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STUDIES ON THE PHOTOCATALYTIC DECOMPOSITION OF ORGANIC DYES USING MESOPOROUS METAL OXIDES

BY

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Abstract. In this study, the ultraviolet irradiation behaviour of three dyes (methylene blue - MB, phenol red - FR and crystal violet - CV) is presented in the presence of a mesoporous oxide material based on $ZnO\text{-}CeO_2$.

The three dyes were degraded to the corresponding leucoderivates in different times, methylene blue (conc. 10^{-5}M) in 25 min, crystal violet (conc. $2\cdot10^{-5}$M) in 90 min, and phenol red (conc. $4.5\cdot10^{-5}$M) in 140 min. Also, the calculated photodegradation yield showed that MB and CV degraded by 98% and RF only by 78%. It was also investigated the influence of the photocatalyst concentration on the reaction rate for MB.

Keywords: crystal violet; photodegradation; phenol red; methylene blue.

1. Introduction

The topic chosen for this work is justified by the current interest in waste water purification. One of the most difficult tasks in wastewater treatment plants from the textile, leather and food industries is the incomplete removal of

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the effluent color (water coming out of the treatment plant), mainly because the dyes and pigments are synthesized to withstand biodegradation and other classical treatment processes so that they stay in the environment for a long time. The discharge of water used in industrial processes by various economic agents is regulated by standards and norms which set the limits of pollutant loading of industrial and urban waste water to evacuation to natural receptors (NTPA-001/2002), and the conditions for evacuation of waste water in Sewerage networks of localities directly in treatment plants (Normative NTPA-002/2002 of 28 February 2002).

Many research groups have sought solutions to streamline wastewater purification processes, with good results being obtained in photocatalytic processes (Minero *et al*., 1996; Naeem and Ouyang, 2013; Lv *et al*., 2016; Zhou *et al*., 2016) and the research still continues.

A photocatalyst is a (semiconductor) material that generated electron-hole pairs when a quantum of energy is absorbed and produces chemical transformations in the reaction participants that come into contact with it and also regenerates its chemical composition after each cycle of such interactions (Fox and Dulay, 1993).

Photocatalysis is a process for purifying water financially relatively convenient, easy to implement and with good results. Because of the total energy emitted by the sun, only 5% is ultraviolet radiation, the current trend is to move from active photocatalytic materials in the ultraviolet field to active materials in the visible field, so as to use as much of the light emitted by the sun (Nagarajan *et al*., 2017; Sharma *et al*., 2017; Wang *et al*., 2016). It is also possible to work with tandem photocatalysts, following the proper combination of two or more materials or by doping to obtain optimum results.

2. Experimental

Catalytic photodegradation of three dyes was performed using a nanostructured oxide material based on $ZnO\text{-}CeO_2$, irradiated with UV radiation produced by a mercury lamp. The $ZnO\text{-}CeO_2$ powder was synthesized by solvothermal method (Apostolescu *et al*., 2015). The intensity of the incident radiation was 2.1 W/m^2, and was measured by a Hamamatsu C9536-01 meter with H9958 detector for 310-380 nm, scaled between 1 $\mu W/cm^2$ and 100 mW/cm^2.

The dyes used were methylene blue, abbreviated MB (cationic dye), phenol red abbreviated RF (anionic dye) and crystal violet abbreviated CV (cationic dye) with concentrations in the range of 4 ppm to 16 ppm. All chemicals used in this study were of analytical grade and all solutions were prepared using distilled water, obtained from a commercial distillation system.

For determining the wavelength when absorption maxima occurs for solutions of dyes, were initially developed absorption spectra UV-Vis, using a

SP-870 plus METERTECH, optical path length of 1 cm. The spectra are presented in Fig. 1.

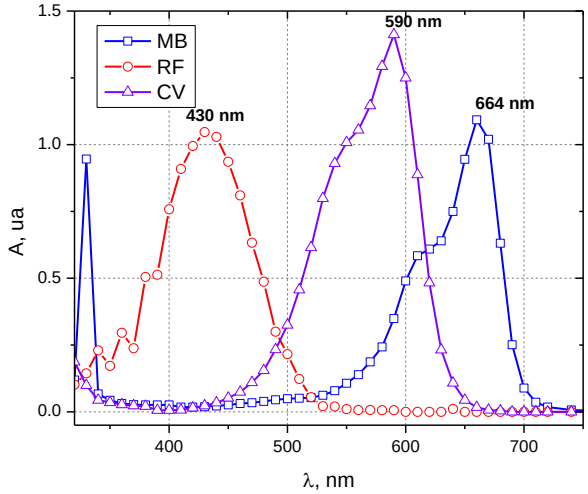
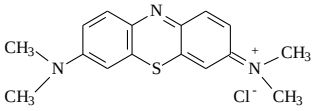
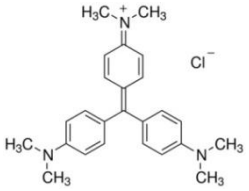
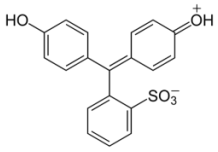


Fig. 1 – UV-Vis absorbance spectra of phenol red, crystal violet and methylene blue.

From the allure of the graph were chosen working wavelengths, given in Table 1, with the main characteristics of the dyes used.

Table 1

Characteristics of Organic Compounds Subject to Degradation

Dye	The chemical structure	Molecular formula	λ_{max} [nm]	Molar mass [g/mol]
Methylene Blue (MB)		$C_{16}H_{18}ClN_3S$	664	319.85
Crystal Violet (CV)		$C_{25}H_{30}ClN_3$	590	407.99
Phenol Red (RF)		$C_{19}H_{14}O_5S$	430	354.38

3. Results and Discussions

Photocatalytic degradation procedure

The photocatalytic activity ZnO-CeO_2 catalysts was measured by monitoring the degradation of MB, RF and CV solution under UV irradiation in a photocatalytic reaction system, using a 18 W high-pressure mercury lamp as light source.

In 50 mL of aqueous dye solutions of different concentrations were introduced varying amounts of photocatalytic material powder. The reaction systems thus prepared were stirred magnetically for 30 min, in the dark, for stabilisation of the equilibrium adsorption - desorption between the pollutant and the surface of the photocatalyst.

Before starting the stirring and after 30 min of stirring, the dyes absorbance was measured by spectrophotometric method at specific wavelengths, as specified in Table 1.

After the adsorption equilibrium, the reaction systems were irradiated with the ultraviolet radiation. At regular time intervals samples were taken from the solution (about 4 mL) and were centrifuged to separate the catalyst and then the absorbance value was determined for each colorant at specific wavelengths. The following equation was used for photocatalytic degradation of organic dye (Mehrabian and Esteki, 2017):

$$R\% = \frac{A_0 - A}{A_0} \cdot 100 = \frac{C_0 - C}{C_0} \cdot 100 \quad (1)$$

where: A_0 is the UV–Vis absorption of the original solution; A is the UV–Vis absorption of same solution at time t (min) and specific λ; C_0 (mol/L) represents the initial concentration of dyes; C (mol/L) is the final concentration at time t (min).

Fig. 2 shows the change of the absorbance of the solution of MB of concentration 10^{-5}, measured at 664 nm, irradiated with ultraviolet radiation, in the presence of different doses of the photocatalyst (0.02 g/L, 0.03 g/L and 0.04 g/L). Photocatalytic degradation process took approximately 25 min; it is observed that a greater amount of the photocatalyst does not lead to more rapid fading of the dye. The degree of discoloration was approximately 98% for all three catalyst doses and was achieved within 25 min. These results suggested that the dose of 0.02 g cat / L dye solution is optimal. According with Tschirch *et al*. (2008), the equation of the chemical reaction proposed for the conversion of MB into mineralization compounds is:

$$C_{16}H_{18}N_3SCl + 25.5O_2 \xrightarrow{h\upsilon > E_g} 16CO_2 + 6H_2O + 3HNO_3 + H_2SO_4 + HCl \quad (2)$$

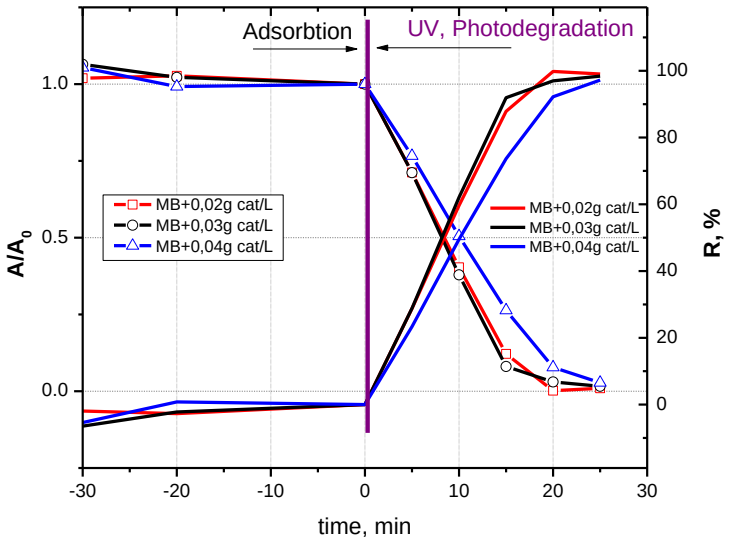


Fig. 2 – Time-course variation of A/A_0 of MB 10^{-5} M under UV irradiation over various catalyst dose and corresponding photo-decolourisation behaviour (R, %).

Fig. 3 shows the variation of absorbance for the crystal violet solution of $2 \cdot 10^{-5}$ mol/L, measured at 590 nm, irradiated with UV in the presence of different doses of photocatalyst (0.02 g/L, 0.03 g/L and 0.04 g/L).

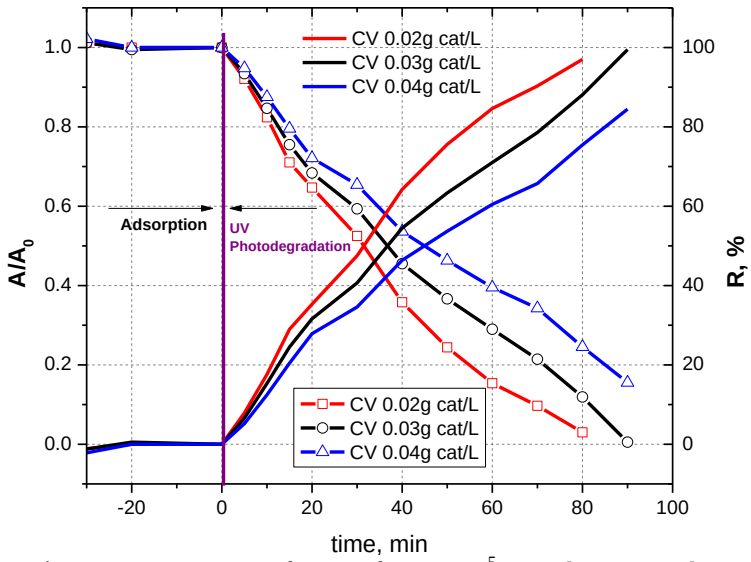


Fig. 3 − Time-course variation of A/A_0 of CV $2 \cdot 10^{-5}$ M under UV irradiation over various catalyst dose and corresponding photo-decolourisation behaviour (R, %).

Photocatalytic degradation took about 90 min. Also for this colorant, a larger amount of photocatalyst does not lead to faster fading, the experimental results suggesting that the dose of 0.02 g of catalyst / L of dye solution is optimal. The CV degradation rate is 98% achieved in 60 min. The equation of the chemical reaction of photocatalytic decomposition of CV is:

$$C_{25}H_{30}N_3Cl+34.5O_2 \xrightarrow{h\upsilon>E_g} 25CO_2+10H_2O+3HNO_3+HCl \quad (3)$$

Fig. 4 shows the variation of the absorbance for the RF solution at a concentration of $4.5\cdot10^{-5}$ M, measured at λ = 430 nm, under UV irradiation, in the presence of different photocatalyst doses (0.02 g/L, 0.03 g/L and 0.04 g/L).

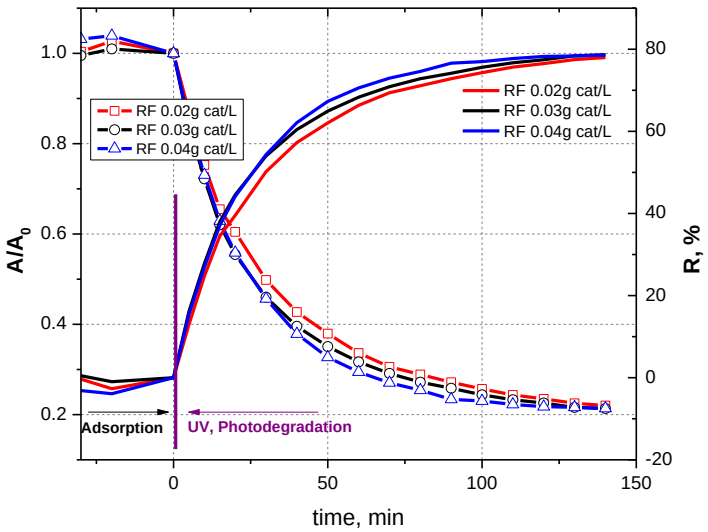


Fig. 4 − Time-course variation of A/A_0 of RF $4.5\cdot10^{-5}$ M under UV irradiation over various catalyst dose and corresponding photo-decolourisation behaviour (R, %).

For the RF solution, ultraviolet radiation degradation took about 140 min but was not complete. The behaviour of the RF dye in the presence of different doses of photocatalyst revealed that a higher amount of photocatalyst led to its degradation more rapidly. The RF degradation rate is most slowly and incomplete, only 78%, achieved in 140 min.

The equation of the chemical reaction of photocatalytic decomposition of RF is:

$$C_{19}H_{14}O_5S+21.5O_2 \xrightarrow{h\upsilon>E_g} 19CO_2+6H_2O+H_2SO_4 \quad (4)$$

According to the data reported by Madhu *et al*. (2008) the photocatalytic degradation of the methylene blue follows a pseudo-first-order kinetic model (Eq. 5).

$$\ln(C_0/C) = kt \tag{5}$$

According to this equation, if the experimental data verifies a kinetic of the first order, a line must be obtained in the coordinates $\ln(C_0/C)$ - t. Therefore a pseudo first-order kinetic model was used to fit the experimental data presented in Fig. 5.

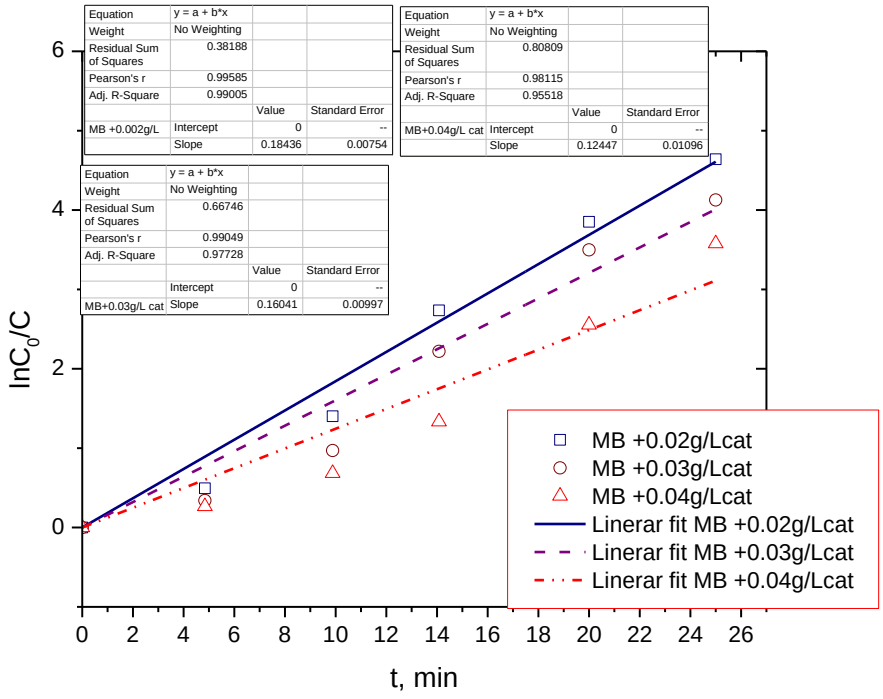


Fig. 5 – First-order rate graph of photocatalytic degradation of MB/ under UV irradiation.

The reaction rate for photocatalytic reactions are independent of radicals concentration (Guettai and Amar, 2005). For first-order reactions, the half-life does not depend on the initial reagent concentration but only on the rate constant. The half-life time was calculated for the three catalyst dose as

$$t_{1/2(\mathrm{MB}0.02g/L)} = \frac{\ln 2}{k} = \frac{0.693}{0.1843\,\mathrm{min}^{-1}} = 3.76\,\mathrm{min} \tag{6}$$

$$t_{1/2(\mathrm{MB}0.03g/L)} = \frac{\ln 2}{k} = \frac{0.693}{0.1604\,\mathrm{min}^{-1}} = 4.32\,\mathrm{min} \quad (7)$$

$$t_{1/2(\mathrm{MB}0.04g/L)} = \frac{\ln 2}{k} = \frac{0.693}{0.1244\,\mathrm{min}^{-1}} = 5.57\,\mathrm{min} \quad (8)$$

This results illustrated that MB rate decreased with increasing the catalyst concentration, working with the same photocatalysis conditions.

4. Conclusions

The heterogeneous photocatalysis processes have a net benefit in the degradation of some contaminants from the aqueous medium (dyes, microorganisms, toxins, pollutants), including: non-selective degradation of pollutants (organic or inorganic) to very low concentrations (ppb), normal pressure and temperature, use of oxygen as the primary oxidant, the possibility of simultaneous induction of both oxidation reactions and reduction reactions.

In the present paper we reported a microstructured ZnO-CeO_2 oxide powder with good photocatalytic activity for the degradation of some organic dyes (methylene blue, crystal violet and phenol red), which are usually less affected by ultraviolet radiation.

One advantage is that this material has good photocatalytic properties, is easy to prepare, and can be used successfully in removing organic pollutants from the water.

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STUDII PRIVIND DESCOMPUNEREA FOTOCATALITICĂ A UNOR COLORANȚI ORGANICI FOLOSIND OXIZI METALICI MEZOPOROȘI

(Rezumat)

În acest studiu este prezentată comportarea la iradiere cu radiație ultravioletă a trei coloranți (albastru de metilen, roșu de fenol și cristal violet) în prezența unui material oxidic mezoporos pe bază de $ZnO\text{-}CeO_2$.

Cei trei coloranți au fost degradați la leucoderivații corespunzători în diferite intervale de timp, astfel: albastru de metilen (de concentrație 10^{-5}M) în 25 min, cristal violet (de concentrație $2\cdot10^{-5}$M) în 90 min și roșu de fenol (de concentrație $4.5\cdot10^{-5}$M) în 140 min. De asemenea, gradul de fotodegradare a arătat că MB și CV s-au degradat în procent de 98% iar RF doar 78%. De asemenea, a fost investigată influența concentrației fotocatalizatorului asupra vitezei de reacție pentru MB.