

## AEROBIC PHOTOCATALYTIC OXIDATION OF MIXED TEXTILE AZO DYES BY SPRAYED NANOSTRUCTURED TITANIUM DIOXIDE

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**ABSTRACT.** Azo dyes are considered as xenobiotic compounds which are very recalcitrant to remove from industrial wastewaters by traditional techniques for treating. Advanced oxidation processes for effective treatment of single azo dyes by heterogeneous nanostructured TiO<sub>2</sub> have showed promising results for photocatalytic decolorization. However, mixture of three or more azo dyes with one, two and three azo-groups possesses different behavior at photocatalytic degradation process. In this report, several operational parameters for aerobic photocatalytic oxidation of mixture of phenylazophenol, reactive black 5 and chlorazol black E azo dyes were investigated by using of spray pyrolysis prepared nanostructured TiO<sub>2</sub>. The experimental data showed that the initial concentration of azo dyes in dye mixture significantly affect their degradation efficiency. Initial dye concentration, photocatalytic dosage, pH adjustment and water hardness greatly influence the destruction reaction.

## АЕРОБНО ФОТОКАТАЛИТИЧНО ОКИСЛЕНИЕ НА СМЕСЕНИ ТЕКСТИЛНИ АЗО БАГРИЛА ЧРЕЗ НАНОСТРУКТУРИРАН ТИТАНИЕВ ДИОКСИД

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**РЕЗЮМЕ.** Азо багрилата се считат за ксенобиотични съединения, които са много устойчиви и неподатливи към премахване от промишлени отпадни води чрез традиционните техники за третиране. Окислителните процеси за ефективно разрушаване на единични азо багрила посредством хетерогенен наноструктуриран титаниев оксид показаха обещаващи резултати при фотохимичното обезцветяване. Въпреки това смес от три или повече азо багрила с една, две и три диазо-групи притежават различни свойства при процесите на фотокаталитична деградация. В този доклад няколко оперативни параметри за аеробно фотокаталитично окисление на смес от азобагрилата фенилазофенол, реактивно черно 5 и хлоразол черно Е са изследвани чрез използване на наноструктуриран TiO<sub>2</sub> получен посредством спрей пиролиза. Експерименталните данни показват, че първоначалната концентрация на азобагрилата в смес оказва съществено влияние върху ефективността на деградацията. Концентрацията на багрилата, фотокаталитичната доза, фиксираното рН и твърдостта на водата силно повлияват реакцията на деструкция.

### 1. Introduction

The abundant class of synthetic coloring organic azo dyes compounds can be characterized by the presence of –N=N– groups linked between aromatic rings in their molecular structure (Konstantinou and Albanis 2004; Jin et al., 2008). A number of technologies for removal of dye pollutants have been investigated, such as adsorption, biodegradation, advanced oxidation, and membrane filtration (Karcher et al., 2008; Karbus et al., 2003; Sen and Demirer 2003; Golob and Ojstrsek 2005; Ojstrsek et al., 2007).. However, the above mentioned processes are unable to completely eliminate the dye pollutants, since they mostly transfer the dye compounds from aqueous to another phase, leading to secondary pollution problems and posing a major drawback of such the treatment processes. Heterogeneous photocatalytic oxidation using TiO<sub>2</sub> as catalyst is highly considered as a promising destructive technology (Fox and Dulay 1993; Hoffmann et al., 1995;

Lachheb et al., 2002; Carp et al., 2004). Titanium dioxide possess several advantages as environmentally friendly material, the photo-destruction is carried out under mild conditions, i.e. room temperature and atmospheric pressure. It can bring complete degradation of most organic pollutants, without causing secondary pollution problems and the polluting compounds are decomposed into ending non-toxic substances. Several reports about photocatalytic properties of nanostructured TiO<sub>2</sub> powders and thin films as high-effective material have been published (Akpan and Hameed 2009). In most report the catalyst power is demonstrated with single azo dye. However, the industrial wastewaters usually contain a mixture of various organic dyes. To demonstrate the industrial application, the catalytic material must show no high specificity toward target organic dyes. The aim of this report is to show that nanostructured TiO<sub>2</sub> thin films obtained by spray pyrolysis method possess high effectiveness and catalytic power to various azo dyes. To prove these properties of our advanced

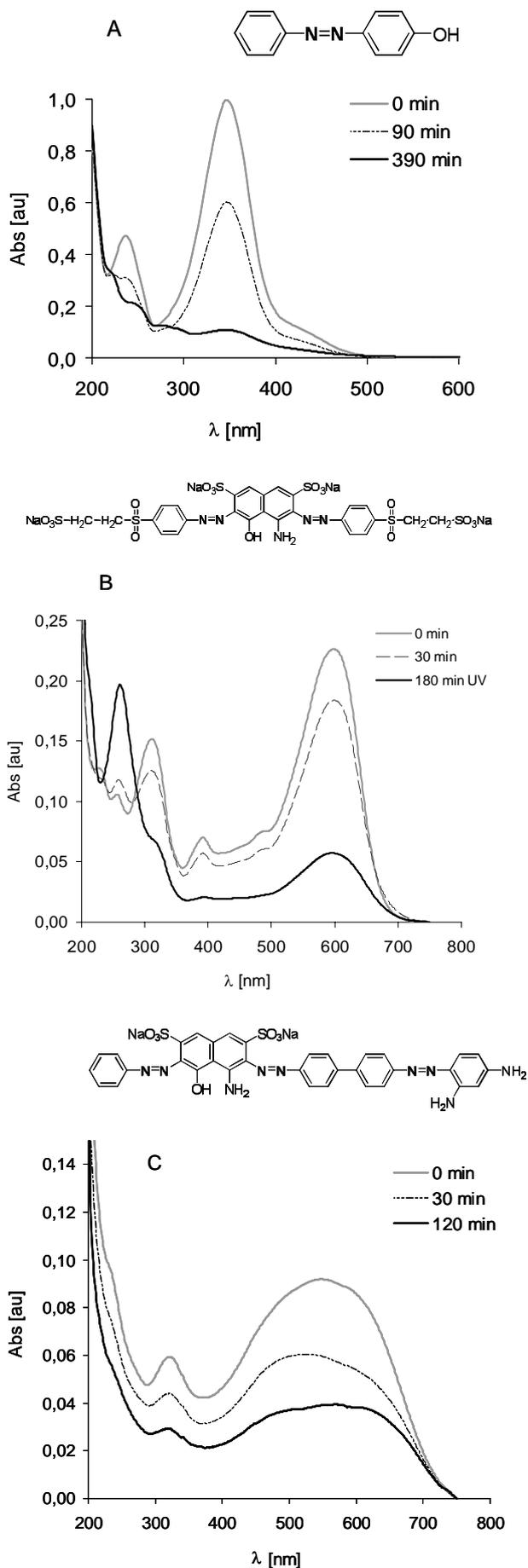


Fig. 1. Chemical structure and UV-VIS spectra of treated single azo dyes (A) phenylazophenol, (B) reactive black 5, (C) chlorazol black E.

nanomaterials it was tested with a mixture of azo-dyes containing one, two and three azo bonds. The experimental data show that the number of azo-groups is not significant factor for the rate and effectiveness of reaction destruction.

## 2. Experimental procedures

### 2.1. Preparation of nanostructured $TiO_2$ by spray pyrolysis.

The aluminum foil plates (75 x 75 mm, thickness 0.3 mm) and glass microscopic slides (76 x 26 mm, Waldemar Knittel Glasbearbeitungs – GmbH) were cleaned successively in hot ethanol and acetone. They were further used for the deposition of thin  $TiO_2$  films. An alcoholic solution (EtOH – 98 % purity) of titanium tetraisopropoxide (TTIP) (98% purity, Acros) was hydrolyzed by a water-ethanol mixture in molar ratio TTIP:H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH = 1:1:30. Acetyl acetone (AcAc) was added as a complexing agent so that the ratio TTIP:AcAc = 1:1 (solution A). The solution A was diluted with a mixture of isopropanol and butyl carbitol (C<sub>4</sub>H<sub>9</sub>OC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OH) and then stirred intensively for 1 hour at room temperature. The prepared mixture was used for the spray procedure. The aerosol precursor solution was generated by pneumatic glass nebulizer and transported with carrier gas Ar to the heated substrate at 300-400 °C. The substrate-nozzle distance was 20 cm. The spraying of the solutions on the substrate was carried out at regular time intervals of 10 s thus maintaining a constant substrate temperature.

### 2.2. Decolorization of model solutions of single phenylazophenol, reactive black 5 and chlorazol black E and mixture by nanostructured $TiO_2$ .

To study the photocatalytic degradation of model solution of phenylazophenol (PP), reactive black 5 (RB5) and chlorazol black E (CE), the experiments were conducted by an UV-A light source (UV lamp with maximum emission at 370 nm). The photocatalytic reactor contained 150 ml water solution of single dye or mixture with concentration 10 mg/L and pH = 2.70. The photocatalytic degradation was evaluated by taking aliquote of the solution and measuring the residual concentration using spectrophotometer in the wavelength range from 200 to 750 nm at regular time intervals. The actual dye concentration was determined by comparison of the measured absorbance at the wavelength of spectral maximum with absorbance of solutions of known dye concentration.

## 3. Result and discussion

In the photocatalytic activity testing experiments, the UV-visible spectrophotometry was used to investigate the effects of various reaction parameters on the degradation of single and mixed azo dyes. On Fig. 1 are shown the typical absorbance spectra of PP, RB5 and CE. The figure presents also the changes of their spectrum during photocatalytic treatment with nanostructured  $TiO_2$  at acidic pH. The acidic conditions favor the electrostatic attraction between the positively charged  $TiO_2$  surface and investigated azo-dyes. It is seen that the adsorption peaks corresponding to  $\lambda_{max}$  for azo group (-N=N-) are located in different ranges of the VIS-spectrum, which are respectively 344 nm for phenylazophenol, 596 nm for reactive black 5 and 540 nm for the wide spread peak of chlorazol black E. For the mixture of PP, RB5 and CE it is clear that their  $\lambda_{max}$  values did not change upon their mixing (see Fig. 2). This indicates that the decreases in absorbance at their  $\lambda_{max}$  values can be reliably used to evaluate the degradation performance for each dye.

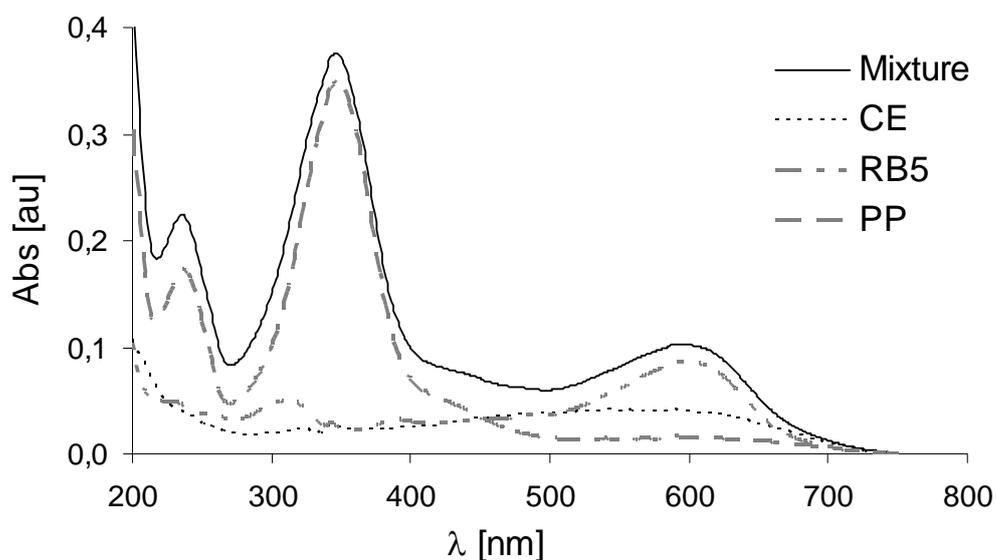


Fig. 2. UV-VIS spectra of single azo dyes and mixed model solution

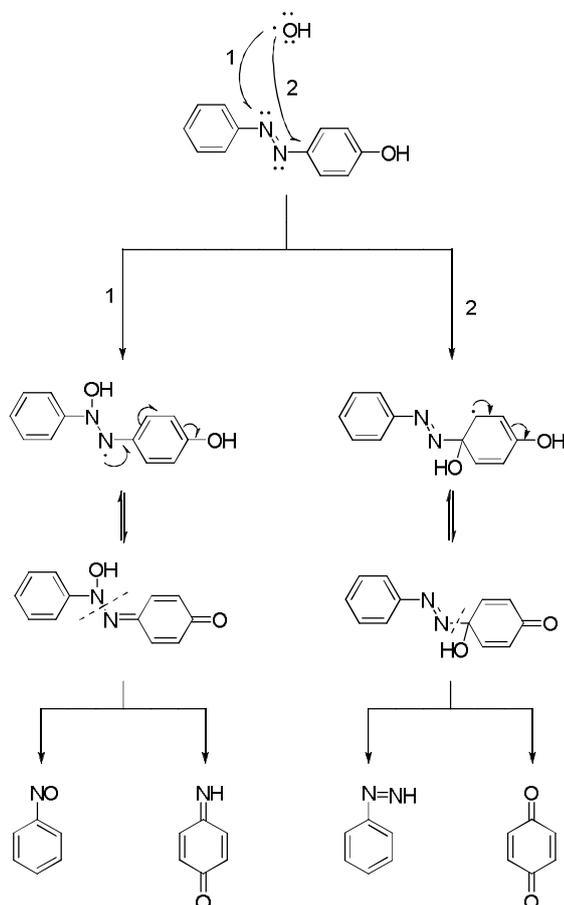


Fig. 3. Reaction mechanism of photooxidation reaction of phenylazopenol dye

Three model solutions with fixed concentration (10 mg/L) of PP, RB5 and CE were used to investigate the effect of initial dye concentration on the photocatalytic degradation performance. It is observed that all of them are completely decolorized within few hours. However, over 95 % of the dye amount is destructed for 3 hours. This is due to the fact that the oxidation of azo-group and obtained aromatic derivatives follows precise regularity, which can be predicted in the time. As it is shown on Fig. 3 in the first step of photo-degradation the azo bond lose its unsaturated character and

is transformed into hydroxyl structure. Further oxidation leads to  $-N-$  bond splitting and formation of nitro group and aromatic derivatives. The total amount of nitrogen-containing ions presented in the solution at the end of the experiment is usually lower than the expected from stoichiometry indication that N-containing species remain adsorbed on the photocatalyst surface or most probably, that significant quantities of  $N_2$  and/or  $NH_3$  have been produced and transferred to the gas phase. Due to the generation of ammonia the pH of reaction mixture is increasing from 2.70 to 3.35 in our experiment.

The presence of water hardness in water supply at high degrees can cause several operational problems in industry, and most wastewaters contain a significant level of water hardness. Hardness is generally referred to calcium and magnesium cations present in water with a typical Ca-to-Mg ratio of 3:2, and a typical total hardness concentration found in tap water is about 60-180 mg/L. The results indicate that for any studied system, the degradation efficiency tended to decrease with hardness concentration. However, at the same total hardness concentration, Mg more negatively affects the photocatalytic degradation efficiency than Ca.

On Fig. 4 is shown UV-VIS spectra of mixed model solution contain respectively PP, RB5 and CE in equal concentrations. The total amount of the organic dyes in solution is 10 mg/L and pH = 2.7. On this spectrum the CE peaks are masked, because of the high intensity peaks of PP and RB5. The important result from this experiment is that the decolorization progress of the mixed azo dyes follows or is similar to the degradation rate, which was measured in the case of single dyes in model solution (as in Fig. 1). The higher degradation efficiency of any given dye in the mixture as compared to the single dye is theoretically possible because the other dye, with suitable concentration, acts as a mediator in reducing the complete interaction/repulsion between the dye molecules and the photocatalyst surface, resulting in greater possibilities for the dye molecules to reach the photocatalyst surface and be attacked by the oxygen active species generated by photoinduced mechanism at the photocatalyst surface.

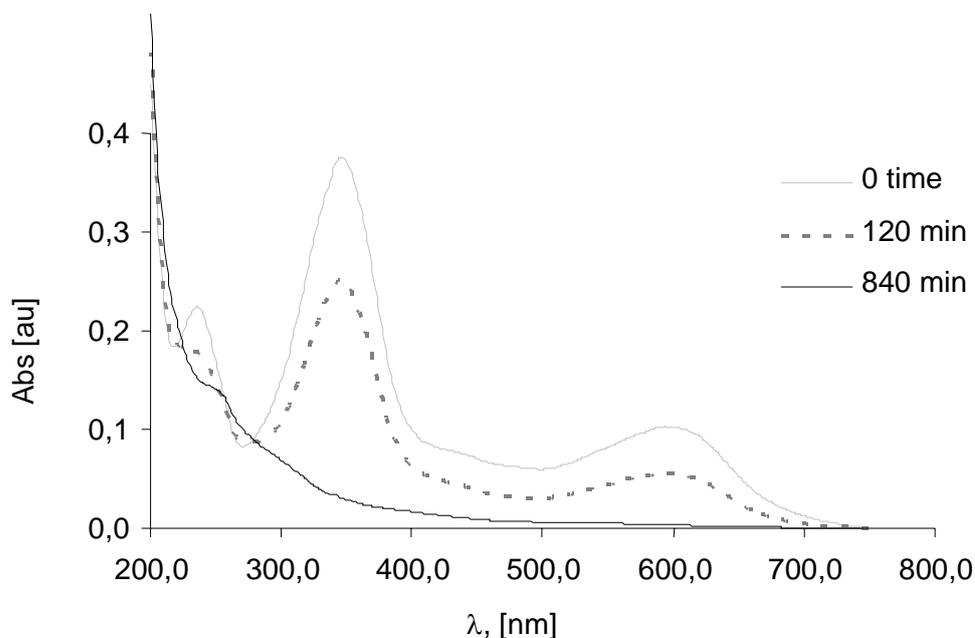


Fig. 4. Absorption spectra of mixed PP, RB5 and CE azo dyes. They are photo-catalytically oxidized by nanostructured titanium dioxide obtained by sol-gel pyrolysis

As it is seen from Fig. 4 complete decolorization of the azo dyes mixture is achieved within few hours. However, some amount of benzene aromatic derivatives remains in the reaction mixture. Similar phenomenon was registered in the case of reactive black 5 (Fig. 1 B). However the peaks corresponding to azo-groups (at 344 nm and 590 nm) and naphtene- groups (306 nm) are completely disappeared.

#### 4. Conclusion

In this work, nanostructured titanium dioxide obtained by sol gel pyrolysis method was used to investigate the photocatalytic degradation of mixture of three azo dyes: phenylazophenol, reactive black 5 and chlorazol black E. Various reaction parameters, i.e. type of dye, numbers of azo-groups within the molecule, dye concentration, pH and water hardness were systematically studied on the photocatalytic degradation performance. The photocatalytic activity results showed that the optimum conditions for the maximum photocatalytic degradation of all azo dyes were obtained at concentration 3 mg/L – 10 mg/L. The acidic pH adjustment significantly increases the photocatalytic degradation of single or mixed dyes. The complete decolorization of single and mixed azo dyes is achieved within hours. The decolorization progress of mixed azo dyes follows or is similar to the degradation rate, which was measured in the case of single dyes in model solution.

#### Acknowledgements

The support of this project by the Bulgarian National Scientific Fund (Project No. DDVU 02-36/2010) is gratefully acknowledged.

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