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Preliminary study of the use of β-SiC foam as a photocatalytic support for water treatment

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ABSTRACT

In this study we used a medium sized surface area of β-SiC foam, being a three-dimensional medium for the preparation of photocatalytic materials. The study's objective was to optimize the deposition of TiO_2 photocatalyst on the β-SiC Foam by using the sol–gel process. To this end, various parameters were applied via varying temperatures of the thermal treatment; variation in the ratio of acetic acid/Ti of sol–gel; and differing level of oxidation of the β-SiC support. The relative performances of the various prepared materials were evaluated against their ability to degrade an aqueous solution of Diuron (herbicide) under UV irradiation. As an outcome, we obtained an efficient TiO_2/β-SiC material for photocatalytic degradation of organic compounds in water.

1. Introduction

Photocatalytic oxidation using semi-conductors is one of the advanced oxidation processes (AOPs) utilised for the rapid degradation of organic pollutants in water and air. However the future of photocatalysis as an efficient method for water treatment in the context of a policy of sustainable development requires that the scientific community and companies involved in this area must resolve a number of challenges. One of the most significant of these challenges is to develop photocatalytic materials that can be integrated into industrial processes for large-scale water treatment.

TiO_2 is an excellent photocatalyst that can mineralise a large range of organic pollutants including some of the most refractory ones such as pesticides, herbicides and dyes [1–3]. The basic process of photocatalysis consists in ejecting an electron from the valence band (VB) to the conduction band (CB) of the TiO_2 semi-conductor thus creating a h^+ hole in the valence band. This in turn induces the formation of extremely reactive radicals such as $^{\circ}OH$ at the semi-conductor surface or by direct oxidation of the polluting species by h^+. The ejected electrons will react with electron acceptors such as adsorbed oxygen.

To achieve an industrial-scale application of this process, it is necessary to deposit the photocatalyst (titanium dioxide) on a suitable medium. The original element of this study is its use of medium surface area β-SiC foam (20–30 $m^2\,g^{-1}$), a three-dimensional photocatalytic medium for the preparation of photocatalytic materials [4]. This β-SiC foam is a tridimensional medium with an alveolar, adaptable and flexible geometry permitting both good performance in light transmission and in optimum fluid flow thus promoting increased contact between the photocatalytic active coating and the polluted water. This support was synthesized using the shape-memory synthesis developed by Ledoux et al. which is a gas–solid reaction between SiO and Carbon [5].

In the relevant literature, very few studies refer to TiO_2/β-SiC composite in an environmental application and, to our knowledge none to the TiO_2 deposited on β-SiC foam by the sol–gel method. Currently, Rodriguez et al. [6] have used a process of TiO_2 coating on SiC by dip-coating and using TiO_2–P25 suspensions with different formulations. The photocatalytic performance of the resulting material was evaluated by studying the photooxidation of aqueous ammonia. The authors conclude that TiO_2 anchored on β-SiC foam is a promising material for photocatalytic applications and could be exploited as an internal structuration in classical reactors. Yamashita et al. [7] studied the TiO_2–SiC composite prepared by calcination of nano-particles of TiC–SiC precursor obtained by a carbothermic reduction of SiO_2–TiO_2 which showed high photocatalytic reactivity for the degradation of 2-propanol diluted in water. The formation of well-crystallized TiO_2 on SiC and the hydrophobic surface of SiC were found to be related to the photocatalytic efficiency.

The objective of this study is to optimize the process of deposition of TiO_2 photocatalyst on the β-SiC Foam. The performances of the materials prepared as the basis of the study are evaluated

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against their ability to degrade an aqueous solution of Diuron (herbicide) under UV irradiation.

2. Experimental

2.1. Products

All the reagents used in this work were of analytical grade and were used without any further purification: tetraisopropylorthotitanate $Ti(OC_3H_7)_4$ (Aldrich, 97%), ethanol (SdS-France, 99.9%) and acetic acid (Prolabo, 99.5%). Diuron (98% purity, (N-(3,4-dichlorophenyl)-N,N-dimethylurea) was purchases from Aldrich Company. Titanium dioxide P25 from Degussa Corporation (70% anatase and 30% rutile, 99.8% purity, average particle size 30 nm and specific surface of 50 m^2/g) was used as supplied.

The β-SiC Foam samples used in this study were provided by SICAT Company (Otterswiller-France). 35 mm diameter and 10 mm thick pieces were cut and used as catalyst supports. Each piece weighted approximately 1.2 g and the pore diameter size is between 3600 and 4000 μm.

2.2. TiO_2 sol–gel and TiO_2/β-SiC synthesis

2.2.1. Method 1

TiO_2 sol was prepared based on the optimised methodology reported before by Bessekouad et al. [8].

2.2.2. Method 2

TiO_2 powder: Precursor sol of TiO_2 was prepared via sol–gel process. Tetraisopropylorthotitanate ($Ti(OC_3H_7)_4$ (20.4 ml) was dissolved in ethanol (70,8 ml). After vigorous stirring for 30 min at room temperature, the mixture of distilled water (1 ml), ethanol (2 ml) and acetic acid (between 0 and 74 ml according to the CH_3COOH/Ti ratio desired) was added drop by drop into the solution under continuous stirring. The resultant precursor solution was stirred at room temperature for 1 h, and then was kept for 24 h in the dark. A uniform, stable and transparent sol of TiO_2 was obtained

The sol was dried at 110 °C overnight and then heat-treated for 2 h in air with a temperature between 300 and 450 °C to create a range of samples heat treatment being applied at a heating rate increase (and decrease) of 5 °C/min.

β-SiC-TiO_2 foam preparation: The TiO_2 nanofilm was prepared by depositing the TiO_2 sol on β-SiC foam via dip-coating method at room temperature. Prior to the coating process, all SiC foam samples were sonicated for 20 min in ethanol and heated at 110 °C for 2 h. The foam was then immersed into the TiO_2 sol for 3 min and withdrawn at a speed of 9 mm/s. The samples were naturally dried in air for 30 min between two coating operation. Finally the samples were dried at 110 °C in a desiccator overnight before a heat treatment at a temperature between 300 and 450 °C for 2 h (5 °C/min)

2.3. Sample characterisation

Structural characterization of the prepared samples was done by powder X-ray diffraction (XRD) measurements carried out on a D8 Advance Bruker diffractometer, in a q/2q mode and using the Ka_1 radiation of Cu at 1.5406 Å. Scanning Electron Microscopy (SEM) was carried out on a Jeol JSM-6700F working at 3 kV voltage, equipped with a CCD camera. The surface area and porosimetry measurements were carried out on a ASAP2010 Micromeritics using N_2 as adsorbant at liquid N_2 temperature. Before the N_2 adsorption, the material was outgassed at 200 °C for 12 h in order to desorb the impurities or moisture from its surface. The surface area was calculated from the nitrogen adsorption isotherms using the B.E.T. method (S_{BET}), the micropore surface area was derived using the /*t*/-plot method, and the pore size distribution was obtained using the B.J.H. method during the desorption isotherm branch

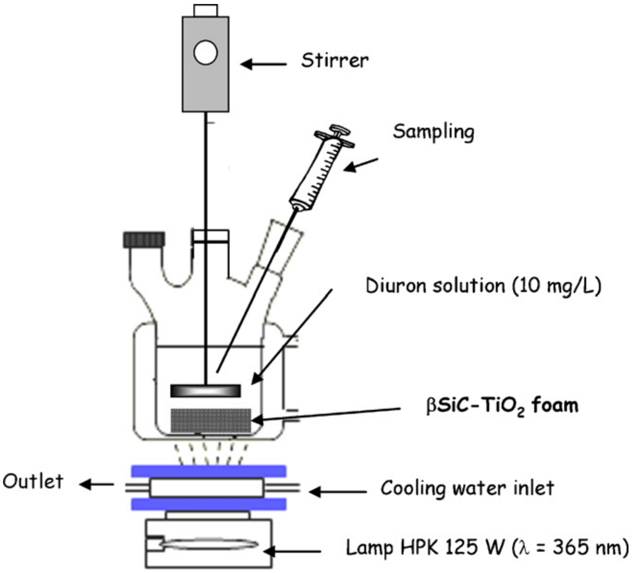

Fig. 1. Schematic diagram of experimental setup.

2.4. Evaluation of photocatalytic efficiency

Pure TiO_2 powders (P25 and SG–TiO_2) or β-SiC/TiO_2 samples were dipped by means of stirring in a volume of 50 ml of Diuron aqueous solution ($C_{Diuron} = 10$ mg/l). Before each irradiation, the suspensions were kept in the dark for 2 h in order to reach the adsorption equilibrium. Irradiation was carried out with a HPK 125 W Philips mercury lamp, emitting in the wavelength range 250–600 nm, with a maximum emission at 365 nm (The average value of UVA irradiance is 130 W/m^2). A circulating water Pyrex-glass tank cooler was positioned between the lamp and the reactor. The suspension was homogenised by a magnetic stirrer and remained in contact with air (Fig. 1). Before analysis, each sample was filtered through a 0.45 mmWhatman filter to eliminate the TiO_2 particles. In the case of TiO_2 suspension experiments, no filtration is necessary for the test with TiO_2/β-SiC. During the photocatalytic test, 2 ml of the solution were extracted at given irradiation time intervals. The remaining concentration of Diuron was determined with a LIBRA S12 UV–vis spectrophotometer ($\lambda = 248$ nm)

3. Results and discussions

3.1. Optimization and evaluation of photocatalytic activity of TiO_2 powder

The photodegradation kinetics of the Diuron in TiO_2 dispersions under UV irradiation have often been modelled on the Langmuir–Hinshelwood equation. When the solution is highly diluted, the reaction is essentially an apparent first order reaction and after integration, the L.H. equation can be reduced to the following equation: $\ln(C_0/C) = k_{ap}t$ where k_{ap} is the apparent rate constant of a pseudo first-order reaction. By plotting $\ln(C_0/C)$ versus t, the apparent rate constant (k_{ap}) can be determined from the slope of the curve obtained.

The effect of the preparation method and the CH_3COOH/Ti ratio of the sol–gel solution on photocatalytic activity of TiO_2 can be observed at Fig. 2.

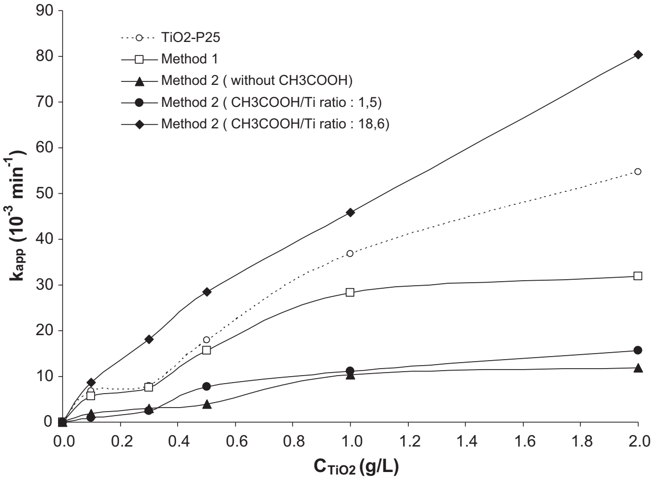

Fig. 2. Apparent rate constants according TiO_2 amount for the photocatalytic degradation of Diuron solution with different samples of TiO_2.

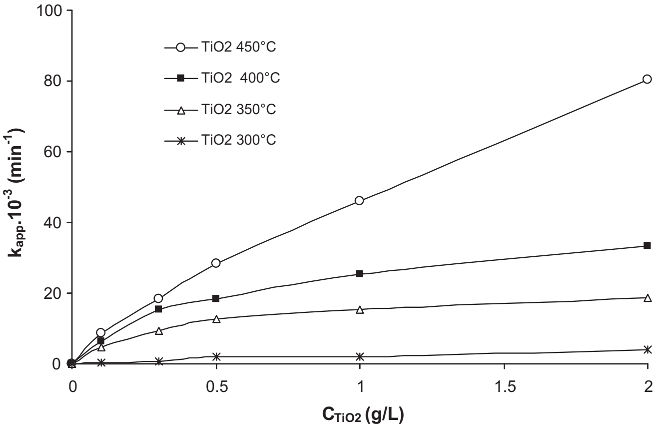

Fig. 4. Effect of heat treatment on the k_{app} according TiO_2 concentration for the photocatalytic degradation of Diuron solution (CH_3COOH/Ti ratio = 18.6).

In Fig. 2, we note that the better photocatalyst for the Diuron degradation was achieved with method 2 with the CH_3COOH/Ti ratio: 18.6. In this condition, prepared TiO_2 was more efficient than TiO_2–P25. Attar et al. [9] have shown that the presence of acetic acid will be useful for controlling the hydrolysis and condensation reactions and prevent the precipitation of undesired phases. Acetic acid displaced two isopropoxide ligands to form the alcoxyde chelate: $Ti(i\text{-}PrO)_2(CH_3COO)_2$. As indicated by Livage et al. [10] by the Ti coordination number becomes equal to 6. The stable TiO_2 sols can be prepared by using acetic acid, unlike method 1 (direct addition of water in the solution of TTIP).

It is very important to obtain a stable solution for several hours (or days), because the procedure for TiO_2 deposit onto the relevant medium can sometimes be lengthy.

As can be seen in Table 1, the main difference between the various prepared TiO_2 samples are the BET area values. For a temperature of sol–gel thermal treatment of 450 °C, the largest area is obtained with the CH_3COOH/Ti ratio: 18.6. This would indicate that this sample has the best photocatalytic level of activity as we have already shown in previous works [11]. By using Scherrer equation the size of crystals were measured and calculated in Table 1. We note that the sizes of the crystals are relatively close and they are smaller for the largest CH_3COOH/Ti ratio.

XRD analysis (Fig. 3) revealed that the outcome of the all samples crystallized phase was anatase. Only the sample prepared from method 1 shows traces of the rutile phase.

We confirmed the significant effect of heat treatment temperature on the level of photocatalytic activity. In Fig. 4, we observe that at 300 °C the photocatalyst is ineffective because TiO_2 is under amorphous phase and that the photocatalytic efficiency increases with the temperature reaching its maximum at 450 °C for method 2 with CH3COOH/Ti ratio: 18.6. We have not exceeded this optimum because at higher temperature than 450 °C, there was mainly a formation of rutile phase.

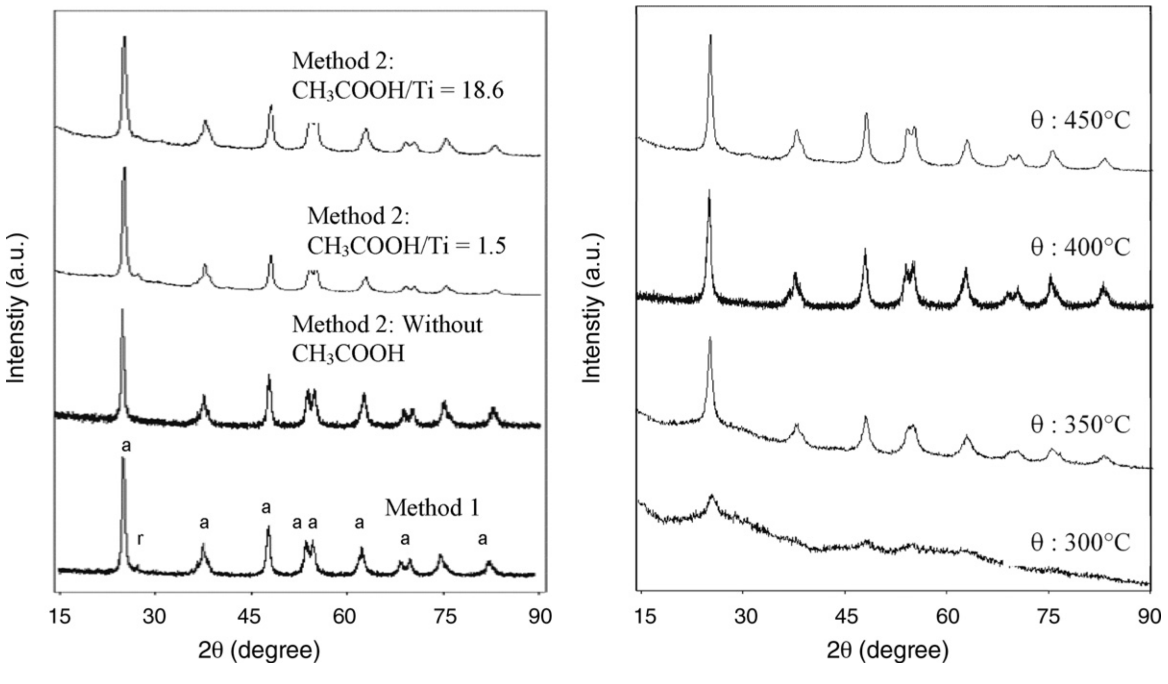

Fig. 3. XRD patterns of TiO_2 nanoparticles synthesis (a: anatase and r: rutile) after heat treatment in 450 °C with different CH_3COOH/Ti ratio (left) and for CH_3COOH/Ti ratio = 18.6 at different temperature of heat treatment for method 2 (right).

Table 1
Main characteristics of TiO_2 photocatalyst samples.

	Calcination temperature	CH_3COOH/Ti in sol–Gel	BET area (m^2/g)	Crystal size (nm)
Method 1	450 °C	/	5	16
	450 °C	/	42	18
	450 °C	1.5	30	16
Method 2	450 °C	18.6	82	12
	350 °C	18.6	158	10
	400 °C	18.6	86	12
P25	/	/	50	30

3.2. *Pretreatment β-SiC foams*

β-SiC foams offer many advantages including a low pressure drop, a large frontal area and low flow resistance reaction because of their open structure [12]. Moreover, β-SiC is chemically inert and thermally stable because it has already heated been to 1450 °C. Its surface is covered with a thin layer of SiO_2/SiO_xC_y of 2 to 4 nm thickness, formed during the final thermal treatment of the material. Anderson and Bard [13,14] demonstrated that a mixed oxide of TiO_2 and SiO_2 produced by sol–gel was a more efficient photocatalyst for the decomposition of Rhodamine-6G or phenol than TiO_2 alone. In this part of the study, an oxidizing heat treatment at different times was carried out on β-SiC foams to increase the thickness of the SiO_2 layer. During the heat treatment in air, we observe an increase in mass for temperatures above 800 °C, which is due to the oxidation of silicon carbide on the foam surface to form SiO_2 by the following reactions:

$$SiC + 3/2O_2 \rightarrow SiO_2 + CO$$

After 2 h of thermal treatment at 1000 °C, the increases of β-SiC mass determined by thermogravimetric analysis correspond to 20%. The formation of SiO_2 was confirmed by XRD measurement, which shows the presence of a diffraction peak at 21.6° corresponding to amorphous SiO_2 (Fig. 5).

The specific surface area (BET) measurements show that BET area decreases during the thermal oxidative treatment (BET = 18 m^2/g for β-SiC and 10 m^2/g for oxidized-β-SiC at 1000 °C).

3.3. *Preparation and optimisation of β-TiO_2-SiC foam composite*

3.3.1. *Coating solution and CH_3COOH/Ti ratio effect*

Although the TiO_2 powder prepared from method 1 presents a good photocatalytic performance, the sol–gel solution from method 1 is inadequate for the deposition of TiO_2 on β-SiC foam. This is due to a very high detachment of TiO_2 particles observed when the material was dipped in Diuron solution (Fig. 6).

In Fig. 6, it was evident that method 2 is more adapted to the context of industrial treatment processes, because no visible detachment of TiO_2 was observed in this case. As we can see in Fig. 7, the CH_3COOH/Ti ratio effect is less important for the composite material than for the TiO_2 alone in the case of photocatalytic degradation of Diuron solution. However, the most effective material is that which has been dipped in the sol–gel with CH_3COOH/Ti ratio: 18.6 as in the case of TiO_2 powder. In this study, each sample contains about 6–7% in weight of TiO_2 (see Table 2), that corresponding to 1.5–1.8 g/L of TiO_2.

The results obtained with β-SiC/TiO_2 materials were less important than the one obtained with corresponding TiO_2 powders. Apparent rate constants are on average 6–8 times lower than for the structured photocatalysts. These decreases should be related to the diffusion problems of the UV radiation into the foam structure (masking effect). The configuration of our photoreactor cannot illuminate all the foam because the lamp is placed below the composite (see Fig. 1). We assume that only a half part of TiO_2 is activated.

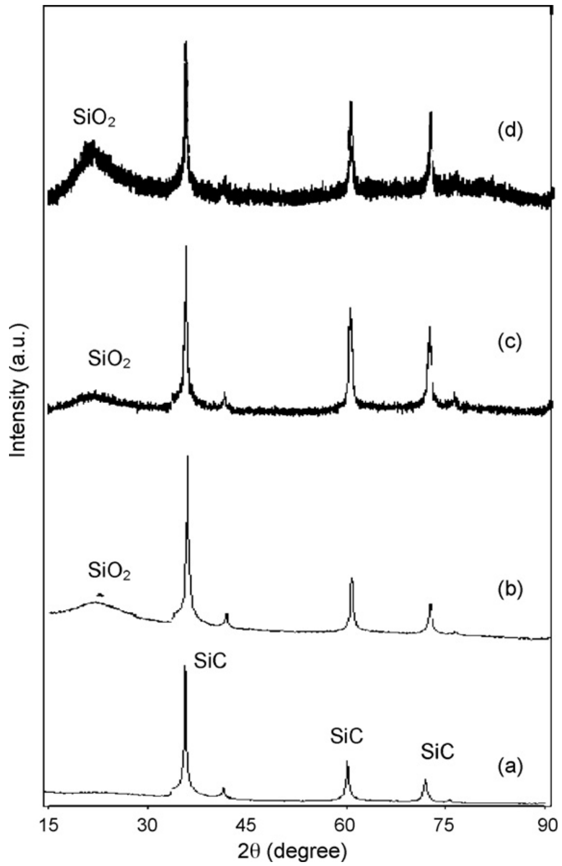

Fig. 5. X-ray diffraction patterns of the β-SiC (a) and oxidized β-SiC at 1000 °C during 2 h (b), 5 h (c) and 10 h (d).

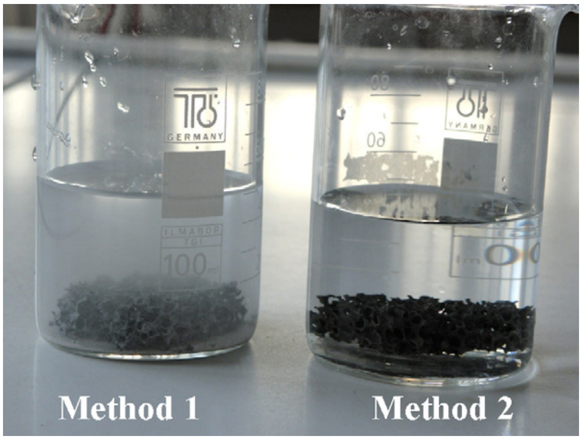

Fig. 6. Stability β-SiC-TiO_2 samples in Diuron water solution.

Table 2
Sample β-SiC/TiO_2 composition and concentration in Diuron solution.

Samples	m_{SiC/TiO_2}	% TiO_2 in weight	C_{TiO_2} (g/L) in Diuron solution	$k_{app} \times 10^{-3}$ (min^{-1})
Method 1	1.27	6.76	1.60	5.5
Method 2 (without CH_3COOH)	1.28	6.89	1.76	2.5
Method 2 (CH_3COOH/Ti ratio = 1.5)	1.21	6.29	1.52	5.6
Method 2 (CH_3COOH/Ti ratio = 18.6)	1.32	6.8	1.56	10.3

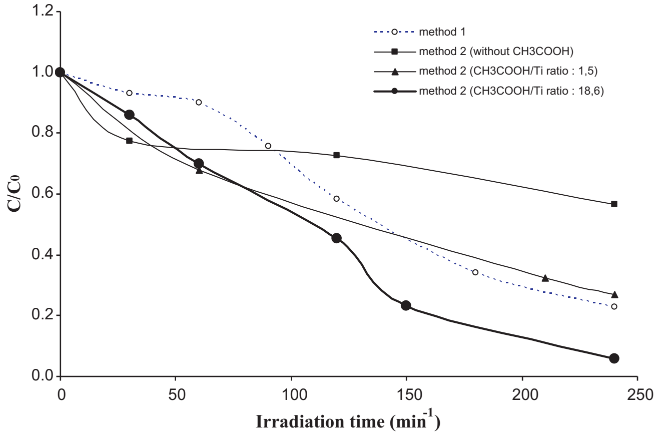

Fig. 7. Photocatalytic degradation of Diuron according to different β-SiC/TiO_2 composites treated at 450 °C (experimental conditions are summarized in Table 2).

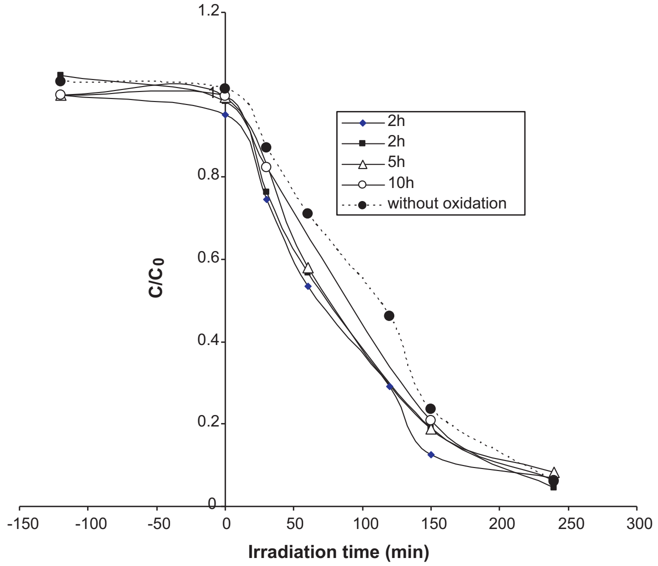

Fig. 8. Effect of the oxidation of β-SiC on the degradation kinetic of Diuron with TiO_2/β-SiC.

Another reason is the possibility of rate limitation due to liquid to solid mass transfer. This effect is negligible for a suspension, whereas Turchi and Ollis [15] have shown that the mass transfer can explain the flow rate dependence for the photocatalytic reaction rate in the case of immobilized photocatalysts. However, this lower photocatalytic activity is compensated for by the fact that filtering the solution after treatment is not necessary, the media being easily reusable and they can work in continuous flow.

3.3.2. *Effect of pre-oxidation of β-SiC foam*

Different samples of β-SiC foams have been air-heated at 1000 °C during 2, 5 and 10 h to increase the thickness of the SiO_2 layer. TiO_2 was deposit according the method 2 (CH_3COOH/Ti ratio: 18.6 and calcination temperature: 450 °C). In Fig. 8, we observe that a SiO_2 layer increase has a very little influence on the kinetics of photodegradation of Diuron. We assume that the silica layer formed during the preparation of SiC foam is sufficient (2–4 nm) and TiO_2 is deposited uniformly over the entire surface of the foam. Therefore it is not necessary to increase the layer of SiO_2.

4. Conclusion

Titanium dioxide nanoparticles and TiO_2 supported on β-SiC foam were prepared via sol–gel methods. Several parameters (CH_3COOH/Ti ratio, temperature of calcination) were used to optimize the efficiency of the prepared materials. In correlation with the increase of the CH_3COOH concentration in the sol–gel solution, the photocatalytic oxidation of Diuron also increases. The optimized TiO_2/β-SiC foam material was very stable. TiO_2 remains strongly attached to the surface of the foam. The photocatalytic efficiency obtained with β-SiC/TiO_2 materials was less significant than the efficiency obtained with corresponding TiO_2 powders. However, these results are very promising because this lower activity is compensated by the fact that filtering the solution after treatment is not necessary, the media being easily reusable and they are suitable to work in continuous flow. In addition, the β-SiC foam can be formed in any shape. It can thus be adapted for industrial reactors for the photocatalytic treatment of contaminated water.

References

[1] A. Mills, S. Le Hunte, J. Photochem. Photobiol. A 108 (1997) 1–35.
[2] A.G. Agrios, P. Pichat, J. Appl. Electrochem. 35 (2005) 655–663.
[3] M. Lewandowski, D.F. Ollis, in: V. Ramamurthy, K.S. Schanke (Eds.), Semiconductor Photochemistry and Photophysics, Basel, New York, 2004, pp. 249–258.
[4] S. Hajiesmaili, M. Grandcolas, D. Bégin, V. Keller, N. Keller, C. Pham, Huu et al., PCT patent N PCT2009/1093, "Photocatalyseurs à base de mousses tridimensionnelles structurées en carbures de silicium".
[5] M.J. Ledoux, S. Hantzer, J. Guille, D. Dubots, US Patent No. 4 914 070.
[6] P. Rodriguez, V. Meille, S. Pallier, M.A. Al, Sawah, Appl. Catal. A 360 (2009) 154–162.
[7] H. Yamashita, Y. Nishida, S. Yuan, K. Mori, M. Narisawa, Y. Matsumura, T. Ohmichi, I. Katayama, Catal. Today 1020 (2007) 163–167.
[8] Y. Bessekhouad, D. Robert, J.V. Weber, J. Photochem. Photobiol. A 157 (2003) 47–53.
[9] A.S. Attar, M.S. Ghamsari, F. Hajiesmaeilbaigi, S. Mirdamadi, J. Mater. Sci. 43 (2008) 173–178.
[10] J. Livage, C. Sanchez, M. Henry, S. Doeuff, Solid State Ionics 32 (1989) 633–638.
[11] O. Heintz, D. Robert, J.V. Weber, J. Photochem. Photobiol. A 135 (1) (2000) 77–80.
[12] D. Edouard, S. Ivanova, M. Lacroix, E. Vanhaecke, C. Pham, C. Pham-Huu, Catal. Today 141 (2009) 403–408.
[13] C. Anderson, A.J. Bard, J. Phys. Chem. 99 (1995) 9882–9885.
[14] C. Anderson, A.J. Bard, J. Phys. Chem. B 101 (1997) 2611–2616.
[15] C.S. Turchi, D.F. Ollis, J. Phys. Chem. 92 (1988) 6852–6853.