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PHOTOCATALYTIC DEGRADATION OF CATIONIC TRI-ARYLMETHANE DYE - METHYL VIOLET 10B ON ZnS CATALYSTS UNDER UV IRRADIATION

BY

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Abstract. The presence of tri-arylmethane dyes in waste water is an issue of major concern due to the toxic potential to the environment. The conversion of these pollutants into mineral products with minimal energy is a major goal of the world scientific community. In this study, we investigate the photocatalytic degradation under UV light of Methyl Violet 10B, a complex dye with antibacterial, anthelmintic and antifungal effects, used in local administration or in the textile industry. The reaction conditions (irradiation time, radiation nature and catalyst loading) were evaluated in order to obtain an optimum time to discolouration, the results suggesting that the used ZnS can be successfully used to degrade the Methyl Violet 10B dye.

Keywords: Methyl Violet 10B; photocatalysis; ZnS catalysts; UV light; wastewater.

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1. Introduction

In recent years, many research laboratories have focused on reducing the quantity of colored organic compounds from wastewater by photo-catalytic methods. The use of these methods is due to the fact that they are easy to apply, financially accessible and also because photo-catalytic materials have low toxicity towards the environment. Methyl Violet 10B dye is a Tri-Aryl-methane cationic compound with multiple uses; it is an antibacterial reagent (active for both gram-positive and gram-negative bacteria), presents anthelmintic and antifungal properties, being used in local administration as treatment for skin infections of bacterial or mycotic origin. It is also used as additive in prevention and treatment of Chaga disease. As an industrial reagent, it is used in textile industry, for coloring paper and some products such as fertilizers, anti-freeze materials, detergents, constituents in blue or black inks for ballpoint pens. Methyl-Violet 10B is a toxic compound for aquatic creatures (Docampo and Moreno, 1990; Tonogai *et al*., 1982), in large quantities, localizing in the gills and can even suppress their functioning. However, due to its antimicrobial activity, MV 10B is used for the treatment of skin and eye infections for animals and sometimes for fish, but in many countries it is not accepted for use in aquaculture (Arbiser *et al.*, 2009). To eliminate this dye (with low biodegradability) from waste water, various techniques are used, such as: adsorption on different adsorbent materials (Bajpai and Jain, 2012) or photocatalytic techniques, knowing that this type of dyes is quite sensitive to ultraviolet radiation, which leads to de-methylation and, in the presence of oxygen, to oxidation. The process is taking place with higher rate in the presence of semiconductor materials with photocatalytic properties (Chandraboss *et al*., 2015, Saeed *et al*., 2017). Also, more complex degradation methods, such as plasma gliding arc (Tiya-Djowe *et al*., 2015) or using nano-zeolites (Shojaei *et al.*, 2019) or photocatalytic methods (Ameur *et al*., 2019; Ranjith *et al*., 2019) were used. ZnS is a photo-catalytic material with low toxicity and multiple uses due to the UV activity that can be extended, by suitable doping, in the visible domain, being a good choice for different applications such as solar cells, photoluminescence, OLEDs, photo-catalytic decontamination or biomedical applications (Dafeh *et al*., 2019; Nayakm and Choudhary, 2019; Palanisamy *et al*., 2019).

2. Experimental

Zinc sulfide was synthesized in our laboratories using a hydrothermal method. The used reagents were: Thiourea ($(NH_4)_2CS$), zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), and Poly (vinyl alcohol) (Sigma-Aldrich). For all experiments bidistilled water was used.

The used dye-reagent was Methyl Violet 10B (Sigma Aldrich), a cationic compund type Tri-Arylmethane with a molar weight of 407.99 g·mol^{-1}, presenting an UV-Vis absorption maximum peak at 590 nm; (IUPAC name: N-[4-[bis[4-dimethyl-amino)-phenyl]-methylene]-2, 5-cyclohexadien-1-ylidine]-N-methyl-methanaminium chloride). Its structure is presented in Fig. 1.

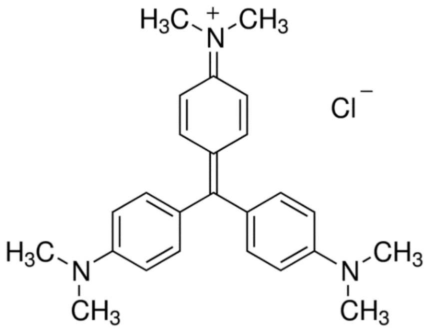

Fig. 1 – MV 10B structure.

The initial solution of MV 10B, having a concentration of (2.5·10^{-4} mol/L) was dilluted until the value of (1.25·10^{-5} mol/L ≈ 5ppm), which is the concentration of the solutions used for photo-degradation process. The pH value, measured with a Biobase PH-20S pH-meter was 6.5.

Photocatalytic tests were analyzed at room temperature, using previously presented materials and bidistilled water. The photocatalyst concentration in the analyzed systems varied from 0.02 g/L to 0.06 g/L. Initially, the system consisting of the dye solution and ZnS was kept in the dark for 30 min, with continuous stirring, to establish the adsorption-desorption balance between the solid surface and the dye molecules. After 30 min, the systems were irradiated with UV radiation (λ = 254 nm) produced by a Phillips lamp (18 W). The intensity of UV radiation was measured with a Hamamatsu UV sensor - C9536-01 (controller) + H9958 (detector 310-380 nm, 1 µW/cm^2 – 100 mW/cm^2), the average value being 2.1 W/m^2. The lamp was placed 20 mm from the surface of the reaction mixture.

For specific time intervals, 4 mL of the mixture was taken out of the solution, was centrifuged to remove ZnS and then UV-Vis analysed. Each experiment was performed 2 times in order to verify the reproducibility of the results. The degradation efficiency (R, %) was calculated according to the equation.

$$R(\%) = \frac{A_0 - A_i}{A_0} \times 100 \quad (1)$$

where, A_0 and A_i are the dye absorbance before and after photo-irradiation.

3. Results and Discussions

The effectiveness of ZnS for Methyl Violet 10B degradation (MV 10B) was measured as the ratio between the absorbance values at different time intervals to the initial absorbance (Liu *et al.*, 2013). The degradation rate of the MV 10B solution depending on the time of reaction with ZnS nanoparticles is graphically shown in Fig. 2. It was shown that the presence of the synthesized ZnS nanoparticles initiated the degradation process of MV 10B which then, gradually increased in time.

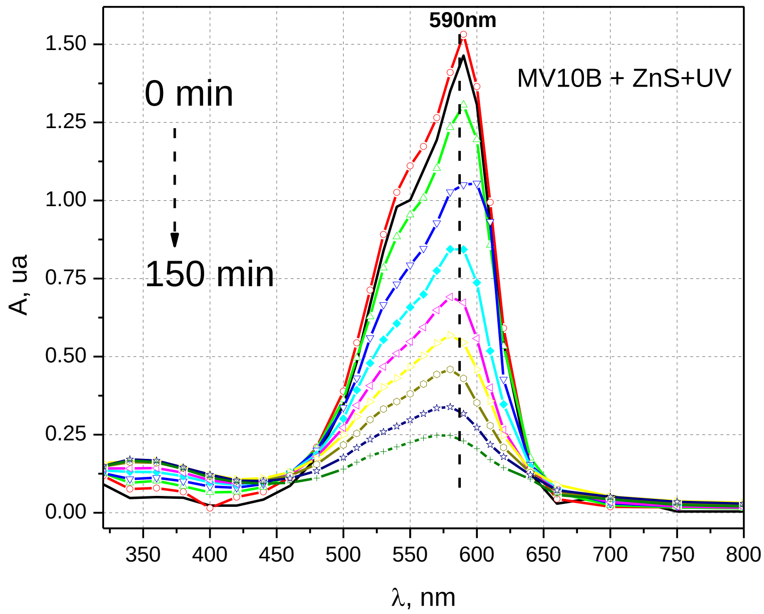

Fig. 2 – UV-Vis evolution spectra in time for MV 10B.

It was observed that, at light irradiation, the intensity of the adsorption band at 590 nm of MV 10B decreased rapidly. The amplitude of the absorption band decreases with the increasing of irradiation time. This indicates the photocatalytic potential of the synthesized ZnS, established by degrading the characteristic species of color absorption (chromophores) from the dye (Tiya-Djowe *et al.*, 2015). It should be noted that discolouring the dyes when adding nanoparticles and exposure to ultraviolet light were considered results of the dye degradation.

Analysing the obtained values for the absorption ratio (A_i/A_0) for the irradiation behaviour of the systems: (1) MV 10B 5ppm + ultraviolet radiation + ZnS 30 ppm, (2) MV 10B 5 ppm + visible light irradiation + ZnS 30 ppm and (3) MV 10B + UV light without catalyst, it is observed that for the last two systems there are no significant changes, while for the first one, there is a major discoloration of the analysed system (Fig. 3).

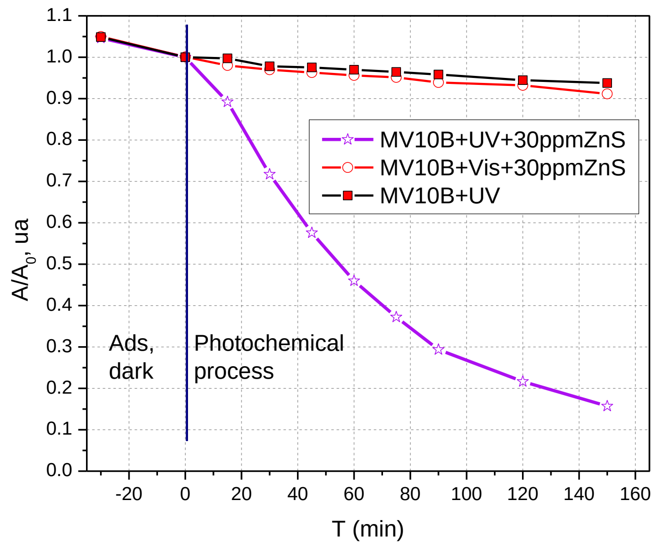

Fig. 3 – A/A_0 curves for MV 10B – ZnS system.

For 150 min irradiation time, only 6% of the initial dye was degraded in the presence of ultraviolet radiation without catalyst, 8.9% of the dye was degraded in the presence of the catalyst and visible light radiation, compared to about 85% in the case of photocatalysis (Fig. 4).

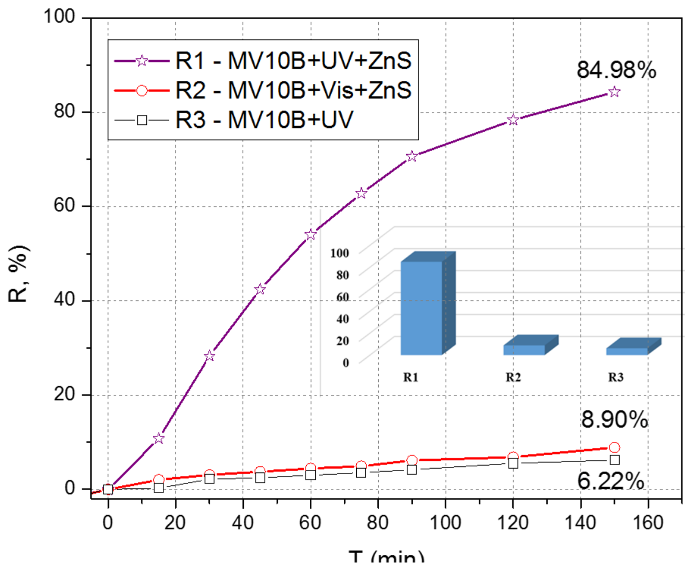

Fig. 4 – R(%) for MV 10B – ZnS system.

The effects of the photocatalyst dose were studied for 0.02 g/L, 0.03 g/L, 0.04 g/L and 0.06 g/L, using a solution containing 5 ppm dye for time exposure of 150 min. The results are shown in Fig. 5.

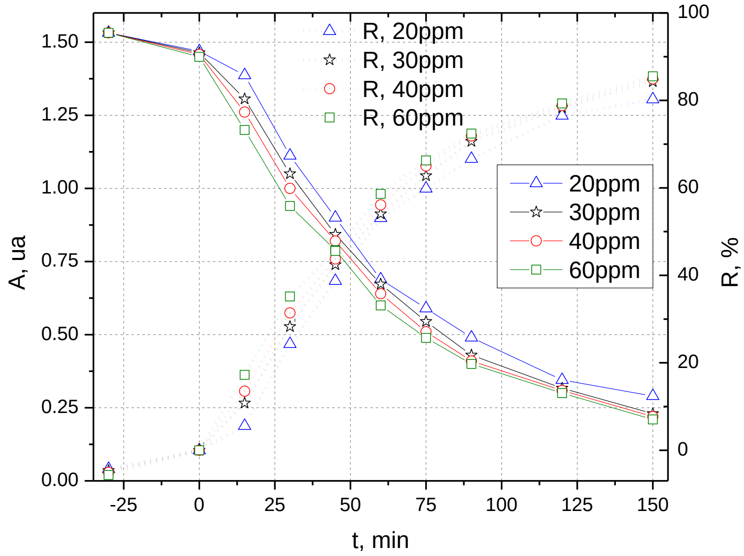

Fig. 5 – The effect of the photocatalyst concentration.

The photo-degradation process constantly increases with the increasing of photocatalyst concentration. There are slight differences regarding the photocatalytic action of ZnS related to the used dose. Thus, for a concentration of 20 ppm ZnS, the degradation efficiency is 80.25%, 84.28% for 30 ppm, 84.91% for 40 ppm and 85.51% for 60 ppm ZnS.

Although the obtained efficiency degradation values are slightly increased with the increasing of ZnS dose, it was preferred to use a concentration of 0.03g ZnS/L solution, ie 30 ppm ZnS, since the addition of a larger quantity of ZnS is not justified, due to economic and environmental protection considerations.

Based on the above, a possible explaining mechanism for the photo-catalytic properties of ZnS can be described by the Eqs. (2) - (7) (Tie *et al.*, 2019) presented below:

$$ZnS + h\nu \rightarrow ZnS(e^-_{CB}) + ZnS(h^+_{VB}) \quad (2)$$

$$e^-_{CB} + O_2 \rightarrow O_2^{-\cdot} \quad (3)$$

$$h^+_{VB} + H_2O \rightarrow HO^{\cdot} + H^+ \quad (4)$$

$$O_2^{-\cdot} + \text{dye} \rightarrow \text{degradation products} \quad (5)$$

$$HO^{\cdot} + \text{dye} \rightarrow \text{degradation products} \quad (6)$$

The general photo-catalytic reaction is:

$$C_{25}H_{30}N_3Cl + 36O_2 \xrightarrow{\text{ZnS ,UV }(h\upsilon > E_g)} 25CO_2 + 13H_2O + 3HNO_3 + HCl \quad (7)$$

Under the incidence of UV radiation, e^-/h^+ pairs are generated in ZnS particles, the holes being situated in the valence band and the electrons in the conduction band (CB). The e^-/h^+ pairs determine the formation of reactive (unstable) species $O_2^{-\cdot}$, $HO^{\cdot}$ which rapidly react with the dye MV 10B, leading to its degradation.

4. Conclusions

In this study, the possibility of using ZnS for the degradation of some Tri-Arylmethane - MV 10B organic compounds from wastewater was analysed, the experimental data suggesting that ZnS presents a good photo-catalytic action (R = 84.98%).

The reaction systems were studied for 150 min, at the natural pH value of the solution, resulting that the percentage of photo-degradation process increases with the increasing of ZnS concentration.

Considering that both the concentration of the photo-catalyst (30 ppm) and the used dose of ultraviolet radiation (2.1 mW/cm^2) were very low, it can be concluded that ZnS can be successfully used to remove some dyes from waste waters.

REFERENCES

Ameur S.B, BelHadjltaief H., Duponchel B., Leroy G., Amlouk M., Guermazi H., Guermazi S., *Enhanced Photocatalytic Activity Against Crystal Violet Dye of Co and Indoped ZnO thin Films Grown on PEI Flexible Substrate under UV and Sunlight Irradiations*, Heliyon, **5** (2019).

Arbiser J.L., *Gentian Violet is Seif*, J. Am Acad Dermatol, **61**, *2*, doi: 10.1016/j.jaad.2009.03.029 (2009).

Bajpai S.K., Jain A., *Equilibrium and Thermodynamic Studies for Adsorption of Crystal Violet onto Spent Tea Leaves (STL)*, Water, **4**, 52-71 (2012).

Chandraboss V.L., Kamalakkannan J., Prabha S., Senthilvelan S., *An Efficient Removal of Methyl Violet from Aqueous Solution by an AC-Bi/ZnO Nanocomposite Material*, RSC Advances, **33** (2015).

Dafeh S.R., Iranmanesh P., Salarizadeh P., *Fabrication, Optimization, and Characterization of Ultra-Small Superparamagnetic Fe_3O_4 and Biocompatible Fe_3O_4@ZnS Core/Shell Magnetic Nanoparticles: Ready for Biomedicine Applications,* Materials Science and Engineering: C, **98**, 205-212 (2019).

Docampo R., Moreno S.N., *The Metabolism and Mode of Action of Gentian Violet*, Drug Metab Rev., **22**, *2-3*, 161-78 (1990).

Liu S., Wang X., Zhao W., Wang K., Sang H., He Z., *Synthesis, Characterization and Enhanced Photocatalytic Performance of Ag_2S-Coupled ZnO/ZnS Core/Shell Nanorods*, Journal of Alloys and Compounds, **568**, 84-91 (2013).

Nayakm D., Choudhary R.B., *Augmented Optical and Electrical Properties of PMMA-ZnS Nanocomposites as Emissive Layer for OLED Applications*, Optical Materials, **91**, 470-481 (2019).

Palanisamy G., Bhuvaneswari K., Chinnadurai A., Bharathi G., Pazhanivel T., *Magnetically Recoverable Multifunctional ZnS/Ag/$CoFe_2O_4$ Nanocomposite for Sunlight Driven Photocatalytic Dye Degradation and Bactericidal Application*, Journal of Physics and Chemistry of Solids, (https://doi.org/10.1016/j.jpcs.2019.109231) (2019).

Ranjith R., Renganathan V., Chen S.-M., Selvan N.S., Rajam P.S., *Green Synthesis of Reduced Graphene Oxide Supported TiO_2/Co_3O_4 Nanocomposite for Photocatalytic Degradation of Methylene Blue and Crystal Violet*, Ceramics International, **45**, *10*, 12926-12933 (2019).

Saeed K., Khan I., Gul T., Sadiq M., *Efficient Photodegradation of Methyl Violet Dye Using TiO_2/Pt and TiO_2/Pd Photocatalysts*, Appl Water Sci, **7**, 3841-3848, DOI 10.1007/s13201-017-0535-3 (2017).

Shojaei S., Ahmadi J., Farahani M.D., Mehdizadeh B., Pirkamali M., *Removal of Crystal Violet Using Nanozeolite-X from Aqueous Solution: Central Composite Design Optimization Study*, J. Water Environ. Nanotechnol., **4**, *1*, 40-47 (2019).

Tie L., Sun R., Jiang H., Liu Y., Xia Y., Li Y.-Y.. Chen H., Yu C., Dong S., Sun J., Sun J., *Facile Fabrication of N-Doped ZnS Nanomaterials for Efficient Photocatalytic Performance of Organic Pollutant Removal and H_2 Production*, Journal of Alloys and Compounds, **807**, 151670 (2019).

Tiya-Djowe A., Acayanka E., Lontio-Nkouongfo G., Laminsi S., Gaigneaux E.M., *Enhanced Discolouration of Methyl Violet 10B in a Gliding Arc Plasma Reactor by the Maghemite Nanoparticles Used as Heterogeneous Catalyst*, Journal of Environmental Chemical Engineering, **3**, *2*, 953-960 (2015).

Tonogai Y., Ogawa S., Ito Y., Iwaida M., *Actual Survey on TLm (Median Tolerance Limit) Values of Environmental Pollutants, Especially on Amines, Nitriles, Aromatic Nitrogen Compounds and Artificial Dyes*, J. Toxicol. Sci., **7**, *3*,193-203 (1982).

DEGRADAREA FOTOCATALITICĂ A COLORANTULUI CATIONIC TRI-ARILMETAN - METIL VIOLET 10B PE CATALIZATORI ZnS CU RADIAȚIE UV

(Rezumat)

Prezența coloranților de tip tri-arilmetan în apele uzate este o problemă îngrijorătoare majoră datorită potențialului toxic al acestora pentru mediu. Transformarea acestor poluanți în produse minerale cu consum energetic minim, este un obiectiv prioritar al comunității științifice mondiale. În acest studiu, s-a investigat procesul de degradare fotocatalitică sub lumina UV a colorantului Metil Violet 10B, un colorant complex cu efecte antibacteriene, antihelmintice și antifungice, utilizat în administrația locală sau în industria textilă. Variind condițiile de reacție (timpul de iradiere, natura radiațiilor și concentrația catalizatorului) pentru a obține un timp optim de decolorare și analizând rezultatele, se concluzionează că sulfura de zinc folosită poate fi utilizată cu succes pentru a degrada colorantul Metil Violet 10B.