Combination of Adsorption on Activated Carbon and Oxidative Photocatalysis on TiO_2 for Gaseous Toluene Remediation

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Abstract: The influence of activated carbon on the activity of TiO_2 in toluene photooxidation was studied to verify the efficiency of both materials working ensemble. Results showed that surface pH and more strongly the surface area of activated carbon influence the TiO_2 photoactivity. Results suggest that toluene adsorbed on carbon diffuses to TiO_2 where photooxidation takes place. In conclusion, TiO_2-activated carbon was able to perform the photooxidation of toluene for at least two consecutive runs more efficiently than TiO_2 alone. Combination of adsorption on activated carbon and oxidative photocatalysis on TiO_2 is a promising direction for removal of pollutant from air.

Keywords: Photocatalysis, toluene, TiO_2, activated carbon.

1. INTRODUCTION

Industrial activities are responsible of emission of different volatile organic compounds (VOC's) and most of them as toluene are very harmful for human [1]. In addition, toluene is a common reagent in the preparation of a great variety of compounds such as benzaldehyde, benzoic acid, benzyl alcohols, etc. Thus, besides in air, toluene can be found in many industrial waste effluents. From different advanced oxidation processes, heterogeneous photocatalysis has shown to be an effective technology to control environmental pollution both in aqueous and in gaseous phases. In particular, studies about photocatalytic oxidation of toluene in gas phase on irradiated TiO_2 [2-5] has been shown promising results for air pollution remediation and efficiency is limited by the adsorption capacity of photocatalysts. However, recent studies in gas phase showed that combination of TiO_2 with adsorbents as activated carbon filters [6] or TiO_2-embedded carbon nano filters [7] appeared to have higher photocatalytic efficiency in comparison with TiO_2 alone. Having this in mind, the objective of this work is to study the influence of powdered activated carbon (AC) on the photocatalytic activity of TiO_2 during toluene oxidation in two photocatalytic consecutive runs to verify the efficiency of both processes, adsorption and photocatalysis ensemble.

2. EXPERIMENTAL

Toluene was acquired from National Institute of Standards and Technology (NIST) in a compressed gas cylinder (99.9%) with nitrogen as balanced gas. Experiments were performed in presence of steam with a relative humidity of 35%. Photocatalyst was TiO_2 P25 from Degussa. Activated carbon (AC) was prepared from *Tabebuia Pentaphyla* wood by physical activation with CO_2 at 700ºC and 900ºC by 1h and denoted $AC_{CO2\text{-}700}$ and $AC_{CO2\text{-}900}$. Surface properties of AC and TiO_2 have been reported previously [8] and they are summarized in Table **1**. TiO_2-AC samples were prepared by mixing 25mg TiO_2 and 5mg AC in 5mL water continuously stirred for 80min and then filtered and dried at 110ºC by 2h and then introduced into the photoreactor. Experimental set-up has been reported previously by some of us [5]. The experimental procedure is summarized as follows. Gaseous stream of toluene was generated using a permeation tube (Calibrage) at $117ng.min^{-1}$ at contact temperature of 50ºC. A N_2 gas at a constant flow rate of $50mL.min^{-1}$ was passed over the permeation tube and then mixed with O_2 and water vapor at gas flow rates corresponding to target toluene concentration of 190ppb. The final gas stream humidity and temperature was measured using a thermohygromer (Rotonic Hydropalm 1). Photoreactor was a stainless steel cylindrical tube of 85mL volume and with optical window diameter of 7cm. UV-irradiation was provided by a high pressure Hg lamp (Phillips HPK 125W). Radiation was filtered by a circulating-water cell (thickness 2.5cm) with cut-off filter (Corning 0-52). Photocatalytic test consisted in the adsorption in the dark of toluene by 120min followed by 40min of UV-irradiation. In a second run, adsorption process was carried out only by 30min before UV-irradiation because kinetic trends of adsorption during the first run showed that this time was enough to achieve equilibrium of adsorption in the dark. Toluene concentration was measured by GC-FID equipment.

3. RESULTS AND DISCUSSION

3.1. Adsorption in the Dark

Fig. (**1**) shows the kinetics of toluene adsorption in the dark during the first and second runs. Adsorption equilibrium is reached in about 30min in both adsorption

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Table 1. BET Surface Area (S_{BET}) and Surface pH (pH_{PZC}) of TiO_2 and AC

Photocatalysts	S_{BET} (m^2/g)	pH_{PZC}
TiO_2	50 ± 2	6.5
$AC_{CO2-700}$	574 ± 14	8.0
$AC_{CO2-900}$	907 ± 21	9.1
TiO_2-$AC_{CO2-700}$	104 ± 3	7.3
TiO_2-$AC_{CO2-900}$	145 ± 4	7.8

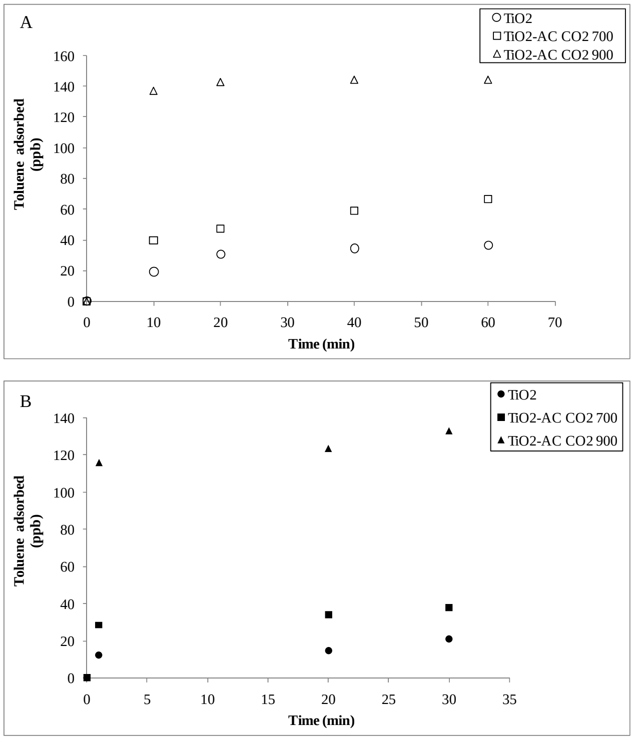

Fig. (1). Kinetics of toluene adsorption in the dark. **A**) First run. **B**) Second run.

runs. In the first run (Fig. **1A**), toluene adsorption on TiO_2-$AC_{CO2-900}$ is considerably higher than that adsorbed on TiO_2-$AC_{CO2-700}$ (about 75% toluene adsorbed against 35%) which showed a lightly higher toluene adsorption than that obtained on TiO_2 alone (about 20%). In the second run (Fig. **1B**), results showed the same adsorption trends: TiO_2-$AC_{CO2-900}$ >> TiO_2-$AC_{CO2-700}$ > TiO_2. However, it is important to remark that after the second adsorption process TiO_2-$AC_{CO2-900}$ showed a decrease of only 7% in adsorption capacity (70 against 75% toluene adsorbed at equilibrium) while TiO_2-$AC_{CO2-700}$ decreases in about 40% (20 against 35% toluene adsorption) and TiO_2 decreases remarkably in about 50% (10 against 20%). It can be seen from data in Table **1** that S_{BET} of TiO_2-$AC_{CO2-900}$ is clearly higher than that of TiO_2-$AC_{CO2-700}$ (145 against $104m^2.g^{-1}$). This suggest that differences in toluene adsorption in the dark between TiO_2-$AC_{CO2-700}$ and TiO_2-$AC_{CO2-900}$ can be ascribed to the differences in surface area more than to the light difference in pH_{PZC} of AC. This results in gas phase agree with recent results in aqueous phase [8] concerning to 4-chlorophenol photodegradation on the same type of TiO_2-carbon based photocatalysts where surface area of AC remarkably influence the adsorption of pollutant and concomitantly to the photoefficiency of TiO_2 as we discuss as follows.

3.2. Toluene Photodegradation

Fig. (**2**) shows the kinetics of toluene photooxidation on UV-irradiated TiO_2, TiO_2-$AC_{CO2-700}$, and TiO_2-$AC_{CO2-900}$ for the two consecutive photocatalytic runs and after achieves the equilibrium of adsorption in the dark described above. After 20min reaction in the first photocatalytic run (Fig. **2A**), toluene conversion reached about 90% on TiO_2-$AC_{CO2-900}$, 85% on TiO_2-$AC_{CO2-700}$ and 80% on TiO_2. After 40min reaction, toluene conversion increases to 95%, 87% and 85% on TiO_2-$AC_{CO2-900}$, TiO_2-$AC_{CO2-900}$ and TiO_2, respectively. In the second run (Fig. **2B**) toluene conversion follows the same trends than in the first photocatalytic run and after 40min reaction, conversion was about 92%, 82% and 80% on TiO_2-$AC_{CO2-900}$, TiO_2-$AC_{CO2-900}$ and on TiO_2, respectively. It can be inferred from the kinetic trends in Fig. (**2**) that toluene photodegradation follows an apparent first-order rate. In agreement with this, linear transformation of kinetic results, $Ln(C_o/C_t) = f(t)$, are shown in Fig. (**3**). Linear regression from the kinetic data of Fig. (**2**) was employed to estimate the apparent rate constant of first-order (k_{app}) for the photodegradation of toluene that can be employed to compare the efficiency of photocatalysts. A summary of kinetic results of toluene degradation showing the apparent first-order constant (k_{app}), the quadratic value of the linear regression (R^2) and the interaction factor (I_F) between both solids are presented in Table **2**. I_F is defined by comparison between the apparent constant obtained on the mixed system against value obtained on TiO_2 alone:

$$I_F = [k_{app}(TiO_2\text{-}AC_i)/k_{app}(TiO_2)]. \quad (1)$$

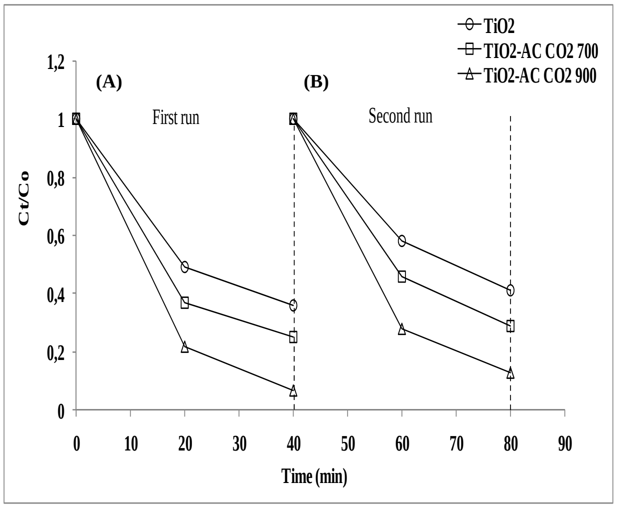

Fig. (2). Kinetics of toluene photodegradation. **A**) First run. **B**) Second run.

I_F permits to verify the influence of AC on TiO_2 photoactivity. From the apparent rate constant of first-order (k_{app}) in Table **2**, it can be seen a clear correlation between photocatalytic activities with surface area and pH_{PZC} of AC.

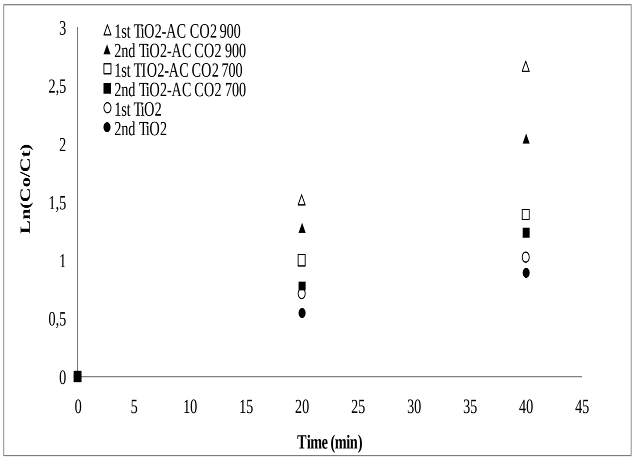

Fig. (3). Linear regression from kinetic data of Fig. (**2**).

Table 2. Apparent First-Order Rate Constants (k_{app}) and Interaction Factor (I_F) Detected During the Photodegradation of Toluene

System	First Run			Second Run		
	k_{app} (min^{-1})	R^2	I_F	k_{app} (min^{-1})	R^2	I_F
TiO_2	0.0276	0.9403	1.00	0.0233	0.9806	1.00
TiO_2-$AC_{CO2\text{-}700}$	0.0377	0.9290	1.36	0.0325	0.9746	1.39
TiO_2-$AC_{CO2\text{-}900}$	0.0683	0.9924	2.47	0.0535	0.9759	2.30

For example, results of I_F in Table **2** show that TiO_2-$AC_{CO2\text{-}700}$ and TiO_2-$AC_{CO2\text{-}900}$ are about 1.4 (0.0377 against 0.0276min^{-1}) and 2.5 (0.0683 against 0.0276min^{-1}), respectively, more photoactive than TiO_2 alone in the first photocatalytic run of toluene photodegradation. It is important to note that in spite of k_{app} decrease for the second photocatalytic run for the three photocatalysts, I_F values from Table **2** suggest that photoactivity of TiO_2-$AC_{CO2\text{-}700}$ and TiO_2-$AC_{CO2\text{-}900}$ practically reminds the same after the second photocatalytic run. In other words, TiO_2-$AC_{CO2\text{-}700}$ and TiO_2-$AC_{CO2\text{-}900}$ are about 1.4 and 2.3 times more photoactive than TiO_2 alone after two consecutive photocatalytic runs. This enhancement in photoactivity of TiO_2-$AC_{CO2\text{-}700}$ and TiO_2-$AC_{CO2\text{-}900}$ in comparison of TiO_2 alone can be attributed to the higher toluene adsorptions indicated previously suggesting that TiO_2-$AC_{CO2\text{-}900}$ would be able to perform several adsorption runs while TiO_2. In this work, the intermediate products of toluene photodegradation were not quantified but the main products detected in all photocatalysts studied were benzaldehyde and p-cresol in agreeing with works from other authors [2,3,5]. The decrease in toluene adsorption and concomitantly in photoactivity during the second run, mainly on TiO_2 alone and lightly on TiO_2-$AC_{CO2\text{-}700}$ could be consequence of competition for the adsorption sites [9] between toluene and intermediate products formed during its photooxidation. This effect would affect more strongly to TiO_2 because adsorption sites of TiO_2 are clearly lower than that on TiO_2-AC based photocatalysts. Also, as we have already discuss in previous works, the enhanced TiO_2-$AC_{CO2\text{-}900}$ photoactivity can be also explained by the creation of a common contact interface [10] between TiO_2 and AC which permits that adsorbed pollutants diffuse from AC to TiO_2 for photooxidation. Once the pollutant diffused, AC is able to adsorb more pollutants from gaseous stream and diffusing again to TiO_2 and so on. This pollutant transfer cycle from gaseous phase to AC and then to TiO_2 is a driven force that could be responsible for the improved pollutant removal.

4. CONCLUSIONS

TiO_2-AC was able to perform the photooxidation of toluene for at least two consecutive runs more efficiently than TiO_2 alone suggesting that combination of adsorption on AC and photocatalysis on TiO_2 is a promising direction for pollutant removal from air.

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REFERENCES

[1] Legrini O. Photochemical processes for, water treatment. Chem Rev 1993; 93: 671-98.
[2] Martra G, Augugliaro V, Coluccia S, *et al*. Photocatalytic oxidation of gaseous toluene on polycrystalline TiO_2: FT-IR investigation of surface reactivity of different types of catalysts. Stud Surf Sci Catal 2000; 130: 665-70.
[3] Marci G, Addamo M, Augugliaro V, *et al*. Photocatalytic oxidation of toluene on irradiated TiO_2: Comparison of degradation performance in humidified air, in water and in water containing a zwitterionic surfactant. J Photochem Photobiol A: Chem 2003; 160: 105-14.
[4] Tomasic V, Jovic F, Gomzi Z. Photocatalytic oxidation of toluene in the gas phase: Modelling an annular photocatalytic reactor. Catal Today 2008; 137: 350-6.
[5] Sleiman M, Conchon P, Ferronato C, Chovelon JM. Photocatalytic oxidation of toluene at indoor air levels (ppbv): Towards a better assessment of conversion, reaction intermediates and mineralization. Appl Catal B: Environ 2009; 86: 159-65.
[6] Ao CH, Lee SC. Indoor air purification by photocatalyst TiO_2 immobilized on an activated carbon filter installed in an air cleaner. Chem Eng Sci 2005; 60: 103-9.
[7] Kim S, Lim SK. Preparation of TiO_2-embedded carbon nanofibers and their photocatalytic activity in the oxidation of gaseous acetaldehyde. Appl Catal B: Environ 2008; 84 : 16-20.
[8] Cordero T, Duchamp C, Chovelon JM, Ferronato C, Matos J. Surface nano-aggregation and photocatalytic activity of TiO_2 on h-type activated carbons. Appl Catal B: Environ 2007; 73: 227-35.
[9] Matos J, Laine J, Herrmann JM, Uzcategui D, Brito JL. Influence of activated carbon upon titania on aqueous photocatalytic consecutive runs of phenol photomineralization. Appl Catal B: Environ 2007; 70: 461-9.
[10] Matos J, Laine J, Herrmann JM. Synergy effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon. Appl Catal B 1998; 18: 281-91.

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