



## Photocatalytic decolorization of methylene blue in the presence of TiO<sub>2</sub>/ZnS nanocomposites

A. Franco<sup>a</sup>, M.C. Neves<sup>b</sup>, M.M.L. Ribeiro Carrott<sup>c</sup>,  
M.H. Mendonça<sup>a</sup>, M.I. Pereira<sup>a</sup>, O.C. Monteiro<sup>a,\*</sup>

<sup>a</sup> CCMM and Department of Chemistry and Biochemistry, University of Lisbon, Campo Grande, Ed. C8, 1749-016 Lisboa, Portugal

<sup>b</sup> CICECO, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>c</sup> CQE, Department of Chemistry, University of Évora, Colégio L.A. Verney, 7000-671 Évora, Portugal

### ARTICLE INFO

#### Article history:

Received 13 December 2007

Received in revised form 28 March 2008

Accepted 30 March 2008

Available online 6 April 2008

#### Keywords:

TiO<sub>2</sub>

Methylene blue

Decolorization

Photocatalysis

TiO<sub>2</sub>/ZnS nanocomposites

### ABSTRACT

The synthesis of distinct nanocrystalline TiO<sub>2</sub> capped ZnS samples was carried out using a chemical deposition method. The materials characterization showed that the presence of ZnS onto TiO<sub>2</sub> surface results in a red shift of the material band edge when compared with the initial semiconductor. The photocatalytic activity of the prepared nanocomposites was tested on the decolorization of methylene blue (MB) aqueous solutions. The dye photodecolorization process was studied considering the influence of experimental parameters such as catalyst concentration, TiO<sub>2</sub>/ZnS ratio, pH and methylene blue adsorption rate. The material with the best catalytic activity towards the methylene blue photodecolorization was the TiO<sub>2</sub> doped with 0.2% of ZnS. The complete photodecolorization of a 20 ppm methylene blue solution, at natural pH was achieved in less than 20 min, nearly 70 min faster than the TiO<sub>2</sub> photoassisted process.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Nowadays, heterogeneous photocatalysis processes are one of the most efficient methods for destroying organic pollutants in aqueous media [1–3]. Over the past decades, many studies have revealed that nanosized TiO<sub>2</sub> particles can photocatalytically oxidize many organic wastes into inorganic substances [1,4,5]. However the TiO<sub>2</sub> photoefficiency, activity and photo response makes it unsuitable for direct application in environmental processes due to the band gap energy of about 3.2 eV (the light absorption of TiO<sub>2</sub>, takes place in only approximately 3% of the visible spectrum), and the high recombination rate of the photo-generated electron/hole pairs.

An important advance in this field is the development of visible light responsive TiO<sub>2</sub> photocatalyst by doping it with metals [6,7], or non-metallic elements like C, N, S, F and B [1,8,9]. Unfortunately, those metal/non-metal-doped TiO<sub>2</sub> materials are generally difficult to prepare with needs of lattice exchange at high temperature and multi-step experimental process.

It is also expected that the photocatalytic activity of the solitary TiO<sub>2</sub> will be greatly improved, by the enhancement of charge

separation and minimization or inhibition of charge-carrier recombination, via preparation of nanoscale coupled semiconductors: when both semiconductors are illuminated, electrons accumulate at the low-lying conduction band of one semiconductor while holes accumulate at the valence band of the other compound. These processes of charge separation are very fast and the efficiency of reduction or oxidation of the adsorbed organics remarkably increases.

Several methods have been published concerning the photosensitization of TiO<sub>2</sub> by M<sub>x</sub>S<sub>y</sub> nanoparticles for heterogeneous photocatalysis applications [10]. Photocatalytic active TiO<sub>2</sub>/ZnS composites were prepared by homogeneous hydrolysis of a mixture of titanium oxo-sulphate and zinc sulphate in aqueous solutions with thioacetamide. These composites exhibit better UV characteristic compared with the bulk TiO<sub>2</sub> and ZnS [11]. Homogeneous ZnS-coating onto TiO<sub>2</sub> nanoparticles can also be prepared by a simple one pot sonochemical method [12]. Photoactive ZnS/TiO<sub>2</sub> nanocomposites can be prepared via a microemulsion-mediated solvothermal method. In this case factors including the interactions between the ZnS and TiO<sub>2</sub> phases and a strong adsorption of the substrate at the ZnS/TiO<sub>2</sub> nanocomposites surface are responsible for this enhanced photocatalytic activity [13].

On the basis of these considerations, in this work we report a study concerning the effect of the ZnS doping level on the catalytic properties of TiO<sub>2</sub> for the methylene blue (MB) photodecoloriza-

\* Corresponding author. Tel.: +351 217500000; fax: +351 217500088.  
E-mail address: [ocmonteiro@fc.ul.pt](mailto:ocmonteiro@fc.ul.pt) (O.C. Monteiro).

tion process, under UV–vis radiation. In order to deconvolute the catalytic activity of the ZnS from TiO<sub>2</sub>, and considering that SiO<sub>2</sub> is a photo-inert material, the preparation of SiO<sub>2</sub>/ZnS nanocomposites was also performed. The synthesis of the nanocomposites was achieved by a single-source deposition method [14]. This method makes use of zinc dithiocarbamate, which acts as single-source, for the ZnS growth on the TiO<sub>2</sub> and SiO<sub>2</sub> surface. MB was chosen as a pollutant in this study, due to its high importance as dye in textile industries and in a variety of other applications [15]. It can also have various harmful effects on human beings; on inhalation it can give rise to difficult breathing, while injection through mouth produces burning sensation, nausea, vomiting, diarrhoea and gasestrics, painful micturation and methemoglobinemia like syndromes [16].

## 2. Experimental

All reagents were of analytical grade (Aldrich and Fluka) and were used as received. The solutions were prepared with Millipore Milli-Q ultra-pure water. TiO<sub>2</sub> Degussa P-25 (ca. 80% anatase, 20% rutile; BET area ca. 50 m<sup>2</sup> g<sup>-1</sup>) was used for the preparation of the TiO<sub>2</sub> nanocomposite materials.

### 2.1. Materials synthesis

#### 2.1.1. ZnS precursor

The precursor for ZnS, zinc diethyldithiocarbamate, {Zn[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>}, was prepared as previously reported [17]. 20 mmol of the ethylenediamine {C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>} and 13.5 mmol of CS<sub>2</sub> were added to a suspension containing 10 mmol of ZnCl<sub>2</sub> in water (50 mL). The mixture was stirred over 2 h and a white solid was obtained. The zinc complex was identified by using IR spectroscopic technique.

#### 2.1.2. SiO<sub>2</sub> microparticles

The SiO<sub>2</sub> was prepared using the Stöber method reported in the literature [18]: 0.73 g of tetraethoxysilane (TEOS) was added to 5 mL of absolute ethanol containing 0.06 g of distilled water, and the mixture was allowed to stand for 30 min. Subsequently, 2 mL of NH<sub>4</sub>OH solution (25%) was added, and the solution was left to stand for more 30 min. The SiO<sub>2</sub> colloid formed was filtered and washed thoroughly with water and ethanol. The SiO<sub>2</sub> particles were used after a thermal treatment at 700 °C for 4 h. This thermal treatment increased the degree of dehydroxylation of the silica surface.

#### 2.1.3. Nanocomposites

The XO<sub>2</sub>/ZnS (X = Ti, Si) nanocomposite particles have been prepared by adding drop-wise ethylenediamine (2.5 mL) to an acetone solution (47.5 mL) containing the metal dithiocarbamate complex and 0.125 g of TiO<sub>2</sub> or 0.250 g of SiO<sub>2</sub> particles. The suspension formed was then refluxed with stirring. The white solids obtained, after 4 h, were collected by centrifugation, washed with acetone and dried at room temperature in a desiccator over silica gel [17]. TiO<sub>2</sub>/ZnS nanocomposites with different TiO<sub>2</sub>/ZnS ratio were obtained by varying the {C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>};{Zn[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>} proportion. The solids prepared were approximately 10, 0.5 and 0.2% of ZnS on TiO<sub>2</sub>.

### 2.2. Studies in the absence of light

Before the photocatalytic experiments, studies have been carried out, using 25 mL of a 20 ppm MB aqueous solution with 50 mg of the nanocomposite, under stirring for 1 h in dark conditions. The sampling has been performed periodically, and after centrifu-

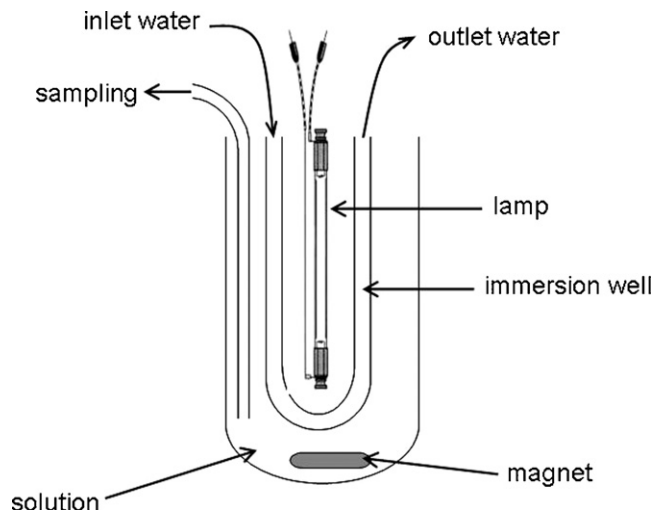


Fig. 1. Photochemical experimental setup.

gation, the MB concentration was estimated by measuring their absorbance at 665 nm.

### 2.3. Photodecolorization experiments

The photodecolorization experiments have been conducted using an Ace Glass photoreactor cooled by water circulation (Fig. 1). The reaction vessel (250 mL) was made of borosilicate glass and suitable to accommodate an immersion well. The quartz immersion well, was a double-walled, with inlet and outlet tubes for cooling. The inlet tube extends down the annular space and ensures the upward flow of coolant from the bottom of the well upward to the outlet. The reactor had one angled joint for the sparger tube, one vertical joint for the condenser and one Ace-Thread side arm for the thermometer. The reactor bottom is flat to allow the use of a magnetic stirrer. The radiation source was a 450-W medium-pressure mercury-vapour lamp (from Hanovia). Of the total radiated energy, approximately 40–48% is in the ultraviolet portion of the spectrum and 40–43% in the visible (see supplementary material for the lamp spectral energy distribution). The radiated watt density was 0.37 W/cm<sup>2</sup>.

Suspensions have been prepared by adding 50 mg of the nanocomposite powder into a 100 mL of 20 ppm MB aqueous solution, at natural pH. Prior to irradiation, the suspensions were stirred in dark conditions for 15 min. During irradiation, the suspensions were sampled at regular intervals and centrifuged. The concentrations of the MB solutions were calculated by measuring their absorbance at the maximum absorption peak of the MB (665 nm).

### 2.4. Characterization

X-ray powder diffraction was performed using a Philips X-ray diffractometer (PW 1730) with automatic data acquisition (APD Philips v3.6B) using Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) and working at 30 kV/40 mA. The diffraction patterns were collected in the range  $2\theta = 20\text{--}60^\circ$  with a  $0.01^\circ$  step size and an acquisition time of 2.5 s/step. The UV–vis spectrophotometer (Jasco V560) was used for monitoring the absorption of the MB solutions and the diffuse-reflectance spectra of the powders, in the range 200–900 nm at a scanning speed of 400 nm/min. The scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) measurements were carried out on a JEOL (JSM-35C) system operating at 15 keV. The specific surface areas were obtained from the analysis of the adsorption isotherms by the Brunauer–Emmett–Teller

(BET) method [19]. The nitrogen adsorption–desorption isotherms at 77 K were determined on a CE Instruments Sorptomatic 1990, after outgassing the samples at 453 K for 8 h. The X-ray photoelectron spectroscopy (XPS) spectra were taken in CAE mode (30 eV), using an Al (non-monochromate) anode. The accelerating voltage was 15 kV. The quantitative XPS analysis was performed using the Avantage software. The chemical oxygen demand (COD) of the samples was determined by commercially available test tubes (Macherey & Nagel, Germany). After digestion at 421 K for 2 h of the tubes containing the sample, sulfuric acid, mercuric sulfate and chromic acid, the COD concentration was obtained by photometric determination, using a MN Nanocolor 500 D photometer.

### 3. Results and discussion

#### 3.1. Material characterization

The  $\text{MO}_2/\text{ZnS}$  ( $M=\text{Ti}, \text{Si}$ ) nanocomposites were prepared by the reaction of the zinc dithiocarbamate complex with ethylenediamine in the presence of  $\text{SiO}_2$  or  $\text{TiO}_2$  particles [17]. The characterization by electronic microscopy did not demonstrate relevant changes of the  $\text{TiO}_2$  morphology after ZnS deposition (Fig. 2a).

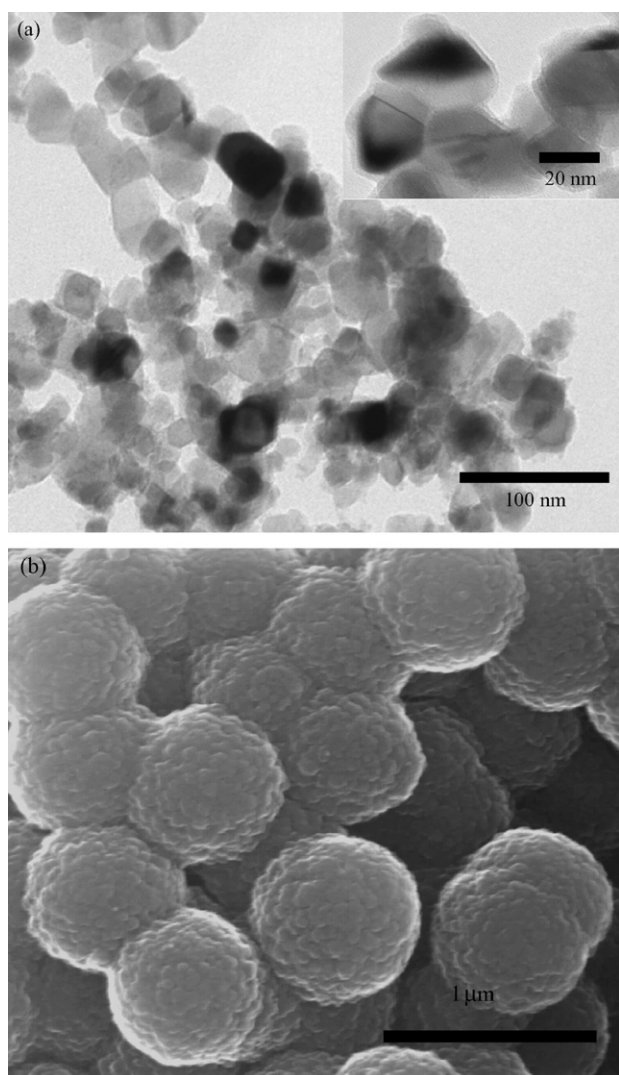


Fig. 2. TEM image for the  $\text{TiO}_2/\text{ZnS}$  (a) and SEM image for the  $\text{SiO}_2/\text{ZnS}$  (b) nanocomposite particles.

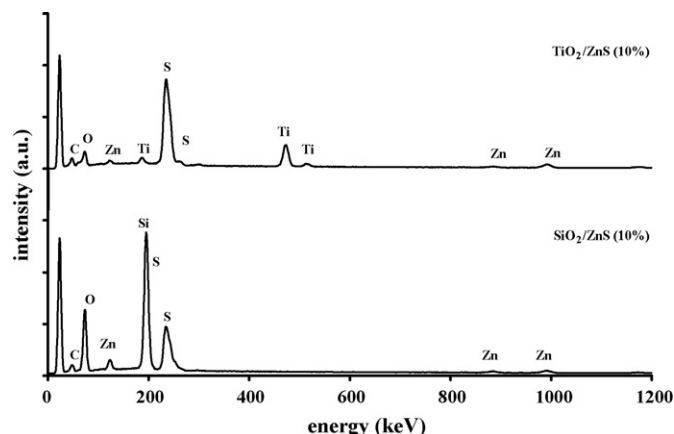


Fig. 3. EDS spectra of  $\text{TiO}_2/\text{ZnS}$  (10%) and  $\text{SiO}_2/\text{ZnS}$  (10%) powder samples. Some peaks identification was removed for convenience.

On the other hand the SEM images of  $\text{SiO}_2/\text{ZnS}$  (10%) particles show the presence of a deposited phase on the  $\text{SiO}_2$  surface (Fig. 2b). This difference is probably due to the more defined morphology and larger size of  $\text{SiO}_2$  comparatively to the  $\text{TiO}_2$  particles. By EDS the existence of Zn and S were detected in both samples (Fig. 3). The poor crystallinity and small amount of the ZnS present, in addition to the high crystallinity and small size of the  $\text{TiO}_2$  or the amorphous nature of the  $\text{SiO}_2$  were factors that contribute to the difficulty of the ZnS identification by XRD. However the presence of ZnS, over the substrates, was recognized by XPS.

The band gap energy of the  $\text{TiO}_2/\text{ZnS}$  (0.2%) sample was calculated from the Kubelka–Munk (KM) spectrum (after conversion of diffuse-reflectance to KM) show in Fig. 4, by plotting the function  $f_{\text{KM}} = (F_{\text{KM}}/h\nu)^2$  versus  $h\nu$  [20]. The estimated  $E_g$  value was 3.21 eV for the  $\text{TiO}_2/\text{ZnS}$  (0.2%) sample. This value is red shifted from the typical  $E_g$  of the  $\text{TiO}_2$  used (3.28 eV). This result suggests the possibility of using this material as photocatalyst on degradation processes with lower energetic requirements than  $\text{TiO}_2$ .

As the surface area is a very important parameter for the efficiency of the photocatalysts, this was also evaluated for  $\text{TiO}_2$  and  $\text{TiO}_2/\text{ZnS}$  (0.2%). The BET specific total surface areas were found to be 47 and 43  $\text{m}^2 \text{g}^{-1}$ , respectively, thereby indicating that some reduction occurred. However, it can be considered that the preparation method for obtaining the composite did not cause important alterations in the specific surface area.

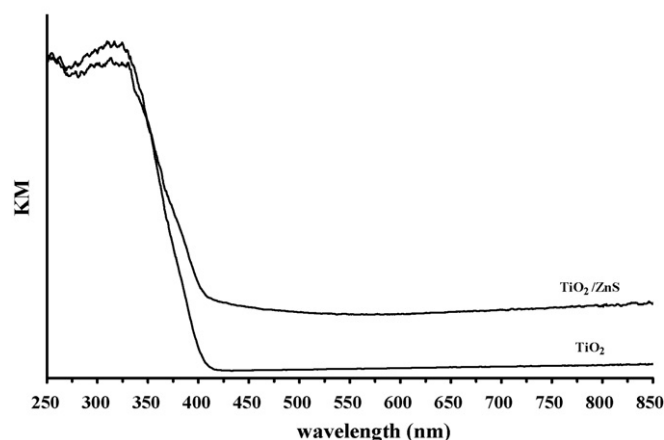


Fig. 4. KM vs. wavelength for the  $\text{TiO}_2$  and  $\text{TiO}_2/\text{ZnS}$  (0.2%) samples.

### 3.2. Adsorption process

Since the photo-oxidation reaction usually takes place at the catalyst surface, the adsorption characteristics of the system are expected to be quite important on the photocatalytic process. The ability of the MB to be adsorbed on the nanocomposite surface was tested using suspensions of MB and  $\text{TiO}_2/\text{ZnS}$  in dark conditions. The dye adsorbs onto the  $\text{TiO}_2/\text{ZnS}$  particles and after the first 15 min a clear decrease on the MB solution concentration can be visualized (Fig. 5 for time zero). After this period the adsorption–desorption equilibrium is achieved and no more decrease on the MB concentration occurs.

The ability of the semiconductor phases ( $\text{TiO}_2$  and ZnS) to adsorb MB was also tested using  $\text{TiO}_2$ ,  $\text{SiO}_2/\text{ZnS}$  (10%) and  $\text{SiO}_2$  particles. The experiments were not conclusive, as the MB adsorption takes place on all the materials. However, the MB adsorbed percentage is higher for the materials containing ZnS. These results are in agreement with other authors, and suggest that the MB photodecomposition may occur with the dye adsorbed onto the catalyst surface [21].

### 3.3. Photodecolorization process

#### 3.3.1. Influence of catalyst composition

The photocatalytic efficiency of 50 mg of  $\text{TiO}_2/\text{ZnS}$  materials on the decolorization of a 20 ppm MB solution was tested during 120 min (Fig. 5). The MB decolorization in the absence of catalyst (photolysis) was also evaluated. After 120 min of photolysis, less than 20% of the MB, in solution, disappeared. On the other hand, in the presence of the  $\text{TiO}_2$ , only 90 min were needed for the complete MB decolorization. A similar result was obtained using  $\text{TiO}_2/\text{ZnS}$  (10%). For  $\text{TiO}_2/\text{ZnS}$  (0.5%) the decolorization time was reduced to 60 min, and the minimum time (20 min) needed to the complete MB decolorization was achieved using the  $\text{TiO}_2/\text{ZnS}$  (0.2%). Analysing these results it is possible to say that using 0.05% (w/v) (50 mg nanocomposite/100 mL 20 ppm MB solution) of this photocatalyst,  $\text{TiO}_2/\text{ZnS}$  (0.2%), corresponding to a 0.04 g dye/g catalyst, the complete photodecolorization occurs in less than 20 min, nearly 70 min faster than the  $\text{TiO}_2$  photoassisted process.

From these facts it can be concluded that the introduction of very small amounts of ZnS into the  $\text{TiO}_2$  surface results in nanocomposite materials with improved performance for the MB photodecolorization.

These results are based on the spectrophotometrical analysis of the dye solutions. In order to verify whether the dye decolorization is accomplish with its degradation, chemical oxygen demand (COD) measurements of the dye solutions, before and at the end of the assays, have been performed. The initial (before adsorption) and

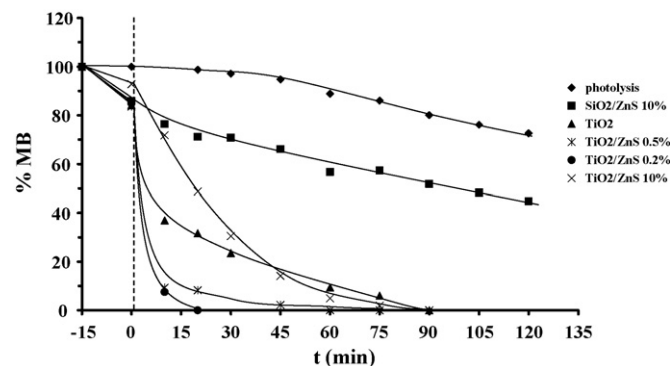


Fig. 5. Photocatalytic decolorization of a 20 ppm MB aqueous solution (100 mL) using 50 mg of catalyst.

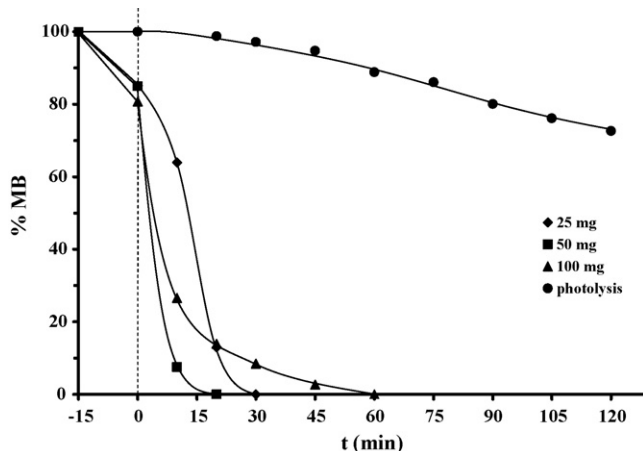


Fig. 6. Effect of photocatalyst amount on the MB decolorization process ( $\text{TiO}_2/\text{ZnS}$  (0.2%), 100 mL of MB aqueous solution).

final (after photo-irradiation) COD values of the aqueous dye solutions indicate a COD removal of 33% during the photo-irradiation process. The results show that using  $\text{TiO}_2/\text{ZnS}$  (0.2%) as photocatalyst the color is removed faster than COD.

Considering that  $\text{SiO}_2$  is a photocatalytic inert material, the ability of the ZnS to photocatalyse the MB decolorization, was tested using the  $\text{SiO}_2/\text{ZnS}$  (10%) nanocomposite (in these conditions a complete coverage of the  $\text{SiO}_2$  surface with ZnS was obtained). As Fig. 5 shows the pathway of the MB photodecolorization, in the presence of  $\text{SiO}_2/\text{ZnS}$  (10%), it is approximately parallel to the pathway of the photolysis process. It must be noted that after being submitted to the photo-radiation the solid remained blue. These two facts suggest that only photolysis has taken place and the complete desorption of the dye, and/or its blue degradation products, does not occur during irradiation. These results suggest that ZnS, when covering the  $\text{SiO}_2$  surface and under the experimental conditions tested, do not show significant photocatalytic activity.

#### 3.3.2. Influence of the catalyst amount

The effect of the catalyst concentration on the MB photodecolorization (Fig. 6) was investigated for the nanocomposite  $\text{TiO}_2/\text{ZnS}$  (0.2%), since it was the material with the best photoactivity, concerning the MB decolorization. Fig. 6 shows that during light-off (first 15 min needed to reach the adsorption–desorption equilibrium), an increase of the percentage of the MB adsorbed was observed with the increase on the amount of the nanocomposite, as expected.

After light-on the rate of MB decolorization is dependent on the  $\text{TiO}_2/\text{ZnS}$  (0.2%) concentration. The complete MB photodecolorization was achieved within 20 min using 50 mg of  $\text{TiO}_2/\text{ZnS}$  (0.2%). Longer times were required when 25 mg and 100 mg were used, 30 and 60 min, respectively. These results can be explained by two main reasons: first, and taking into account the 25 and 50 mg experiments, it must be considered that increasing the catalyst concentration the number of dye molecules adsorbed will increase and the number of photons absorbed will increase too. As a result of the high density of molecules in the area of illumination, the decolorization rate will be increased. However for a very high particles concentration (in this case 100 mg) the suspensions turbidity increases. In this situation the light penetration decreases, as a result of an enhanced light scattering effect, and consequently the photodecolorization will be less effective [22,23].

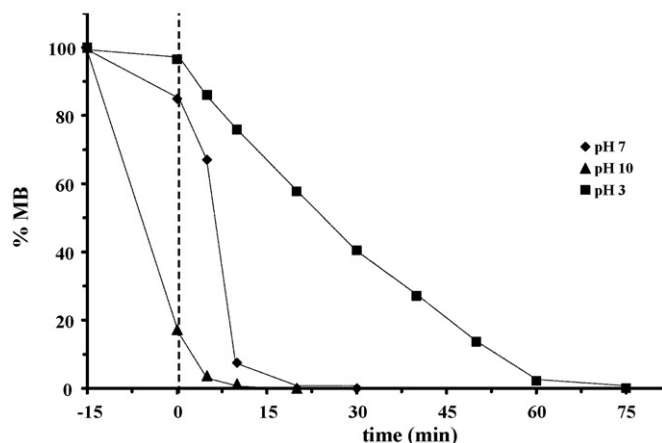


Fig. 7. Photocatalytic decolorization of a 20 ppm MB solution using different initial pH values (50 mg TiO<sub>2</sub>/ZnS (0.2%), 100 mL of MB aqueous solution).

### 3.3.3. Influence of the pH

Usually pH plays an important role in the industrial wastewaters characteristics and could be considered as one of the most important parameters that influence the photo-oxidation processes. The effect of the pH, on the decolorization rate, can be explained mainly by the modification of the electrical double layer of the solid-electrolyte interface, which affects the adsorption-desorption processes and the separation of the photogenerated electron-hole pairs in the surface of the catalyst particles [21].

Normally, in aqueous solution, the P-25 TiO<sub>2</sub> surface is positively charged in acidic media and negatively in alkaline media, with a PZC of about pH 6–7 [24]. Thus, adsorbates would prefer to adsorb on the TiO<sub>2</sub> surface by a negatively charged or electron-abundant group in acidic solutions and by a positively charged group in alkaline solutions due to the electrostatic interaction. According to this, the efficiency of the MB photodecolorization, in the presence of TiO<sub>2</sub>, is expected to increase with pH owing to the electrostatic interactions between the negative TiO<sub>2</sub> surface and the MB cations.

Taking into account these facts the study of the pH influence on the MB decolorization process was performed. For pH 3 a slight adsorption onto the TiO<sub>2</sub>/ZnS surface was visualized. This result can be correlated with the cationic behaviour of both, TiO<sub>2</sub>/ZnS (0.2%) and MB, for this pH. Conversely, for pH 10 a very high amount of the dye was adsorbed. However in this experiment, a violet solid coloration was observed, probably correlated with the dye protonation/deprotonation process [25]. For neutral pH an intermediate adsorption situation was observed.

Concerning the adsorption results, the photodecolorization was performed at pH 3, 7 and 10, during 90 min (Fig. 7) in the presence of TiO<sub>2</sub>/ZnS (0.2%). At pH 3 the time requested for the complete decolorization process was less than 75 min. This value is higher if compared with the 20 min needed at pH 7 and lower if compared with the 10 min necessary for pH 10. However at pH 10 it must be remembered that at the starting irradiation time the percentage of the MB adsorbed was still very high, close to 83%. After 10 min of irradiation the solution was completely decolorized but the catalyst remained violet. Increasing the irradiation time the color of the catalyst did not change anymore. This fact can be associated with a strong adsorption/interaction between the violet dye form and the TiO<sub>2</sub>/ZnS (0.2%) surface, at pH 10 [26].

The strong adsorption leads to a major decrease of the active centres and consequently a decrease of the absorbed light on the catalyst's surface. This could be the reason why the initial rate of decolorization is lower in alkaline solutions than in neutral pH (Fig. 7). In acid solutions an identical decrease of the initial decol-

orization rate was observed (Fig. 7) reflecting the difficulty of the dye molecules to approach the catalyst surface due to electrostatic interaction. As a result the optimum pH, among those studied and under the experimental conditions tested, appears to be the neutral one. Similar observations have been made by other researchers for dyes and other types of pollutants photodegradations studies [21,23].

Considering the good results obtained for the use of TiO<sub>2</sub>/ZnS on the MB photodecolorization process, under UV-vis radiation, it is possible to propose these materials as potential photocatalysts under solar light irradiation. The photodecolorization of MB and others pollutants, such as phenol and Orange II, using these materials, under visible light irradiation, are now in progress in our lab.

## 4. Conclusions

Nanocomposites TiO<sub>2</sub>/ZnS with different ZnS:TiO<sub>2</sub> ratios have been prepared using a chemical deposition method. The obtained materials were tested as photocatalysts on the MB decolorization process. The presence of small ZnS percentages on the nanocomposite surface (0.5% and 0.2%) promotes an increase on the catalyst photoactivity, when compared with the original TiO<sub>2</sub>. The material with the best catalytic performance on the MB photodecolorization was the TiO<sub>2</sub>/ZnS (0.2%) using 0.05% (w/w) of this photocatalyst the complete decolorization of a 20 ppm MB solution, at natural pH was achieved in less than 20 min, nearly 70 min faster than the TiO<sub>2</sub> photoassisted process.

## Acknowledgments

O.C. Monteiro thanks Fundação para a Ciência e Tecnologia (FCT) for the grant SFRH/BPD/14554/2003. Márcia C. Neves thanks the University of Aveiro for a PhD grant. This work is supported by FCT, POCI and co-financed by FEDER (POCI/QUI/59615/2004).

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2008.03.133.

## References

- [1] D. Chatterjee, S. Dasgupta, Visible light induced photocatalytic degradation of organic pollutants, *J. Photochem. Photobiol. C* 6 (2005) 186–205.
- [2] V. Ramaswamy, N.B. Jagtap, S. Vijayanand, D.S. Bhang, P.S. Awati, Photocatalytic decomposition of methylene blue on nanocrystalline titania prepared by different methods, *Mater. Res. Bull.* 43 (2008) 1145–1152.
- [3] M. Janus, A.W. Morawski, New method of improving photocatalytic activity of commercial Degussa P25 for azo dyes decomposition, *Appl. Catal. B* 75 (2007) 118–123.
- [4] P.V. Kamat, D. Meisel, Nanoscience opportunities in environmental remediation, *C. R. Chim.* 6 (2003) 999–1007.
- [5] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. C* (2005) 186–205.
- [6] X. Zhang, M. Zhou, L. Lei, Co-deposition of photocatalytic Fe doped TiO<sub>2</sub> coatings by MOCVD, *Catal. Commun.* 7 (2006) 427–431.
- [7] M.R. Nunes, O.C. Monteiro, A.L. Castro, D.A. Vasconcelos, A.J. Silvestre, A new chemical route to synthesize TM-doped (TM = Co, Fe) TiO<sub>2</sub> nanoparticles, *Eur. J. Inorg. Chem.*, 2008, doi:10.1002/ejic.2007.00.978.
- [8] S. Yang, L. Lou, K. Wang, Y. Chen, Shift of initial mechanism in TiO<sub>2</sub>-assisted photocatalytic process, *Appl. Catal. A* 301 (2006) 152–157.
- [9] H. Li, J. Li, Y. Huo, Highly active TiO<sub>2</sub>N photocatalysts prepared by treating TiO<sub>2</sub> precursors in NH<sub>3</sub>/ethanol fluid under supercritical conditions, *J. Phys. Chem. B* 110 (2006) 1559–1565.
- [10] D. Robert, Photosensitization of TiO<sub>2</sub> by M<sub>x</sub>O<sub>y</sub> and M<sub>x</sub>S<sub>y</sub> nanoparticles for heterogeneous photocatalysis applications, *Catal. Today* 122 (2007) 20–26.
- [11] V. Stengl, S. Bakardjieva, N. Murafa, V. Houšková, K. Lang, Visible-light photocatalytic activity of TiO<sub>2</sub>/ZnS nanocomposites prepared by homogeneous hydrolysis, *Micropor. Mesopor. Mater.* 110 (2008) 370–378.
- [12] S.S. Lee, K.-T. Byun, J.P. Park, S.K. Kim, J.Ch. Lee, S.-K. Chang, H.-Y. Kwak, I.-W. Shim, Homogeneous ZnS-coating onto TiO<sub>2</sub> nanoparticles by a simple

- one pot sonochemical method, Chem. Eng. J. (Amsterdam Neth.) 139 (2008) 194–197.
- [13] Y. Xiaodan, W. Qingyin, J. Shicheng, G. Yihang, Nanoscale ZnS/TiO<sub>2</sub> composites: preparation, characterization, and visible-light photocatalytic activity, Mater. Charact. 57 (2006) 333–341.
- [14] O.C. Monteiro, A.C.C. Esteves, T. Trindade, The synthesis of SiO<sub>2</sub>@CdS nanocomposites using single-molecule precursors, Chem. Mater. 14 (2002) 2900–2904.
- [15] F.J. Green, Sigma–Aldrich Handbook of Stains, Dyes and Indicators, Aldrich Chemicals, Milwaukee, 1996.
- [16] K.G. Bhattacharyya, A. Sharma, Kinetics and thermodynamics of methylene blue adsorption on Neem (*Azadirachta indica*) leaf powder, Dyes Pigm. 65 (2005) 51–59.
- [17] O.C. Monteiro, M.C. Neves, T. Trindade, Submicron silica nanocoating with zinc sulfide using a single-source method, J. Nanosci. Nanotechnol. 4 (2004) 146–150.
- [18] W. Stöber, A. Fink, E. Bohn, Controlled growth of monodisperse silica spheres on the micro size range, J. Colloid Interface Sci. 26 (1968) 62–69.
- [19] F. Rouquérol, J. Rouquérol, K.S.W. Sing, Adsorption by Powders and Porous Solids, Academic Press, London, 1999.
- [20] H. Jia, H. Xu, Y. Hu, Y. Tang, L. Zhang, TiO<sub>2</sub>@CdS core–shell nanorods films: fabrication and dramatically enhanced photoelectrochemical properties, Electrochem. Commun. 9 (2007) 354–360.
- [21] M.A. Hasnat, I.A. Siddiquey, A. Nuruddin, Comparative photocatalytic studies of degradation of a cationic and an anionic dye, Dyes Pigm. 66 (2005) 185–188.
- [22] E. Bizani, K. Fytianos, I. Poulios, V. Tsiridis, Photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of titanium dioxide, J. Hazard. Mater. 136 (2006) 85–94.
- [23] S. Senthilkumar, K. Porkodi, Heterogeneous photocatalytic decomposition of crystal violet in UV-illuminated sol–gel derived nanocrystalline TiO<sub>2</sub> suspensions, J. Colloid Interface Sci. 288 (2005) 184–189.
- [24] J. Zhao, H. Hidaka, A. Takamura, E. Pelizzetti, N. Serpone, Photodegradation of surfactants. 11. ζ-Potential measurements in the photocatalytic oxidation of surfactants in aqueous TiO<sub>2</sub> dispersions, Langmuir 9 (1993) 1646–1650.
- [25] M. Zanjanchi, Sh. Sohrabnezhad, Evaluation of methylene blue incorporated in zeolite for construction of an optical humidity sensor, Sens. Actuators B 105 (2005) 502–507.
- [26] S.K. Kansal, M. Singh, D. Sud, Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts, J. Hazard. Mater. 141 (2007) 581–590.