Immobilization of TiO$_2$ and Fe–C–TiO$_2$ photocatalysts on the cotton material for application in a flow photocatalytic reactor for decomposition of phenol in water

Beata Tryba[*]

Szczecin University of Technology, ul. Pulaskiego 10, 70-322 Szczecin, Poland

Abstract

TiO$_2$ and Fe–C–TiO$_2$ photocatalysts have been immobilized on the cotton material and used in a flow photocatalytic reactor for phenol decomposition. The cotton material has been applied as a support for photocatalyst, because can be easily removed and replaced in a reactor, what facilitates the performance of the photocatalytic process. Fe–C–TiO$_2$ photocatalyst has been prepared by modification of TiO$_2$ fine particles of anatase structure with FeC$_2$O$_4$ through heating in Ar at 500 °C. The immobilized photocatalysts could efficiently decompose phenol in multiple use, Fe–C–TiO$_2$ showed higher photocatalytic activity than TiO$_2$, around 15–18 mg and 15–16 mg of phenol have been decomposed after 5 h of UV irradiation on Fe–C–TiO$_2$ and TiO$_2$, respectively. After addition of H$_2$O$_2$ the phenol decomposition and the mineralization degree have been accelerated, especially with immobilized Fe–C–TiO$_2$ photocatalyst, in case of that the photo-Fenton reaction occurred. In the presence of H$_2$O$_2$ around 26–28 mg and 21–24 mg of phenol have been decomposed on Fe–C–TiO$_2$ and TiO$_2$ respectively, after 5 h of UV irradiation.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Photocatalytic reactor; TiO$_2$; Fe–C–TiO$_2$; Immobilization; Phenol decomposition

1. Introduction

The photocatalytic process with using TiO$_2$ photocatalyst is very promising for application in the water purification, because many hazardous organic compounds can be decomposed and mineralized by the proceeding oxidation and reduction processes on TiO$_2$ surface [1]. The most commonly tested compounds for decomposition through the photocatalysis are phenols, chlorophenols, pesticides, herbicides, benzenes, alcohols, dyes, pharmaceutics, humic acids, organic acids and others [1–8]. Many efforts are focused on the practical application of TiO$_2$ in the water treatment system. One of the disadvantage in using TiO$_2$ as a photocatalyst is its difficulty for sedimentation after photocatalytic process. Therefore many researchers have been undertaken some attempts to improve decantability of fine powder TiO$_2$, mounting of TiO$_2$ particles on some supports have been widely reported, such as mounting TiO$_2$ on SiO$_2$, activated carbon, glass, pumice, zeolites, aluminum, polymers, etc. [9–13].

Separation of TiO$_2$ through the membrane and coupling of photocatalysis with the membrane processes such as membrane distillation have been also applied in the water treatment system [14–16].

In the photocatalytic reactors TiO$_2$ is usually fixed to the inner walls of the reactor by means of clay or epoxy resins [17], however some organic binders are not stable, because of their photocatalytic decomposition on the interfacial surface with TiO$_2$ particles under UV irradiation. The fixed TiO$_2$ to the walls of the reactor once is not easy to be replaced with the other photocatalytic material, therefore new resolutions of TiO$_2$ mounting are still welcomed.

In our previous research work we have improved decantability of TiO$_2$ by changing its hydrophility through the carbon coating [18,19] and we have improved photocatalytic activity of TiO$_2$ by developing of a new Fe–C–TiO$_2$ photocatalyst which could work in both, photocatalysis and photo-Fenton processes [20–22].

[*] Tel.: +48 91 4494277; fax: +48 91 4494686.
E-mail address: beata.tryba@ps.pl.

Application of powdered TiO_2 in a real water treatment system is still a great disadvantage of the photocatalytic process. Therefore in this work a new way of mounting TiO_2 for its application in the photocatalytic flow reactor is presented. Previously we have reported about mounting of the photocatalyst to the adhesive tape and fixed to the metal grid, which was placed inside the reactor [20]. Here are the immobilization of a photocatalyst on the cotton material, which can be easily use in the reactor is presented.

2. Experimental

2.1. Photocatalysts

Anatase-type ST-01 was used as base TiO_2 (Ishihara Sangyo Co. Ltd., Japan). Fe–C–TiO_2 photocatalyst was prepared from TiO_2 and FeC_2O_4 by mechanical mixing in the mass ratio of 10:1, and by heating in Ar at 500 °C for 1 h. In this case small amount of carbon was present as residue. Detailed description about preparation and characterization of the photocatalyst has been already reported in the previous papers [21,22].

2.2. Characteristics of the photocatalysts

The photocatalysts were characterized by BET surface area, XRD, content of iron and carbon, and $OH^\bullet$ radicals formation under UV irradiation with or without H_2O_2.

BET surface area was determined from the adsorption isotherm of N_2 at 77 K. XRD analysis was performed using Cu $K\alpha$ radiation. Content of iron in the catalysts (Fe^{2+} and Fe^{3+}) was determined by extraction with 5 mL of 6 M HCl for 2 h, followed by analysis with UV–vis spectrophotometry using a colorimetric method. Iron detection was carried out using the 2,4,6-tris(2-pyridyl)-1,3,5-triazine reagent, which has a very high sensitivity towards Fe^{2+}. Analysis of $OH^\bullet$ radical formation on the surface of the catalysts under UV irradiation and under UV/H_2O_2 was performed by fluorescence technique using terephthalic acid, which easily reacts with $OH^\bullet$ to form the highly fluorescent product 2-hydroxyterephtalic acid. The intensity of the peak attributed to 2-hydroxyterephtalic acid was proportional to the amount of $OH^\bullet$ radicals formed. Content of carbon in Fe–C–TiO_2 photocatalyst has been determined by combustion the sample in air at 1000 °C using thermogravimetric analysis.

2.3. Immobilization of photocatalyst on the cotton material

The suspension of the powdered photocatalyst has been made in 20 mL of the aqueous solution of sodium silicate (Na_2SiO_3). Then this mixture has been homogoneously pasted with a brush on the cotton material of size 19 cm × 24 cm and was left for drying overnight. The cotton material used is a linen textile produced from a raw unbleached linien yarn. Such immobilized photocatalyst was inserted inside the reactor. The excess of the immobilized photocatalyst was rinsed by flowing water through the reactor before photocatalysis, so only a thin layer of photocatalyst remained on the cotton material.
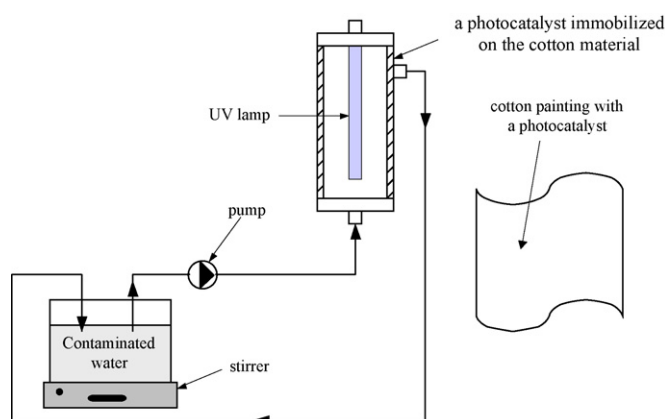

Fig. 1. The scheme of the flow photocatalytic reactor with immobilized photocatalyst on the cotton material.

2.4. Photocatalytic reactor

The commercial cylindrical reactor equipped in UV lamp of Trojan UVMax Company has been used, as shown in Fig. 1. This reactor is easily available and commonly used for the disinfection of water. This is a cylindrical reactor with length of approximately 29.5 cm and the diameter of 6.8 cm. The UV mercury lamp is placed inside the reactor, in the center. The characteristics of this lamp is presented on the UV–vis spectrum in Fig. 2. This lamp emits UV rays in the range of 250–800 nm with high maximum at 254, 436, and 546 nm. The immobilized photocatalyst on the cotton material has been placed inside the reactor from the top in a way to stick to the inner walls along the reactor. The phenol solution has been pump up from the container to the bottom of the reactor by the peristaltic pump and followed the photocatalytic decomposition in the reactor, and then from the top of reactor was going back to the container. This circulation has been performed with the speed of 13.32 dm^3/h for 1.3 dm^3 of circulated phenol solution of concentration 0.03 g/L. Amount of solution inside the reactor was approximately 1 dm^3. Each time after fixing of immobilized cotton material, the reactor was rinsed with water to remove an excess of the photocatalyst.
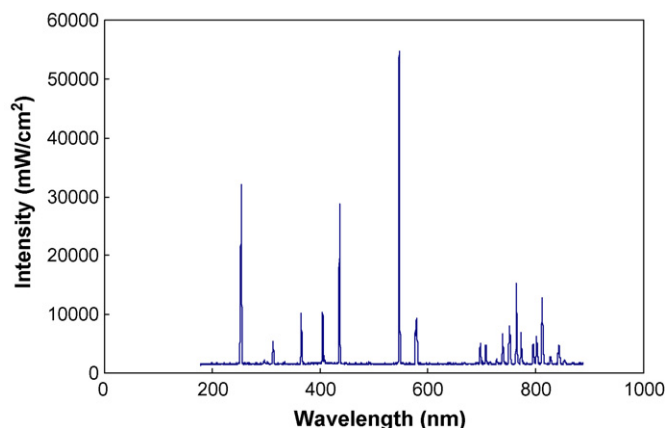

Fig. 2. The characteristics of UV lamp.

2.5. Photocatalytic decomposition of phenol

Phenol decomposition has been performed in the photocatalytic flow reactor equipped in the cotton material with immobilized photocatalyst and switched UV lamp. The experiments have been carried out two to three times for each immobilized photocatalyst. The influence of H_2O_2 addition (9.8 mmol/L) to the reaction mixture on the speed of phenol decomposition has been investigated. The concentration of phenol solution was monitored by sampling of few mL of phenol solution in every 30 min and analysis in UV–vis spectrophotometer by measuring of absorbance at 270 nm. The total organic carbon (TOC) of phenol solution have been measured in Multi N/C analyzer by differential method.

For comparison decomposition of phenol on powdered TiO_2 and Fe–C–TiO_2 has been also performed in a beaker, the results have been published in the previous work [21]. The photocatalysts at a loading of 0.2 g/L were suspended in 500 mL of 0.02 g/L phenol solution. The suspensions were magnetically stirred for 3 h in the dark until saturation with adsorption of phenol. After adsorption, photodecomposition of phenol was carried out under UV irradiation. UV irradiation power inside the reactor was 2.4 mW/cm^2 in the wavelength range 310–400 nm and 1.9 mW/cm^2 in the range 360–470 nm. Experiments were carried out with and without addition of 9.8 mmol/L H_2O_2 to the phenol solution. The concentration of phenol solution was measured by high performance liquid chromatography (HPLC).

3. Results and discussion

The characteristics of photocatalysts are presented in Table 1.
Original TiO_2 exhibited higher BET surface area than Fe–C–TiO_2 and consisted from anatase phase only. $FeTiO_3$ phase appeared in iron modified TiO_2 sample.

In the previous papers [21,22] we have reported the photocatalytic activity of TiO_2 and Fe–C–TiO_2 photocatalysts used as powders in the aqueous phenol solution under UV irradiation with and without addition of H_2O_2 (Fig. 3).

Fe–C–TiO_2 photocatalyst showed lower photoactivity than TiO_2 under UV irradiation but its photoactivity was much higher after addition of H_2O_2 to the reaction mixture. In case of Fe–C–TiO_2 both, photocatalysis and photo-Fenton reactions have been occurred. The presence of carbon in Fe–C–TiO_2 caused that phenol decomposition was going by direct oxidation of phenol on the surface of photocatalyst, addition of H_2O_2 caused oxidation of iron and formation of OH$^\bullet$ radicals, which could attack the organic matter concentrated on the surface of Fe–C–TiO_2 photocatalyst.

The ring products of phenol decomposition has been measured by HPLC. It was checked that in case of TiO_2 ben-
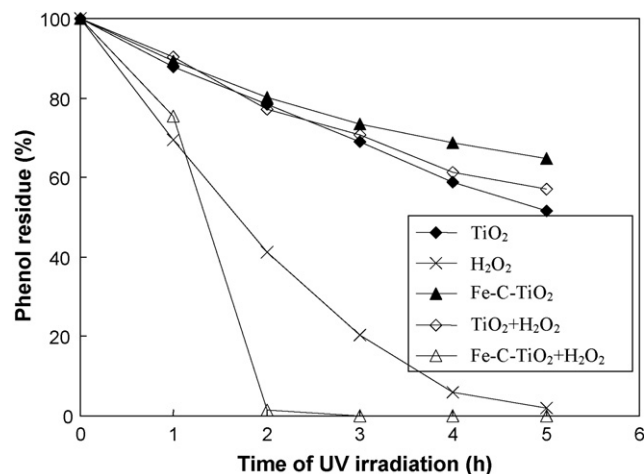

Fig. 3. The phenol decomposition on the powdered TiO_2 and Fe–C–TiO_2 with time under UV irradiation with and without addition of H_2O_2.

zoquinone (BQ) and hydroquinone (HQ) were formed during phenol decomposition, their concentration was increasing with time of UV irradiation. In case of Fe–C–TiO_2 photocatalyst no any ring byproducts of phenol decomposition were detected under UV irradiation. The addition of H_2O_2 to the phenol solution caused that catechol was additionally formed during phenol decomposition under UV irradiation with and without photocatalyst. The ring byproducts of phenol decomposition formed on Fe–C–TiO_2 with H_2O_2 have been completely decomposed after 3 h of UV irradiation but were still remained after 5 h of UV irradiation on TiO_2 with H_2O_2 and in case of H_2O_2 used without any photocatalyst [21].

From the FTIR studies it was proved that hydroquinone was more likely adsorbed on Fe–C–TiO_2 than on TiO_2 and could play a key role in the process of phenol decomposition, some hydroquinones formed in phenol decomposition could reduce iron and accelerate in this way the rate of phenol decomposition by the formation of a ternary HQ–Fe–H_2O_2 complex [23].

OH$^\bullet$ radicals formation on the photocatalyst surface has been measured in order to check the occurring photo-Fenton reaction and to estimate the role of OH$^\bullet$ radicals in the photooxidation of phenol. In Fig. 4 OH$^\bullet$ radicals formation on the photocatalyst surface is presented under UV and UV with addition of H_2O_2. The commercial TiO_2 photocatalyst showed much higher OH$^\bullet$ radicals formation than Fe–C–TiO_2 under UV irradiation, even higher than amount of OH$^\bullet$ produced by photolysis of H_2O_2. Fe–C–TiO_2 photocatalyst showed almost no OH$^\bullet$ radicals formation without addition of H_2O_2. However when H_2O_2 was added to the solution OH$^\bullet$ radicals reduction on TiO_2 has been observed due to the scavenging effect of OH$^\bullet$ radicals

Table 1
Characteristics of TiO_2 and Fe–C–TiO_2 photocatalysts

Sample code	BET (m^2/g)	Carbon (mass%)	Fe^{2+} (mass%)	Fe^{3+} (mass%)	XRD (phases)
TiO_2	300	–	–	–	Anatase
Fe–C–TiO_2	72	2.4	0.70	0.96	Anatase, $FeTiO_3$
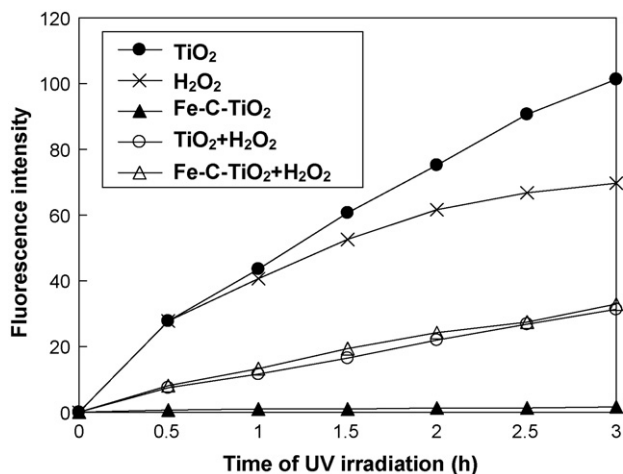
Fig. 4. OH• radicals formation on the surface of TiO_2 and Fe–C–TiO_2 under UV and UV with addition of H_2O_2.

with H_2O_2:

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O \qquad (1)$$
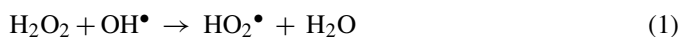
Silmutanously increase of OH• radicals formation on Fe–C–TiO_2 photocatalyst appeared due to the reaction of

iron oxidation:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \qquad (2)$$
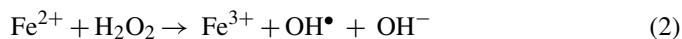
The aim of this work was to find the practical use of the photocatalysts in the water purification, therefore the immobilization of the photocatalyst has been performed.

The photocatalysts after immobilization on the cotton material and placing into the reactor have been rinsed with water in order to remove the excess of the photocatalyst. It was observed that Fe–C–TiO_2 photocatalyst was better fixed to the cotton material than TiO_2, because in case of the latter high excess of the particles have been removed. The immobilized photocatalysts were used for phenol decomposition in a few cycles, with and without addition of H_2O_2. In Fig. 5 the percentage of phenol decomposition with time of UV irradiation is shown. It can be observed the comparable amount of phenol decomposition with cycling on both, TiO_2 and Fe–C–TiO_2, around 50–60% of phenol was decomposed after 5 h of UV irradiation. The fast decreasing of phenol concentration at the beginning can be caused by the phenol adsorption on the photocatalyst surface, however the final amount of decomposed phenol after 5 h of UV irradiation is the same in the cycles. On Fe–C–TiO_2, the lag phase in phenol decomposition is observed
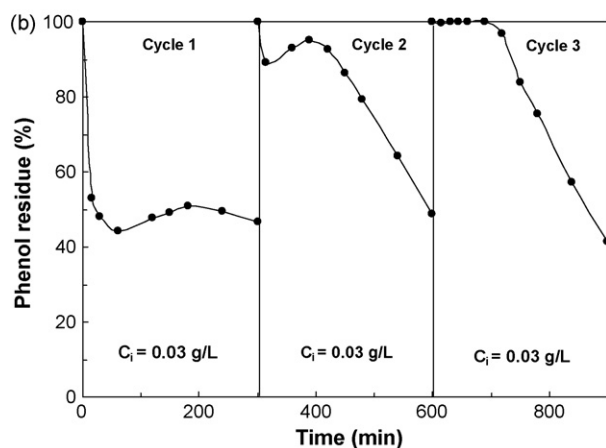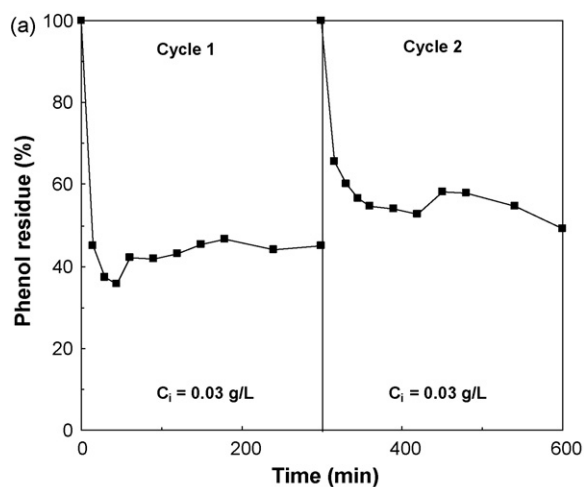

Fig. 5. Cycling decomposition of phenol on (a) TiO_2 and (b) Fe–C–TiO_2 photocatalysts in a flow photocatalytic reactor with time of UV irradiation.
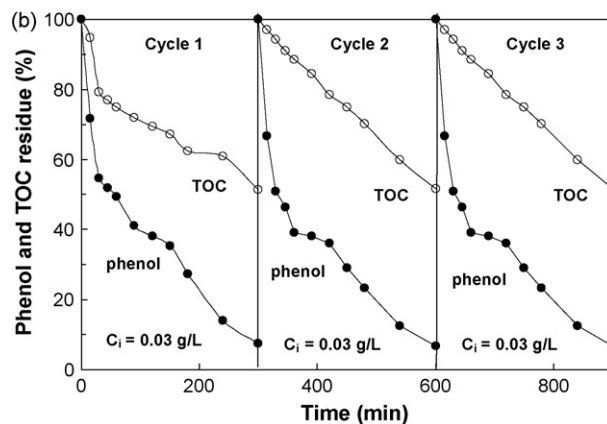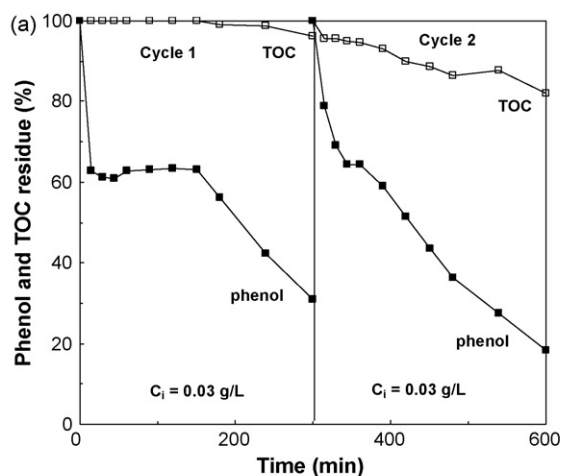

Fig. 6. Cycling decomposition of phenol on (a) TiO_2 and (b) Fe–C–TiO_2 photocatalysts in a flow photocatalytic reactor with time of UV irradiation after addition of H_2O_2.

in the cycles 2 and 3, after that the phenol decomposition is speeded up.

In Fig. 6 phenol decomposition on immobilized photocatalysts is shown with addition of H_2O_2 to the phenol solution. The acceleration of phenol decomposition has been observed, much pronounced on Fe–C–TiO$_2$ photocatalyst, where over 90% of phenol was decomposed after 5 h of UV irradiation with 50% of mineralization degree. By using immobilized TiO$_2$ photocatalyst phenol has been decomposed with 70–80% after 5 h of UV irradiation, however the mineralization degree was rather low, around 20%.

4. Conclusions

Immobilization of photocatalyst on the cotton material and its application in a flow photocatalytic reactor seems to be a good way in the practical use of the photocatalytic process. In the established conditions a stable amount of phenol can be decomposed in the following cycles. The mineralization degree during phenol decomposition can be increased by an addition of H_2O_2 to the reaction mixture.

When process of phenol decomposition was carried out in the beakers with powdered TiO$_2$ photocatalyst, after H_2O_2 addition, the scavenging effect of OH$^\bullet$ radicals has been observed, which caused decreasing a degree of phenol decomposition, however on immobilized TiO$_2$ on the cotton material by means of the Na$_2$SiO$_3$ aqueous solution, addition of H_2O_2 caused increasing the amount of decomposed phenol.

The immobilized Fe–C–TiO$_2$ photocatalyst showed higher photoactivity than TiO$_2$, either with addition of H_2O_2 or not. The cycling decomposition of phenol with using immobilized Fe–C–TiO$_2$ and H_2O_2 showed that amount of decomposed and mineralized phenol was comparable in the cycles. This is a very good example of the application of the heterogeneic-supported photocatalyst for Fenton process.

It is believed that Fe–C–TiO$_2$ photocatalyst can give rise a new kind of heterogenic photocatalyst which can find an application in water purification, giving high degree of mineralization by combination of two processes, photocatalysis and photo-Fenton with H_2O_2 as a Fenton reagent.

References

[1] A. Fujishima, K. Hashimoto, T. Watanabe, TiO$_2$ Photocatalysis Fundaments and Applications, BKC, Inc., May 1999.

[2] E. Piera, M.I. Tejedor, M.E. Zorn, M.A. Anderson, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B: Environ. 47 (2004) 219–256.

[3] I.K. Konstantinou, T.A. Albanis, Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways, Appl. Catal. B: Environ. 42 (2003) 319–335.

[4] T. Sauer, G. Cesconeto Neto, H.J. Jose, R.F.P.M. Moreira, Kinetics of photocatalytic degradation of reactive dyes in a TiO$_2$ slurry reactor, J. Photochem. Photobiol. A: Chem. 149 (2002) 147–154.

[5] J. Arana, O. Gonzalez Diaz, J.M. Dona Rodriguez, J.A. Herrera Melian, C. Garriga i Cabo, J. Perez Pena, M. Carmen Hidalgo, J.A. Navio-Santos, Role of Fe^{3+}/Fe^{2+} as TiO$_2$ dopant ions in photocatalytic degradation of carboxylic acids, J. Mol. Catal. A: Chem. 197 (2003) 157–171.

[6] Z. Guo, R. Ma, G. Li, Degradation of phenol by nanomaterial TiO$_2$ in wastewater, Chem. Eng. J. 119 (2006) 55–59.

[7] J. Wiszniowski, D. Robert, J. Surmacz-Gorska, K. Miksch, S. Malato, J.-V. Weber, Solar photocatalytic degradation of humic acids as a model of organic compounds of landfill leachate in pilot-plant experiments; influence of inorganic salts, Appl. Catal. B: Environ. 53 (2004) 127–137.

[8] P. Calza, V.A. Sakkas, C. Medana, C. Baiocchi, A. Dimou, E. Pelizzetti, T. Albanis, Photocatalytic degradation study of diclofenac over aqueous TiO$_2$ suspensions, Appl. Catal. B: Environ. 67 (2006) 197–205.

[9] D. Dumitriu, A.R. Bally, C. Ballif, P. Hones, P.E. Schmid, R. Sanjines, F. Levy, V.I. Parvulescu, Photocatalytic degradation of phenol by TiO$_2$ thin films prepared by sputtering, Appl. Catal. B: Environ. 25 (2000) 83–92.

[10] T. Yuranova, R. Mosteco, J. Bandara, D. Laub, J. Kiwi, Self-cleaning cotton textiles surfaces modified by photoactive SiO$_2$/TiO$_2$ coating, J. Mol. Catal. A: Chem. 244 (2006) 160–167.

[11] X. Zhang, M. Zhou, L. Lei, TiO$_2$ photocatalyst deposition by MOCVD on activated carbon, Carbon 44 (2006) 325–333.

[12] X.-Y. Chuan, M. Hirano, M. Inagaki, Preparation and photocatalytic performance of anatase mounted-natural porous silica, pumice, by hydrolysis under hydrothermal conditions, Appl. Catal. B: Environ. 51 (2004) 255–260.

[13] B. Sanchez, J.M. Coronado, R. Candal, R. Portela, I. Tejedor, M.A. Anderson, D. Tompkins, T. Lee, Preparation of TiO$_2$ coatings on PET monoliths for the photocatalytic elimination of trichloroethylene in the gas phase, Appl. Catal. B: Environ. 66 (2006) 295–301.

[14] S. Mozia, M. Toyoda, M. Inagaki, B. Tryba, A.W. Morawski, Application of carbon-coated TiO$_2$ for decomposition of methylene blue in a photocatalytic membrane reactor, J. Hazard. Mater. 140 (2007) 369–375.

[15] K. Azrague, P. Aimar, F. Benoit-Marquie, M.T. Maurette, A new combination of a membrane and a photocatalytic reactor for the depollution of turbid water, Appl. Catal. B: Environ. 72 (2007) 197–204.

[16] R. Molinari, L. Palmisano, E. Drioli, M. Schiavello, Studies on various reactor configurations for coupling photocatalysis and membrane processes in water purification, J. Membr. Sci. 206 (2002) 399–415.

[17] J. Grzechulska, A.W. Morawski, Photocatalytic labyrinth flow reactor with immobilized P25 TiO$_2$ bed for removal of phenol from water, Appl. Catal. B: Environ. 46 (2003) 415–419.

[18] M. Janus, M. Inagaki, B. Tryba, M. Toyoda, A.W. Morawski, Carbon-modified TiO$_2$ photocatalyst by ethanol carbonisation, Appl. Catal. B: Environ. 63 (2006) 272–276.

[19] M. Janus, B. Tryba, M. Inagaki, A.W. Morawski, New preparation of carbon–TiO$_2$ photocatalyst by carbonization of *n*-hexane deposited on TiO$_2$, Appl. Catal. B: Environ. 52 (2004) 61–67.

[20] B. Tryba, M. Toyoda, A.W. Morawski, M. Inagaki, Modification of carbon-coated TiO$_2$ by iron to increase adsorptivity and photoactivity for phenol, Chemosphere 60 (2005) 477–484.

[21] B. Tryba, A.W. Morawski, M. Inagaki, M. Toyoda, The kinetics of phenol decomposition under UV irradiation with and without H_2O_2 on TiO$_2$, Fe–TiO$_2$ and Fe–C–TiO$_2$ photocatalysts, Appl. Catal. B: Environ. 63 (2006) 215–221.

[22] B. Tryba, A.W. Morawski, M. Inagaki, M. Toyoda, Effect of the carbon coating in Fe–C–TiO$_2$ photocatalyst on phenol decomposition under UV irradiation via photo-Fenton process, Chemosphere 64 (2006) 1225–1232.

[23] B. Tryba, M. Inagaki, M. Toyoda, A.W. Morawski, FTIR studies of the surface of TiO$_2$, Fe–TiO$_2$ and Fe–C–TiO$_2$ photocatalysts in phenol oxidation via photo-Fenton process, J. Adv. Oxid. Technol. 10 (2007) 25–30.