Application of novel copolymer-TiO$_2$ membranes for some textile dyes adsorptive removal from aqueous solution and photocatalytic decolorization

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Abstract

Novel low density polyethylene-grafted-poly(4-vinylpyridine-*co*-acrylamide) (LDPE-g-P(4-VP/AAm)) films were prepared by means of γ-radiation-induced graft copolymerization as support for photocatalytic application. Nanometer-sized TiO$_2$ particles were immobilized to the grafted LDPE via dip coating technique. The efficiency of immobilized photocatalyst is tested on two target pollutants (textile azo dyes: Remazol red RB-133 (RR RB 133) and reactive blue 2 (RB2)). The efficient photocatalytic ability as reflected in determined photobleaching rate of both dyes was observed and is comparable to that for the non-supported TiO$_2$ used in a typical slurry photoreactor. The LDPE-g-(4-VP/AAm) copolymers supported TiO$_2$ photocatalyst has the practical advantages of easy separation and removal from the polluted environment. It could be a viable technique for the safe disposal of textile wastewater into the water streams.
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1. Introduction

Reactive dyes have been a great concern for protecting the water ecosystem because many azo dyes and their breakdown products have been found toxic to aquatic life [1–6], mutagenic/carcinogenic [7] and gentoxic [8]. Recent studies indicate that approximately 12% of synthetic dyes are lost during manufacturing and processing operations and that 20% of the resultant color enter the environment through effluents from industrial wastewater treatment plants [9]. Color in dye house effluents has often been associated with the application of dyestuffs, during which up to 50% of the dyes may be lost to the effluent, which poses a major problem for the industry as well as a threat to the environment [10–14]. Decolorization of dye effluents has therefore acquired increasing attention during the last two decades. Several studies have been carried out for biological, physical and chemical treatment of dye containing effluents [15–17]. The acti-vated sludge, coagulation and flocculation processes and their combination are widely used in textile wastewater treatment. However, aerobic biological treatment is not sufficient to break down azo double bonds of reactive dyes which cause the color problem in the effluent, while coagulation process is only able to absorb them up to some extent but the sludge produced from both processes becomes more difficult to be disposed [18].

Recent studies indicate that photocatalytic oxidation is a promising technology for the disinfection and detoxification of water and wastewater. When catalytic semiconductor powders, such as the titanium dioxide (TiO$_2$), are suspended in water and irradiated with near UV ($\lambda < 385$ nm), hydroxyl radicals (OH$^\bullet$) and other oxidative species like H$_2$O$_2$ and superoxide radicals (O$_2{}^\bullet$) are generated. The type of TiO$_2$ used plays an important role during the photocatalytic abatement of organic pollutants [19,20]. The use of TiO$_2$ in suspension is efficient due to the large surface area of catalyst available for the reaction. Nevertheless, the catalyst must be removed following the treatment. Post-treatment removal requires a solid liquid separation stage, which adds to the overall capital and running costs of the plant. Alternatively, the catalyst can be immobilized onto a suitable

Formula I
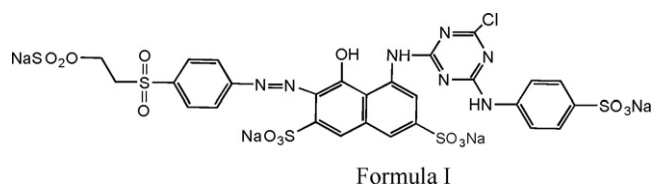
Scheme 1. Remazol red RB-133.

solid support which would eliminate the need of post-treatment removal, but which would also create a decrease in the surface area available for photocatalytic reaction [21]. Reactive polymeric substrate is one of the most appropriate candidates as a support for the immobilization of inorganic or biocatalyst, e.g. photocatalyst, enzymes, etc. The radiation-induced grafting method can be used to modify the chemical and physical properties of the polymeric materials because it imparts desirable properties such as blood compatibility, ion exchange [22,23], dye ability, immobilization of bioactive materials and protein filtration [24].

In the present study, we have tested the photoactivities of easily removable TiO_2 photocatalyst supported over LDPE-g-(4-VP/AAm) copolymers of several composites, in the decontamination of RR RB 133 and RB 2 textile azo dyes.

2. Experimental

2.1. Reagents and materials

2.1.1. Remazol Red RB 133

The commercially available water-soluble reactive dye Remazol Red RB-133 (RR RB-133, of Scheme 1) is obtained from DyStar and used as received without further purification.

#### 2.1.2. Reactive blue 2 or Procion blue HB (RB 2)

Reactive blue 2 or Procion blue HB (RB 2) textile dye of formula in Scheme 2, M. wt = 840.12 g/mol was obtained from Aldrich (Commercial grade) was used as received.

2.1.3. TiO₂ nanoparticles (colloidal solution) were prepared and characterized by XRD as follows [25a,b]

A 25 ml aliquot of titanium isopropoxide (97%, Aldrich) is added drop wise at room temperature, to 125 ml of a 0.1 M nitric acid solution under vigorous stirring. A white precipitate is formed instantaneously. Immediately after the hydrolysis, the slurry is heated to 80 °C and stirred vigorously for 8 h in order to

Formula II
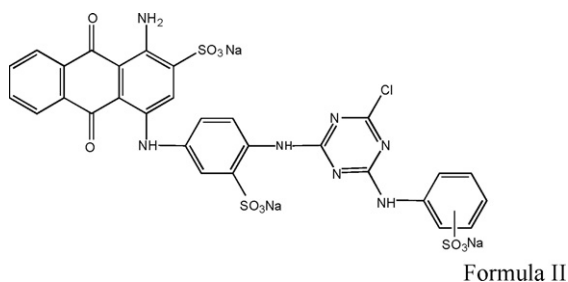
Scheme 2. Procion blue HB.

Formula III
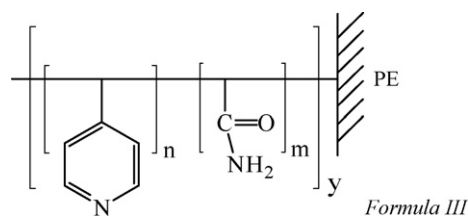
Scheme 3. Low density polyethylene-grafted-(4-vinyl pyridine/acrylamide), where *n* is the number of 4-vinyl pyridine units and m is the number of acrylamide units.

achieve the peptization (i.e., destruction of the agglomerates and redispersion into primary particles). XRD is reported elsewhere [25b].

2.2. Instrumentations

Photostability test experiments are carried out in a batch-type photocatalytic reactor identical to that described in ref. [26]. Transparent thin films of the dyes adsorbed on the supported TiO_2 on the copolymer membranes were exposed to light irradiation at different time intervals. Irradiations are carried out using Xenon arc lamp (PTI-LPS-220 Photon Technology International) adjusted at 70 W. The radiation from this lamp was filtered through a water circulation to reduced incident warming by infrared radiation. The intensity of Xenon lamb is measured using international light research radiometer model IL1700. The intensity of the UV-radiation from this lamp was calibrated at the range (200–400 nm) using the appropriate solar-blind vacuum photodiodes head and the intensity is 170 mW m^{-2}. The pH of the solution is adjusted using a dilute perchloric acid. Complete upload of 100 ml acidic dyes aqueous solution over the surface of TiO_2 immobilized copolymers occurs in about 60–90 min with continuous stirring. Then the concentration of uploaded dyes is determined before irradiation process.

A Unicam UV–vis, double-beam, spectrophotometer from Helios Company has been used.

2.3. Experimental methods

2.3.1. Preparation of reactive polymeric support

LDPE-g-(4-VP/AAm) copolymers (Scheme 3) are obtained by radiation-induced graft copolymerization of 4-VP and AAm binary comonomer mixtures of different molar ratios onto LDPE using ^{60}Co gamma rays at a dose rate 10.28 kGy/h. All samples are washed in excess water to remove the unreacted components and then dried. Sample thickness is 0.02 mm. Table 1 shows

Table 1
The composition and degree of grafting for the studied copolymers

Sample no.	Comonomer composition (mol.%)	Average degree of grafting (wt%)
1	4-VP = 100 AAm = 0	71 ± 1
2	4-VP = 80 AAm = 20	74 ± 1
3	4-VP = 60 AAm = 40	80 ± 2
4	4-VP = 40 AAm = 60	85 ± 1
5	4-VP = 20 AAm = 80	70 ± 5

the studied membranes and the corresponding composition and degree of grafting.

2.3.2. TiO₂ immobilization on LDPE-g-(4-VP/AAm) copolymer

The samples are prepared by the well-established method of dip-coating [27]. The LDPE-g-(4-VP/AAm) copolymer supports are immersed in 50 ml of 0.372 M acidic solution of colloidal TiO_2 for a week with shaking. The polymer samples were removed from solution and then air-dried.

2.3.3. Chemical analysis of titanium dioxide

Following the literature method [28], a sample of 33 cm² of the supported photocatalyst is treated with 17 ml mixture of concentrated H_2SO_4 acid and $(NH_4)_2SO_4$, (H_2SO_4: $(NH_4)_2SO_4 = 129:30$ by weight) and boiled for 15 min. The titanium dioxide dissolved down and several drops of hydrogen peroxide are added to the resulting supernatant to develop color and the solution's absorbance at 410 nm is recorded. The dependence of the absorbance on the concentration of titanium is linear. By establishing a calibration curve for TiO_2, the concentration of TiO_2 uptake could be determined. In this work, TiO_2 content is reported in mg/cm² polymer.

3. Results and discussion

The graft copolymerization of 4VP/AAm binary comonomer system onto LDPE films carried out by direct irradiation of LDPE films immersed in diluted comonomer solution. Radiation-initiated graft copolymerization involves two simultaneous processes in which active sites formed on or near the surface of an existing polymer substrate by irradiation followed by the polymerization of the monomers on these sites. Factors affecting the grafting were optimized. It was found that the equiweight methanol/water co-solvent was the best among other solvents. On the other hand, it was also found that 20 mol.% is the optimal comonomer concentration and 20 kGy is an adequate irradiation dose to obtain appropriate grafted films with good physical properties. The grafting process confirmed using FT-IR to observe the appearance of new peaks characteris-
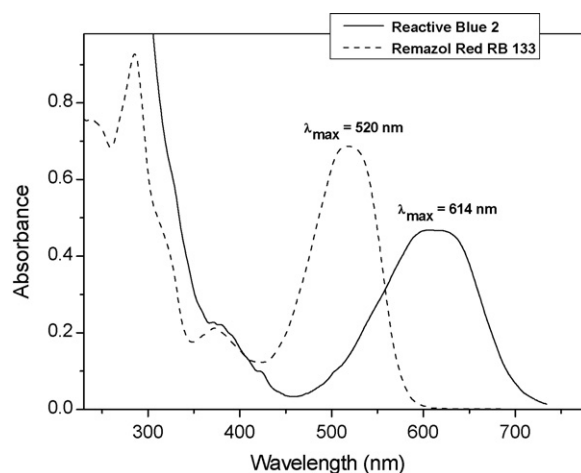

Fig. 1. The electronic absorption spectra of the reactive dye, RR RB;133 3×10^{-5} M and RB; 25×10^{-5} M, in aqueous solution.

Table 2
The amount of supported TiO_2 per 1 cm² of (LDPE-g-(4-VP/AAm) copolymers of different compositions

Membrane no.	Amount of TiO_2 (mg) uptake per cm²
1	0.0085
2	0.012
3	0.0077
4	0.0136
5	0.0712

tic for the amide group and pyridine ring introduced to the LDPE.

The absorption spectra of aqueous solutions of RR RB 133 and RB 2 at 26 °C are shown in (Fig. 1). For more than 1 h of continuous UV irradiation, we have not observed light-induced changes of the absorbance of the aqueous solution of RR RB 133 and RB 2 of pHs equal 5.8 and 5.5, respectively. Both dyes are found to be photostable.

The determined amount of TiO_2 uptake depends on the degree of grafting and copolymer composition (Table 2). Immersion of the of LDPE-g-(4-VP/AAm) copolymer membranes (of different composites and of ≈16 cm² surface area) in 100 ml of
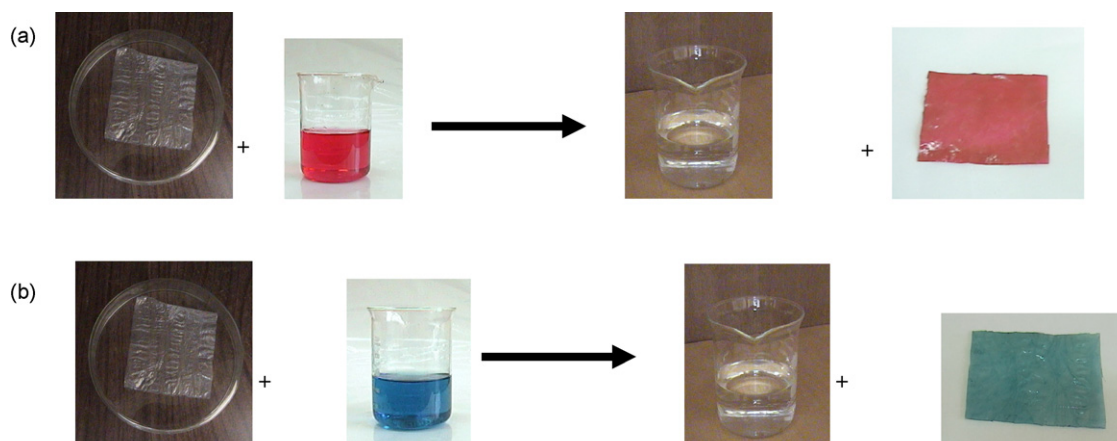

Fig. 2. Images show the complete uptake of RR RB 133 solution (a) and RB 2 solution (b) on TiO_2 immobilized LDPE-g-(4-VP/AAm) copolymer membrane.
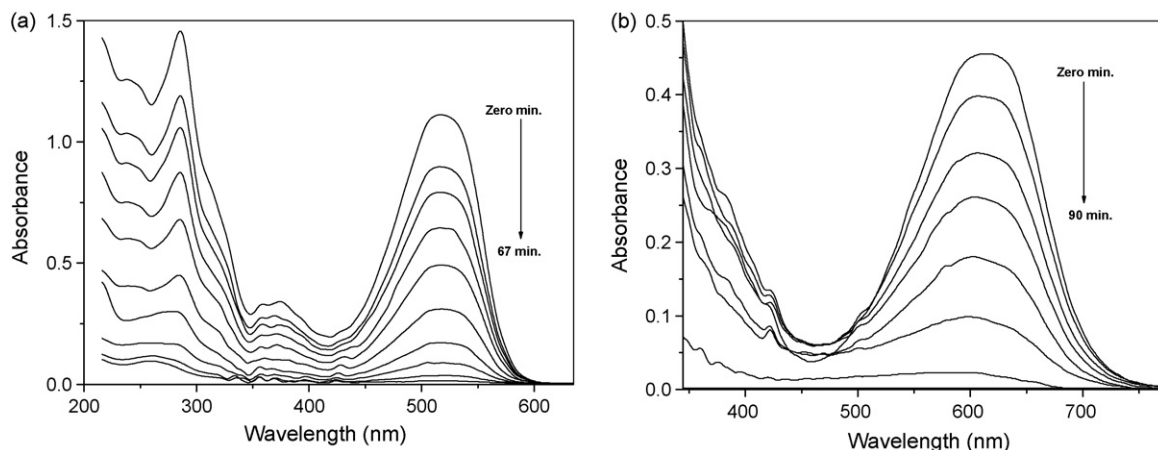
Fig. 3. Variation in absorption spectrum of (a) 5×10^{-5} M aqueous RR RB 133 at pH 5.9 and (b) 5×10^{-5} M aqueous RB 2 at pH 5.5 on TiO$_2$ immobilized LDPE-g-(4-VP/AAm) copolymer sample 4. (Dye volume = 100 ml).

5×10^{-5} M RR RB 133 or RB 2 at pH < 11.5 resulted in complete adsorption of RR RB 133 and RB 2 dyes over the different composites of LDPE-g-(4-VP/AAm) copolymers (Fig. 2). This could be monitored by measuring the absorption spectrum of both dyes at different times of copolymer immersion where a complete adsorption of RR RB 133 and RB2 over the copolymer films occurs after 67 and 90 min, respectively, see (Fig. 3). Moreover, it is of interest to mention that, the TiO$_2$ supported LDPE-g-(4-VP/AAm) copolymer membranes show ability to adsorb excessive concentrations of the dyes compared to the corresponding pure copolymers, see (Fig. 3). Furthermore, at pH > 11.5 the possibility of complete uptake of dye solution on LDPE-g-(4-VP/AAm) copolymer membranes decreases as the [OH$^-$] increases leading to a competitive uptake of OH$^-$ with the dye molecules. The surfaces of both TiO$_2$ and copolymers becomes negatively charged and repelling the negatively charged dye molecules [29]. The variation of adsorption percentage of RR RB 133 and RB 2 on TiO$_2$ supported copolymer membrane in the dark as a function of time is evaluated, see Fig. 4.

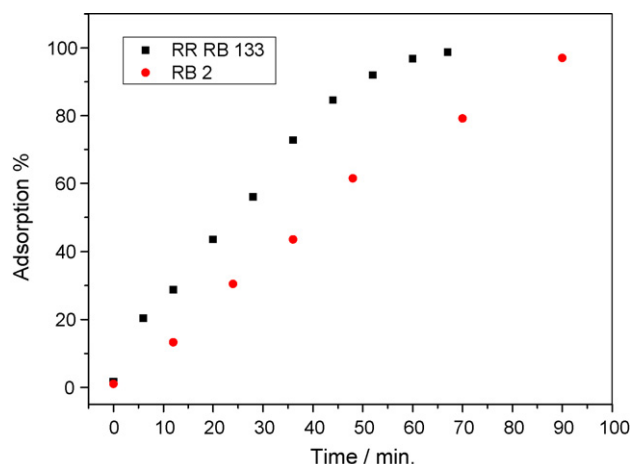The photocatalytic activity of TiO$_2$ immobilized on the different composites of the studied copolymers has been tested by following up the decolorization rate of thin transparent copolymer films of 5×10^{-4} M of impregnated RR RB 133 and RB 2. The degradation reactions follow a first order kinetics; see Fig. 5 as an example.
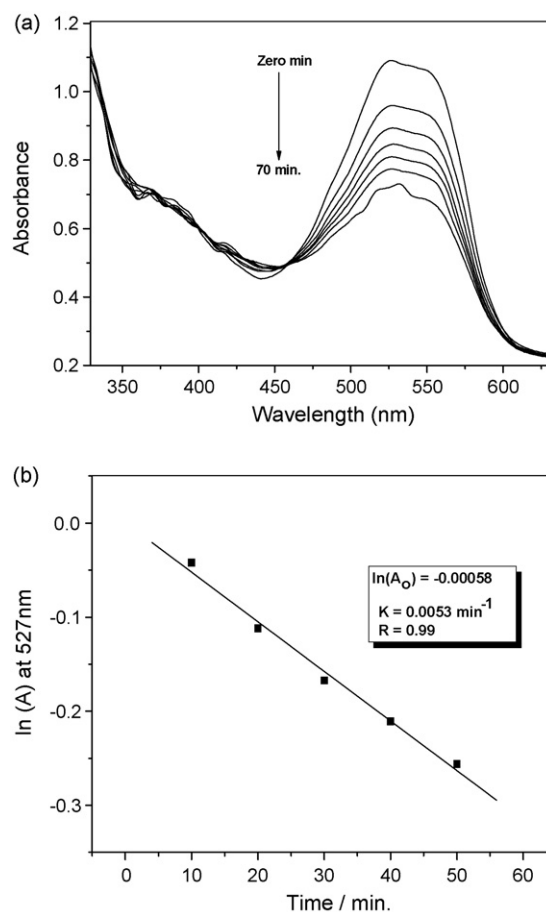

Fig. 5. (a) Irradiation-induced changes of the absorption spectrum of uploaded RR RB 133 in presence of TiO$_2$ immobilized on (LDPE-g-(4-VP/AAm) copolymer membrane (1). (b) Photodegradation [ln(A)–time] rate kinetics of RR RB-133 using TiO$_2$ supported on (LDPE-g-(4-VP/AAm) copolymer membrane (1).

Fig. 4. Variation of adsorption percentage of RR RB 133 and RB 2 on copolymer membrane as a function of time.
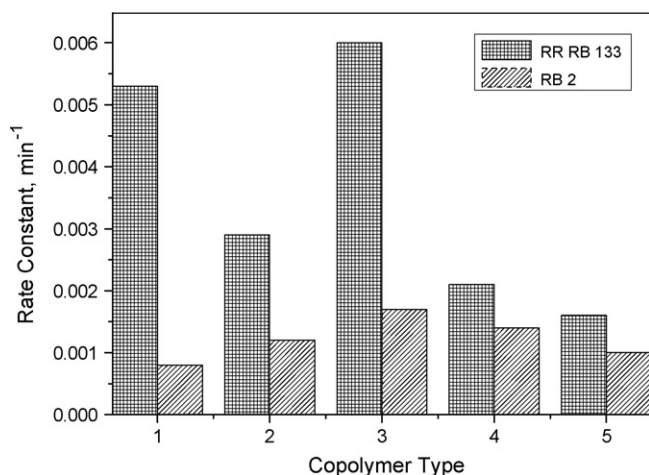
Fig. 6. A comparison illustrates the effect of different compositions of TiO$_2$ supported copolymers (see Table 2) on the rate constants of the photobleaching reactions of impregnated RR RB 133 and RB 2.

The results compared in Fig. 6 show that:

- The photobleaching rate of impregnated RR RB 133 is markedly higher than the corresponding RB 2. This could be explained on the basis of adsorption competition of both RR RB 133 and RB 2 towards TiO$_2$ and/or copolymer sites and obviously on the nature of the two molecules.
- The rate of the color bleaching using copolymer 3 (of least TiO$_2$ content) is noticeably higher than the other types. This phenomenon is closely correlated to the electronic and textural copolymer properties and also may be due to the aggregation of TiO$_2$ particles at high concentrations, causing a decrease in the number of surface active sites [30]. Several authors related this phenomenon to the light scattering and consequent reduction in light penetration through the copolymer films [31–34]. This opens up the possibility of modifying the surface state of titanium dioxide to improve its electronic properties.
- The efficient photocatalytic ability as reflected in the determined photobleaching rate of both dyes is comparable to that for the PVP/AAc hydrogel supported TiO$_2$ catalysts used in a typical slurry photoreactor [35]. However, the practical advantages of direct and ease of removal of the pollutant dyes from the environment by adsorption on the catalyst, makes it a viable technique for the safe disposal of textile wastewater into the water streams.

4. Conclusions

It was found that RR RB 133 and RB 2 have a high degree of photostability and direct photolysis in either aqueous or non-aqueous phases (without TiO$_2$) has not been found effective in their degradation. Upon irradiation of transparent solid thin film samples of RR RB 133 and RB 2 impregnated on the surface of TiO$_2$ supported LDPE-g-(4-VP/AAm) copolymer of different composites, a photo-assisted degradation reaction occurs. The photobleaching reactions obey first order kinetics and the photobleaching rate of impregnated RR RB 133 is markedly higher

than the corresponding RB 2. This could be explained based on adsorption competition of both RR RB 133 and RB 2 towards TiO$_2$ and/or copolymer sites. TiO$_2$ content of the polymer films plays a crucial role in its activity.

References

[1] K.T. Chung, S.E.J. Stevens, C.E. Cerniglia, The reduction of azo dyes by the intestinal microflora, Crit. Rev. Microbiol. 18 (1992) 175–197.
[2] C. Wang, A. Yediler, D. Lienert, Z. Wang, A. Kettmp, Toxicity evaluation of reactive dyestuffs, auxiliaries and selected effluents in textile finishing industry to luminescent bacteria Vibrio fischeri, Chemosphere 46 (2002) 339–344.
[3] C. Wang, A. Yediler, D. Lienert, Z. Wang, A. Kettrup, Ozonation of an azo dye C.I. Remazol Black 5 and toxicological assessment of its oxidation products, Chemosphere 52 (2003) 1225–1232.
[4] Q. Tezcanli-Guyer, N.H. Ince, Degradation and toxicity reduction of textile dyestuff by ultrasound, Ulwas. Sonochem. 10 (2003) 235–240.
[5] F. Zhang, A. Yediler, X. Liang, A. Ketlrup, Effects of dye additives on the ozonation process and oxidation by-products: a comparative study using hydrolyzed C.I. Reactive Red 120, Effects of dye additives on the ozonation process and oxidation by-products: a comparative study using hydrolyzed C.I. Reactive Red 120, Dyes Pigments 60 (2004) 1–7.
[6] S. Meriq, D. Kaptan, T. Olmez, Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process, Chemosphere 54 (2004) 435–441.
[7] K.T. Chung, S.E.J. Stevens, Degradation of azo dyes by environmental microorganisms and helmints, Environ. Toxicol. Chem. 12 (1993) 2121–2132.
[8] A. Gottlieb, C. Shaw, A. Smith, A. Wheatley, S. Forsythe, The toxicity of textile reactive azo dyes after hydrolysis and decolourisation, J. Biotechnol. 101 (2003) 49–56.
[9] A. Reife, H.S. Freemann, Environmental Chemistry of Dyes and Pigments, John Wiley and Sons Inc., Canada, 1996.
[10] H. Zollinger, in: H.F. Eblel, C.D. Brenzinger (Eds.), Colour Chemistry, 1st ed., VCH, New York, 1987, Chapter 16.
[11] C.E. Searle, Chemical carcinogenesis, ACS Monograph, American Chemical Society, Washington, DC, 1976.
[12] M. Qamar, M. Saquib, M. Muneer, Semiconductor-mediated photocatalytic degradation of an azo dye, chrysoidine Y in aqueous suspensions, Desalination 171 (2004) 185–193.
[13] M. Boeninger, Carcinogenicity and metabolism of azo dyes, especially those derived from benzidine. DHHS (NIOSH), Publication No. 80–119, 1980.
[14] J.J. Roxon, A.J. Ryan, S.E. Wright, Reduction of water-soluble azo dyes by intestinal bacteria, Food Cosmet. Toxicol. 5 (1967) 367.
[15] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresource Technol. 77 (2001) 247–255.
[16] S. Ledakowicz, M. Solecka, R. Zylla, Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation processes, J. Biotechnol. 89 (2001) 175–184.
[17] D. Georgiou, P. Melidis, A. Aivasidis, K. Gimouhopoulos, Degradation of azo-reactive dyes by ultraviolet radiation in the presence of hydrogen peroxide, Dyes Pigments 52 (2002) 69-.
[18] R. Ganesh, G.D. Boardman, D. Michelsen, Fate of azo dyes in sludges, Water Res. 28 (1994) 1367–1376.
[19] A. Mills, S. Le Hunte, An overview of semiconductor photocatalysis, J. Photochem. Photobiol. A 108 (1997) 1–35.
[20] D. Blake, P. Maness, Z. Huang, E. Wolfrum, J. Huang, Application of the photocatalytic chemistry of titanium dioxide to disinfection and the killing of cancer cells, Sep. Purif. Methods 28 (1999) 1–50.
[21] D. Robert, A. Piscopo, O. Heintz, J.V. Weber, Photocatalytic detoxification with TiO$_2$ supported on glass-fibre by using artificial and natural light, Catal. Today 54 (1999) 291–296.
[22] H.A. Abd El-Rehim, E.A. Hegazy, A. El-Hag Ali, Selective removal of some heavy metal ions from aqueous solution using treated polyethylene-

g-styrene/maleic anhydride membranes, React. Funct. Polym. 34 (2000) 105–116.

[23] Zhen-Mei Liu, Zhi-Kang Xu, Jian-Qin Wang, Jian Wu b, Jun-Jie Fu, Surface modification of polypropylene microfiltration membranes by graft polymerization of *N*-vinyl-2-pyrolidone, J. Eur. Polym. 40 (2004) 2077–2087.

[24] A. Nabe, E. Staude, G. Belfort, Surface modification of polysulfone ultrafiltration membranes and fouling by BSA solutions, J. Membr. Sci. 133 (1997) 57.

[25] (a) N. Papageorgiou, C. Barbé, M. Grätzel, Morphology and adsorbate dependence of ionic transport in dye sensitized mesoporous TiO_2 films, J. Phys. Chem. B 102 (1998) 4156–4164;
(b) M. Saif, M.S.A. Abdel-Mottaleb, Titanium dioxide nanomaterial doped with trivalent lanthanide ions of Tb, Eu and Sm: preparation, characterization and potential applications, Inorg. Chim. Acta 360 (2007) 2863–2874.

[26] A.A. Essawy, M.S.A. Abdel-Mottaleb, Photosensitized degradation of dinitrosalicylic acid by uranyl ions, Intern. J. Photoenergy 5 (2003) 219.

[27] J.M. Herrmann, H. Tahiri, C. Guillard, P. Pichat, Photocatalytic degradation of aqueous hydroxy-butandioic acid (malic acid) in contact with powdered and supported titania in water, Catal. Today 54 (1999) 131–141.

[28] C. Hu, Y. Wang, H. Tang, Preparation and characterization of surface bond-conjugated TiO_2/SiO_2 and photocatalysis for azo dyes, Appl. Catal. B: Environ. 30 (2001) 277–285.

[29] C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaloui, J.M. Herrmann, Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO_2. Comparison of the efficiencies of powder and supported, J. Photo. Photobiol. A: Chem. 158 (2003) 27–36.

[30] S. Parra, J. Olivero, C. Pulgarin, Relationships between physicochemical properties and photoreactivity of four biorecalcitrant phenylurea herbicides in aqueous TiO_2 suspension relationships between physicochemical properties and photoreactivity of four biorecalcitrant phenylurea herbicides in aqueous TiO_2 suspension, Relationships between physicochemical properties and photoreactivity of four biorecalcitrant phenylurea herbicides in aqueous TiO_2 suspension, Appl. Catal. B: Environ. 36 (2002) 75–85.

[31] J. Bandara, J. Kiwi, R. Humphry-Baker, C. Pulgarin, Oxidative degradation and fluorescence of a non-niodegradble brightener via titania suspensions: implications for the natural cycle, J. Adv. Oxid. Technol. 1 (1996) 126.

[32] L. Le Campion, C. Giannotti, J. Ouazzani, Photocatalytic degradation of 5-nitro-1,2,4-triazol-3-one NTO in aqueous suspention of TiO_2: Comparison with fenton oxidation, Chemosphere 38 (1999) 1561.

[33] Y. Inel, A.N. Okte, Photocatalytic degradation of malonic acid in aqueous suspensions of titanium dioxide: an initial kinetic investigation of CO_2 photogeneration, J. Photochem. Photobiol. A: Chem. 96 (1996) 175.

[34] K.E. Karakitsou, X.E. Verykios, Effects of altervalent cation doping of titania on its performance as a photocatalyst for water cleavage, J. Phys. Chem. 97 (1993) 1184–1189.

[35] H.S. Hafez, A. El-Hag Ali, M.S.A. Abdel-Mottaleb, Photocatalytic efficiency of titanium dioxide immobilized on PVP/AAc hydrogel membranes: a comparative study for safe disposal of wastewater of Remazol Red RB-133 textile dye, Intern. J. Photoenergy 4 (2005) 181.