, (3) mass flow meter, (4) water stripping, (5) ethylbenzene stripping, (6) inlet, (7) photoreactor, (8) outlet/photoreactor and inlet/biofilter, (9) biofilter, (10) outlet, (11) UV lamp, (12) peristaltic pump, and (13) power source.

combination with other semiconductors, are beneficial in decreasing the electron and hole recombination rate and thereby increasing the photocatalytic activity. In photocatalysis, the addition of metals to a semiconductor can change the semiconductor surface properties, and create framework defects thus the metal can enhance the yield of the photocatalytic reaction. Many researchers have attempted to modify the surfaces of photocatalysis by metal doping in order to enhance the reactivity of the catalyst [5,6].

In wastewater treatment technologies, AOP are often used as pretreatment processes to improve performance of the subsequent biological process [7]. However, very little research has been carried out on the combination of AOP and biofiltration to treat high concentrations of recalcitrant or hydrophobic VOCs.

Accordingly, the present study was carried out with the objective of enhancing the degradation rate of ethylbenzene as a model VOC via a photooxidation technology using an indium-doped TiO₂ photocatalyst coupled to a biological process.

2. Materials and methods

2.1. Preparation of catalysts

Titanium (IV) isopropoxide (Aldrich, 97%) and indium acetylacetonate (Aldrich, 99.99%) were used to prepare sol-gel indium TiO₂ doped semiconductors [8]. The quantity of indium acetylacetonate co-gelled with the titanium alkoxide was calculated to provide 1 and 5 wt% of indium oxide in the titanium dioxide. A reference TiO₂ sol-gel sample (TiO₂-SG) was prepared in identical conditions, according to the method described by Rodríguez-González et al. [8], but without the addition of indium acetylacetonate. The semiconductors were characterized by X-ray diffraction, BET surface area analysis, diffuse reflectance UV-vis, FTIR and Raman spectroscopies.

Perlite granules were coated with the catalysts according to the method reported by Hosseini et al. [9] and characterized by SEM microscopy.

2.2. Photocatalytic and biofilter experimental set-up

The experimental device is shown in Fig. 1. The photocatalytic experiments were performed in a Pyrex glass annular plug flow photoreactor with an effective volume of 189 mL. The photoreactor consisted of a 1.5 cm inner diameter quartz tube of housing a 254 nm or 365 nm low pressure mercury UV lamp pen-ray (UVP-11SC). The photoreactor was packed with 23 g of granular

perlite (3 mm) previously impregnated with each catalyst (P25-Degussa, TiO₂, TiO₂-In 1%, or TiO₂-In 5%). EB saturated air was mixed with moistened air and introduced at the bottom of the photoreactor (up-flow mode) with a flow rate of 189 mL min⁻¹ (Mass flow controller-GFC17 model; Aalborg, Orangeburg NY). The photocatalytic systems were operated for 72 min with each catalyst. Photolytic experiments where the reactor was packed with uncoated perlite were carried out at the same previously mentioned wavelengths as controls. For the photocatalytic experiments, EB vapors were fed into the photoreactor for 72 h before the UV-light was turned on to saturate the catalyst coated perlite. Three replicates of the photolytic and photocatalytic experiments were performed.

The biofilter consists of a glass cylindrical reactor with an effective volume of 119 mL. The reactor was packed with 14.4 g of granular perlite (3 mm) previously inoculated with 15 mL of a microbial consortium obtained from hydrocarbon polluted sites and previously acclimatized to ethylbenzene vapors for 45 days [7]. The initial biomass concentration was 12.3 mg_{biomass} g_{dry perlite}⁻¹. The control biofilter was operated for 100 days in a down-flow mode at a flow rate of 119 mL min⁻¹. A 15 mL aliquot of mineral medium, similar to the medium used by Galindo et al. [7], was sprayed into the biofilter every 3 days for the first 50 days, and every day for the next 50 days of biofilter operation in order to maintain the microbial activity, humidity in the bed and to control the pH at 7. Both the photocatalytic and the biological reactors were operated at an empty bed residence time (EBRT) of 1 min and at an inlet EB concentration of 2 g m⁻³. The reactors were maintained at room temperature (28 °C).

The hybrid system for the removal of ethylbenzene, comprised of a photocatalytic system and a biofiltration process, is shown in Fig. 1. The photocatalytic and the biofiltration experiments were operated individually at the conditions mentioned above at the beginning of the experiments. The optimum photocatalytic

Table 1
Physical properties of TiO₂ catalysts.

Catalysts	P-25 Degussa	TiO ₂	TiO ₂ -In 1%	TiO ₂ -In 5%
Crystalline phase	A, R ^a	A	A	A
Energy band gap, E _g (eV)	3.26	3.27	3.24	3.32
Wavelength (nm)	380	327	382	374
Crystallite size (nm)	19.6	11.9	8.4	8.2
Superficial area (m ² g ⁻¹)	52	73	96	112

^a Anatase (A) and rutile (R) crystalline phases.

Table 2
Photocatalytic degradation of ethylbenzene vapors at 254 and 365 nm wavelengths with the catalysts P25-Degussa, TiO₂, TiO₂-In 1% and TiO₂-In 5%.

System	RE ^a (%)	EC ^a (g m ⁻³ h ⁻¹)	Catalysts (g)	Degradation rates (ng m ⁻² min ⁻¹)(ng g ⁻¹ min ⁻¹)	
Photolysis					
254 nm	5.96 ± 2	5.4 ± 0.1	–	–	–
365 nm	3.31 ± 1	2.4 ± 0.02	–	–	–
Photocatalysis					
P25/254 nm	18.49 ± 7	16.3 ± 1.1	2.685	0.286 ± 0.020	14.89 ± 1.04
P25/365 nm	15.07 ± 7	13.2 ± 1.0	2.708	0.257 ± 0.018	13.39 ± 0.93
TiO ₂ /254 nm	25.52 ± 8	22.2 ± 2.0	2.327	0.137 ± 0.011	10.04 ± 0.80
TiO ₂ /365 nm	12.33 ± 10	10.8 ± 1.1	2.856	0.633 ± 0.063	46.57 ± 4.66
TiO ₂ -In 1%/254 nm	19.86 ± 7	17.4 ± 1.2	3.094	0.280 ± 0.020	20.59 ± 1.44
TiO ₂ -In 1%/365 nm	21.92 ± 6	19.2 ± 1.1	2.569	0.414 ± 0.025	30.45 ± 1.83
TiO ₂ -In 5%/254 nm	27.40 ± 8	24.0 ± 1.9	2.408	0.104 ± 0.008	11.77 ± 0.94
TiO ₂ -In 5%/365 nm	23.29 ± 8	20.4 ± 1.6	2.632	0.244 ± 0.019	27.39 ± 2.19

^a RE, removal efficiency; EC, elimination capacity.

system, the reactors was connected to the biofiltration system. This hybrid system was operated for 15 days at an EBRT of 1 min and at an inlet concentration of 3.5 g m⁻³. Gas chromatography samples were taken at the inlet and outlet of the photocatalytic and the biological reactors, respectively.

To evaluate the effect of inlet load on the EC, the gas flow rate was maintained at a constant value while the inlet EB concentration was varied between 0.5 and 7.5 g m⁻³. These inlet load experiments were performed during the last day of biofilter operation, the photocatalytic, and the hybrid systems.

2.3. Analytical methods

2.3.1. Ethylbenzene and CO₂ concentrations

Ethylbenzene concentrations were determined by injecting 100 μL gas samples into a 6890 series gas chromatograph (Agilent Technologies) with a Flame Ionization Detector (FID) and a capillary column (DB-624). Nitrogen, at a flow rate of 25 mL min⁻¹, was used as the carrier gas. The temperature of the injector, oven and detector were maintained at 230, 80 and 230 °C, respectively.

CO₂ production was measured using a TCD gas chromatograph (Agilent Technologies GC-6850) equipped with a capillary column HP-PLOT Q. Helium, at a flow rate of 10.1 mL min⁻¹, was used as the carrier gas. The temperature of the injector, column and detector were 250, 50 and 250 °C, respectively. Because CO₂ is present in the atmosphere, the reported CO₂ values correspond to the difference between the outlet and the ambient CO₂ concentrations.

2.3.2. Byproducts determination

The photocatalytic experiments for the identification of byproducts were performed in the previously described photoreactor for 120 min, but operated in batch mode at an initial EB concentration of 35 g m⁻³. Photooxidation intermediates were identified by GC-MS (Agilent 6890N/EM 5973N) operated in electron impact mode using 70 eV ionization voltage. Photooxidation byproducts were adsorbed on a DVB/CAR/PDMS SPME fiber 50/30 μm (Supelco Bellefonte, PA, USA) during the photooxidation process. After extraction at 25 °C and 10 min, the fiber was directly exposed for 90 s at 240 °C in the GC-MS injector for thermal desorption. The byproducts were identified by comparing the experimental spectra with those of the NIST⁰² database (NIST/EPA/NIH Mass Spectral Library).

2.3.3. Total organic carbon

Total organic carbon (TOC), from solid samples (perlite with TiO₂-In 1% catalyst) taken at the final day of operation of the photoreactor, was measured in duplicate by a TOC analyzer (TOC-VCS/TNM-1, Shimadzu, Japan) equipped with a solid sample module (SSM-5000A, Shimadzu, Japan).

2.3.4. Biomass and protein concentrations

Biomass in the support was measured as volatile solids using a thermogravimetric analyzer (Thermo-Cahn TGA) with a temperature ramp of 10 °C min⁻¹ up to 100 °C. The TGA analyzer was operated with nitrogen at a flow rate of 20 mL min⁻¹. Duplicate measurements were carried out, and the biomass content was expressed in milligrams of biomass per gram of dry perlite.

In addition, protein concentrations from the biofilm samples were determined by the Lowry method previously reported [10]. Samples were hydrolyzed with sodium hydroxide (0.2 M). Serum bovine albumin was used as the standard (Sigma-Aldrich).

2.3.5. SEM analysis

Biofilter sample morphology was analyzed by SEM, using a microscope with automatic stitching control (Philips XL30 ESEM-FEG, FEI Company, Hillsboro, OR). The microscope was operated at 10 kV and 90 Pa under low vacuum mode. Before SEM analysis, samples were set on aluminum plates and sputter-coated with gold (Cressington Sputter Coater, 108 Auto) with an intensity of 40 mA.

3. Results and discussion

3.1. Catalysts characterization

All semiconductors present the anatase TiO₂ crystalline phase which is photocatalytically active under UV-A irradiation (400–200 nm). The average crystallite size was estimated from the X-ray diffraction peak broadening of anatase (1 0 1) plane according to Scherrer's equation, and the calculated results are listed (Table 1). The crystallite sizes of anatase in the case of TiO₂-In catalysts are all smaller than that of undoped TiO₂ and P-25. This observation is consistent with reports that the addition of In to TiO₂ catalysts can restricts the crystallite growth of TiO₂ anatase crystals [8,11]. The band gap energies (E_g) and the wavelength of maximum absorption were obtained from UV-vis spectra and compared to P-25 as a reference. The E_g obtained for the synthesized catalysts had values between 3.24 and 3.32 eV indicating that all semiconductors have adequate E_g to be active photo-catalytically under the UV-A irradiation [12]. It could be interesting to note that the TiO₂-In 1% catalyst had superior physicochemical properties than the others catalysts tested, it had the lower energy band gap and crystallite size; also it had an intense absorption at 382 nm in the UV-vis diffuse reflectance spectra. In summary, indium TiO₂ doped semiconductors have enhanced physicochemical properties and can be excited by UV light as was reported previously [5,8,11].

3.2. Photocatalytic oxidation performance

Results obtained from the photocatalytic oxidation of ethylbenzene vapor are presented in Table 2. Degradation rates were

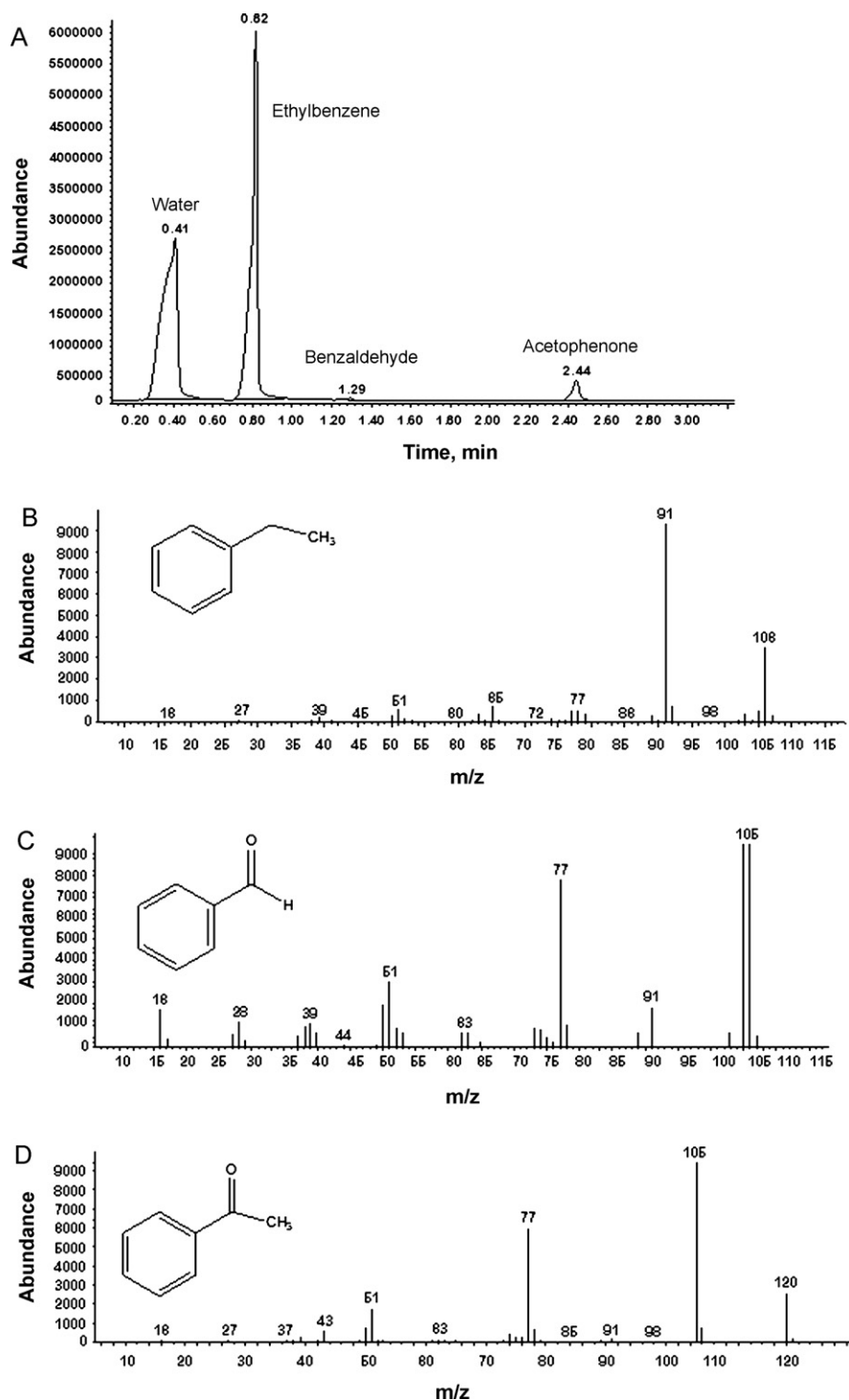


Fig. 2. GC/MS analysis of the outlet stream samples from ethylbenzene photocatalytic oxidation over $\text{TiO}_2\text{-In } 1\%/365 \text{ nm}$ system. (a) Gas chromatogram for the sample. (b), (c) and (d) Mass patterns of ethylbenzene, benzaldehyde and acetophenone, respectively.

calculated from the initial slope obtained by linear regression of the EB concentration versus time profiles and were normalized to the mass and the superficial area of the catalysts. As shown, the removal of ethylbenzene using the photolytic systems with uncoated perlite at 254 nm and 365 nm could be considered negligible due to removal efficiencies ($\text{RE} \approx 5\%$) were lower than those obtained with the photocatalytic systems ($\text{RE} \approx 20\%$). The observed degradation rates of the photocatalytic systems were a function of the physicochemical properties of the catalysts including crystallite size, specific surface area, UV absorption and doping metal. All

EB degradation rates obtained with the catalysts in this study were similar to reported values between 1.54 and $58 \text{ ng g}^{-1} \text{ min}^{-1}$ for Kivanova et al. [13] for the degradation of toluene using kaolinite coated with TiO_2 under UV-A (400–200 nm) and UV-C (283–200 nm) irradiation. According to the RE and the degradation rates obtained as a function of the mass of catalysts and of the specific surface area (see Table 2), the $\text{TiO}_2\text{-In } 1\%/365 \text{ nm}$ was found to be the best system tested for EB degradation. Thus, the $\text{TiO}_2\text{-In } 1\%/365 \text{ nm}$ system was selected as the pretreatment degradation system for EB and coupled to the biofiltration system (see Fig. 1).

The selection of the TiO₂-In 1%/365 nm system for use in the hybrid process is in agreement with the physicochemical properties presented in Table 1. The high performance and photocatalytic activity of this catalyst is well correlated with its superior properties over the others catalysts including a lower energy band-gap, a small crystallite size, the highest specific surface area, and the maximum UV–vis absorption at 382.4 nm. Although the size crystallite, and thus the specific surface area, of the 5% indium doped catalyst were superior physicochemical properties than those of the 1% indium doped catalyst, we selected the catalyst doped with 1% of indium because the pore size distribution was more uniform based on the BET analysis (See Supporting Information (SI) Fig. S1), and the specific degradation rates and removal efficiency were greater. It is important to mention that the synthesized TiO₂ catalyst had greater specific degradation rates but a RE 50% lower than the others catalysts. Also, its physicochemical properties were lower than that obtained with the TiO₂ catalyst doped with 1% of indium.

Taking into account the carbon balance, it was not possible to detect CO₂ production at the outlet of the photocatalytic reactor during operation. However, the loss of EB by adsorption onto the TiO₂-coated perlite during operation is considered to be negligible as the system was saturated with a continuous flow of EB for 72 h before the start the photocatalytic experiments. In addition, the total organic carbon was measured in solid samples of TiO₂-In 1% coated perlite after 15 days of operation for the photocatalytic reactor operated at 365 nm. A TOC content of 0.9 mg g_{dry perlite}⁻¹ was measured. Considering the total mass of support in the reactor (23 g) and the total carbon of EB eliminated (2.6 g of ethylbenzene) during the 15 days of the reactor operation, the 0.7% of the EB degraded was transformed to soluble byproducts (TOC) that remained adsorbed on the solid sample. Additionally, GC–MS analysis was performed during the photocatalytic degradation of EB using the best system of TiO₂-In 1%/365 nm. In addition to ethylbenzene, benzaldehyde and acetophenone were detected as byproducts after 90 min of the photooxidation process (Fig. 2). These by-products had been reported frequently during EB photooxidation [14]. Thus, these results support the feasibility of using photocatalytic systems for VOC degradation as up-stream process to generate more soluble byproducts that could be removed in a subsequent biofiltration process, and thus to enhance the overall removal of VOCs. However, probably the generation of more soluble compounds by using the AOP as a pretreatment process for VOC treatment might not be sufficient to enhance overall degradation rates in a subsequent biofiltration process, as the level of biodegradability of VOCs is a function not only of their solubility, but also of their chemical structure and the type of microorganism used in the biofilter.

3.3. Biofiltration experiments

The results for the biofiltration of ethylbenzene during 100 days of operation are shown in Fig. 3. The adaptation period of the biofilter lasted approximately 12 days. The adsorption of EB on perlite was observed during the first 2 days of reactor operation even though the CO₂ production during this period was high. The high CO₂ production detected at the beginning of the biofilter operation is attributed to remaining carbon sources present in the inoculum during the acclimatization process and also to cellular lysis. After the start-up period, the EC of ethylbenzene varied, but a steady state period was observed from the 39th day of the reactor operation with an average EC of 45 g m⁻³ h⁻¹ (RE = 45%) at an inlet loading rate of 127 ± 9.8 g m⁻³ h⁻¹. The production of CO₂ also reached steady state conditions during this period with average values of 100 g m⁻³ h⁻¹. There is a lack of literature studies regarding the biofiltration of EB as a single pollutant. The majority of the studies reported focus on the biofiltration of BTEX as this

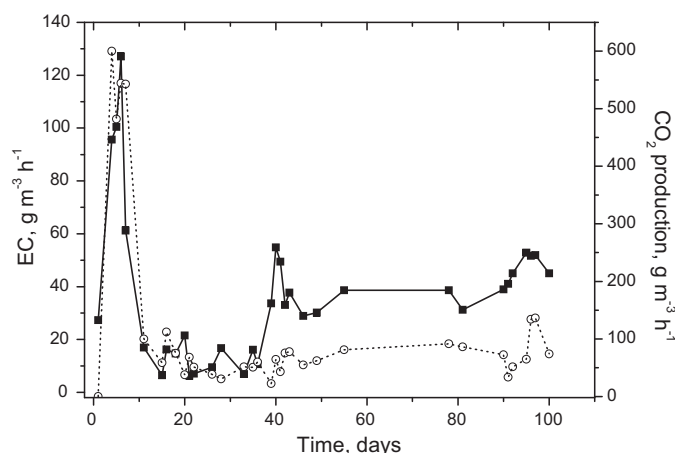


Fig. 3. Elimination capacity (■) and CO₂ production (○) with time for ethylbenzene vapors biofiltration. Inlet loading rate 127 ± 9.8 g m⁻³ h⁻¹.

mixture is more representative of aromatic compound emissions. However, the objective of the present research was focused to study these compounds separately to identify and propose mechanics to enhance the overall degradation rates of each aromatic compound. For example, Kwon and Cho [15] and Abumaizar et al. [16] reported the biofiltration of BTEX using various packing materials, and reported ECs between 86 g m⁻³ h⁻¹ and 23 g m⁻³ h⁻¹ using cork and granular activated carbon (GAC). However, these authors did not report CO₂ production as an indicator of the mineralization of BTEX, thus, the EC reported could be attributed to the adsorption of BTEX on GAC, as has been widely reported. In addition, the EC of ethylbenzene obtained in the present study is in the range of 120 g m⁻³ h⁻¹ and 45 g m⁻³ h⁻¹ reported by Álvarez-Hornos et al. [17] for the biofiltration of EB using a commercial soil amendment and fibrous peat packing materials, respectively.

Integration of the data of Fig. 3 under steady state conditions (from day 39 to 100) showed a consumption of 6.73 g of ethylbenzene (0.425 g C g_{dry perlite}⁻¹), and a production of 13.77 g of CO₂ (0.26 g C g_{dry perlite}⁻¹). The average final biomass was 305 mg g_{dry perlite}⁻¹ with a protein content of about 26% (80 mg protein g_{dry perlite}⁻¹). If 50% of these volatile solids are assumed to be organic carbon, and considering that the biofilter was packed with 14.4 g of perlite, 36% of the consumed ethylbenzene carbon was incorporated to biomass and 62% was mineralized to CO₂. The remaining carbon (2%) can be attributed to the formation of intermediates, or biomass in the leachate. The biomass and protein content measured in the final days of the biofilter operation are similar to the values reported by Arriaga and Revah [10] for a bacterial biofilter degrading hexane and for the thermophilic biofiltration of BTEX in bioreactors packed with perlite [18]. The final bed void fraction of the biofilter (0.22) was reduced 33% from the initial value (0.66) due to the high biomass content (Fig. 4). However, clogging of the biofilter was not registered under these conditions.

SEM analysis from samples taken on the final day of the biofilter operation (Fig. 4) shows a dense biofilm present on the perlite (a) and the typical growth of bacteria (b).

3.4. Hybrid system performance

In Fig. 5, the performance of the hybrid and individual systems during 15 days of operation is shown. The adsorption of ethylbenzene onto perlite coated with the catalyst is considered to be negligible due to a previous saturation process that was performed before starting the UV irradiation. Average EC values of 65 g m⁻³ h⁻¹ (RE = 36%), 85 g m⁻³ h⁻¹ (RE = 47%) and

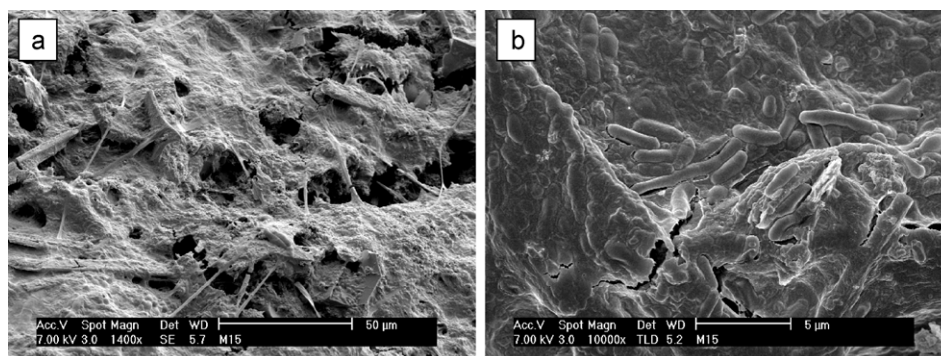


Fig. 4. Samples of the biofilter taken during the coupled process of ethylbenzene degradation. (a) Dense biofilm growth, and (b) bacteria colonizing the support.

$150 \text{ g m}^{-3} \text{ h}^{-1}$ (RE = 83%) for the photocatalytic oxidation, the biofilter, and the hybrid process, respectively. These ECs were stable with respect to time. Thus, the coupled system enhanced the removal of ethylbenzene vapors by 47% and 36% compared to the individual photocatalytic and biofiltration processes, respectively. These results are in agreement with previous studies using hybrid systems consisting of an AOP coupled to a biological process [2–4,19]. Moussavi and Mohseni [20] reported the advantages of using hybrid systems for the degradation of toluene and xylene vapors in an UV/O₃-photocatalytic process coupled with a biofilter. The EC for toluene vapor obtained by these authors had a value of $50 \text{ g m}^{-3} \text{ h}^{-1}$ (RE = 98%), which is lower than the value obtained in the study reported here. However, recently Wei et al. [19] reached a maximum EC of $390 \text{ g m}^{-3} \text{ h}^{-1}$ (RE = 94%) for the degradation of toluene vapor using a photocatalytic system (N-TiO₂/zeolite/UV and visible light irradiation) coupled to a biofiltration system. The EC of EB from the present study was compared with reported values for toluene degradation due to the absence of published reports on ethylbenzene degradation in a hybrid process.

Experiments to determine the effect of inlet loading rate on EC (Fig. 6) showed a maximum EC of $275 \text{ g m}^{-3} \text{ h}^{-1}$ (RE = 61%) for EB vapor, using the coupled system consisting of TiO₂-In 1%/365 nm-biofilter. Thus, the maximum EC obtained in the hybrid system is at least 36% ($175 \text{ g m}^{-3} \text{ h}^{-1}$) and 64% ($100 \text{ g m}^{-3} \text{ h}^{-1}$) greater than the individual values obtained with the biofilter and the photocatalytic process, respectively.

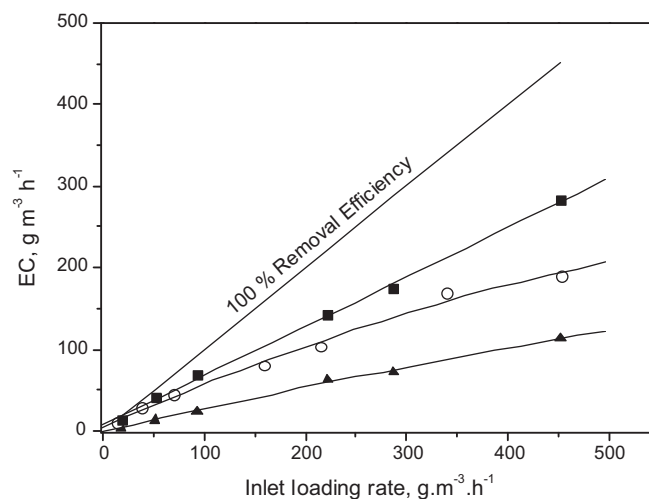


Fig. 6. Effect of the inlet loading rate on ethylbenzene vapors degradation in the TiO₂-In 1%/365 nm (▲), biofilter (○), hybrid system (■) processes.

4. Conclusions

The photolytic processes carried out at 254 nm and 365 nm did not contribute to the degradation of ethylbenzene. The photocatalytic degradation rates were function of the physicochemical properties of the catalysts including the BET surface area. The best photocatalytic process for ethylbenzene degradation consisted of a TiO₂-In 1%/UV 365 nm system because the degradation rate and removal efficiency were greater than for the other photocatalytic systems. The hybrid system provided up to 36% additional removal compared to the individual degradation of the photocatalytic treatment and the control biofilter, demonstrating the synergistic effect of the photocatalytic process on biofilter performance. However, optimization of the coupled process needs to be performed. Thus, the effect of air humidity, empty bed residence time and VOC loading shock conditions needs to be tested. Also, it could be interesting to extend the application of this hybrid system for the abatement of more hydrophobic VOCs and priority indoor air pollutants like formaldehyde.

Acknowledgments

We thank CONACYT for financial support through the SEP-CONACYT-CB-2009-133930 grant. Mariana Hinojosa also thanks CONACYT for the master in science fellowship. The use of the analytical infrastructure of LINAN and LANBAMA are also acknowledged. Special gratitude is expressed to M.C. Dulce Partida, M.C. Guillermo Vidriales, M.C. Gladis Labrada-Delgado, M.C. Beatriz

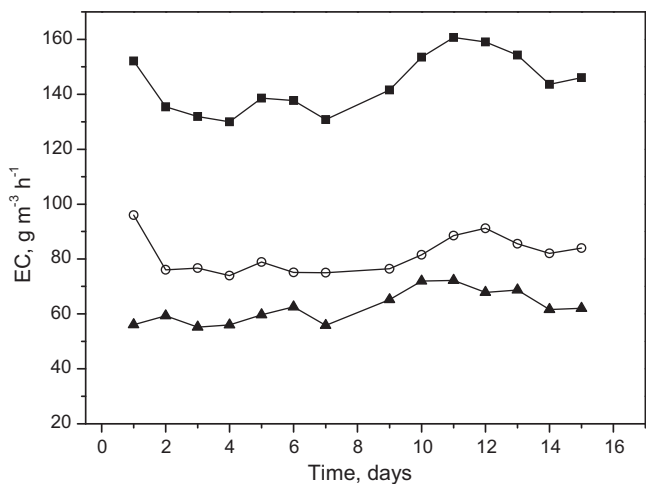


Fig. 5. Ethylbenzene vapors degradation in a photocatalytic system coupled to a biofilter. TiO₂-In 1%/365 nm (▲), biofilter (○), hybrid system (■). Inlet organic loading rate $225 \pm 0.12 \text{ g m}^{-3} \text{ h}^{-1}$.

Rivera Escoto and M.C. Marco García for their technical assistance. We thank Dr. Aitor Aizpuru and Dr. Andrea Pavlick for their suggestions to improve this study.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.01.035.

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