

Band reactor for toxic and recalcitrant water contaminants

Bożena Czech, Wiesława Ćwikła-Bundyra

Maria Curie-Skłodowska University, Faculty of Chemistry, Department of Environmental Chemistry, pl. M. Curie-Skłodowska 3, 20-031 Lublin, Poland, e-mail: czech.bozena@poczta.onet.pl

This paper deals with the problem of the photocatalytic reactor construction. The supported TiO_2 on $\gamma\text{-Al}_2\text{O}_3$ modified with Mo or V addition was used as the photocatalyst, whereas phenol and formaldehyde were chosen as the model pollutants. The counter – current contact of reagents and catalysts is the main advantage of the construction and enables a significant COD reduction of the highly concentrated wastewaters.

Keywords: photocatalysis, photoreactors, $\text{Me-TiO}_2/\text{Al}_2\text{O}_3$, wastewater treatment, phenol, formaldehyde

Presented at VII Conference Wasteless Technologies and Waste Management in Chemical Industry and Agriculture, Międzyzdroje, 12 – 15 June, 2007.

INTRODUCTION

Traditional oxygen processes in biological treatment are not sufficient enough for the removal of industrial wastewaters' pollutants because the chemicals present in wastes are toxic for the activated sludge and the biological membrane of the bed. The biological methods are useful only for the pre-treatment of some types of wastewaters e.g. from knitting or food industry, because beyond the non-biodegradable compounds they consist of the substances yielding to enzymatic decomposition. These processes, however, are long - lasting and cause the BOD reduction but do not change the other water factors e.g. COD, TOC¹.

Heterogeneous photocatalysis with suspended semiconductors: TiO_2 , ZnO , SnO_2 , WO_3 , CdS , ZnS , CdSe , CdTe is a method recently gaining more interest in the organic and inorganic pollutants' removal from the air and water²⁻⁵. The main advantage of this method is that most organic and some inorganic pollutants can be destroyed into CO_2 and H_2O and inorganic acids or transformed into less toxic products working only at room temperature and pressure⁶.

Many factors exert influence on photodegradation: the type of the semiconductor, its surface, light intensity, dissolvent, temperature, pH and the substances present in the solution. Catalysis is applied for the decomposition of the organic compounds containing halogens, nitrogen and sulphur e.g. polychlorinated biphenyls (PCB), pesticides, dioxins, alcohols, aldehydes, ketones, carboxylic acids, ethers, amines, thioethers, merkaptans⁷⁻⁸.

As the catalysts of the mineralization of all organics TiO_2 is chosen, but when used in the form of powder causes a lot of problems with separation after the process. Phenol and formaldehyde are common industrial wastewaters contaminants, therefore, they were chosen as the representatives for the photocatalytic oxidation.

In all the photocatalytic processes two main types of reactors are used:

- with the catalyst immobilized on stationary elements: e.g. nylon fiber net or the reactor walls
- with the catalyst dispersed in the reactor¹³.

The first manner is connected with the replacement of the parts of the apparatus when the catalyst is changed, whis is not only time-consuming but also expensive. There-

fore, the great attention is paid to the reactors having suspended catalysts.

The reactors in the form of tubes, ring and spiral reactors, made out of glass, quartz or plexiglass were used for the photocatalytic oxidation⁹. The lamp is placed inside¹¹, at the top¹⁴, aside¹⁵ or at the bottom¹⁶.

EXPERIMENTAL

The experiments of the photocatalytic degradation of organics in wastewaters were conducted in the band reactor of our construction (Fig. 1.). Into the reactor the mixture of oxygen ($3\text{dm}^3/\text{h}$) and nitrogen ($37\text{dm}^3/\text{h}$) was pumped because the aeration is usually used to prevent or hinder the charge carriers' recombination⁹.

In the counter – current the sample of the wastewaters with the COD value of about $3000\text{mgO}_2/\text{dm}^3$ was pumped in with the peristaltic pump. This COD value is typical for the real wastewaters and simultaneously exceeds the norms, which may indicate highly concentrated (according to the COD) wastewaters. The $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalysts modified with Mo or V were prepared with the procedure described in¹⁰. A catalyst ca. $8\text{g}/\text{h}$, which corresponds to $0.43\text{g TiO}_2/\text{h}$, was placed inside the reactor.

As the oxidizing agents oxygen (from air) and H_2O_2 were selected. The effectiveness was measured in a few configurations: $\text{TiO}_2/\text{UV}/\text{O}_2/\text{H}_2\text{O}_2$, $\text{TiO}_2/\text{O}_2/\text{H}_2\text{O}_2$, $\text{TiO}_2/\text{UV}/\text{O}_2$, TiO_2/O_2 . The $\text{TiO}_2/\text{Al}_2\text{O}_3$ modified with different metals: Co, Mo, were used as the catalysts. Phenol and formaldehyde are widely used in industry and are common in industrial wastewaters. Phenol is also a typical model pollutant studied in photocatalytic oxidation.

The measurements were conducted at room temperature. The sample was taken back after 115 minutes assuming that by the volumetric flow $1.3\text{dm}^3/\text{h}$, the whole sample would be pumped out. The system with a single run or two hours' time is used very often¹¹. The next stage was the analysis of organic compound concentration using the COD method with the dichromate method¹², which is a standard water analysis.

RESULTS AND DISCUSSION

Before the planning of the reactor there was a problem with a proper form of the catalysts. In the suspended form, TiO_2 , needs to be mixed adequately and separated after

the process. The supported TiO_2 could be a solution. Sakhtivel et al.¹⁷ indicated that the high effectiveness of Acid Brown 14 oxidation over $\text{TiO}_2/\text{Al}_2\text{O}_3$ is ascribed to the adsorption properties of the Al_2O_3 support. In order to prevent recombination or to decrease the rate of recombination the factor close to the catalysts surface can be applied. This incorporates the more effective adsorption places, located close to the catalysts' surface. Generated by oxidants ($^{\circ}\text{OH}$) in this way h^+ can reach them before the intermediate products would yield to further reaction that takes place in the presence of strong adsorbents.

The reactor was designed from the organic glass transparent and resistant to the UV light. Two tubes were placed below the UV lamp (254 nm, 50 Hz). The intensity of the UV light was measured by the VLX254 Radiometer (Vilber Lourmat, 254 nm) (Fig.1a and b).

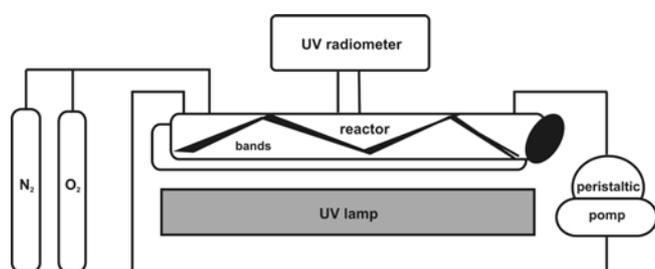


Figure 1a. A scheme of an apparatus for the photooxidation of organic compounds in the water

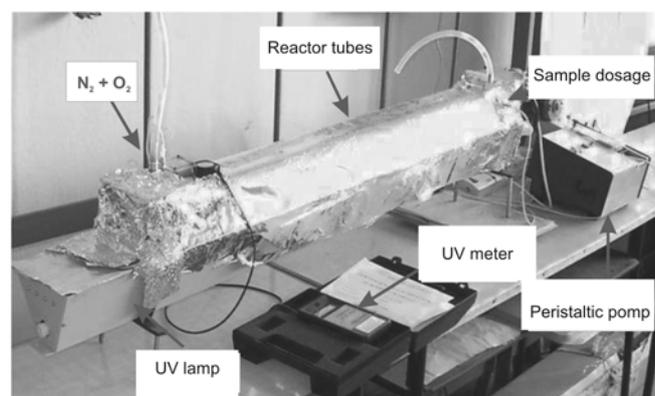


Figure 1b. The reactor for the photocatalytic wastewater treatment

In the reactor the bands are the main mixing system and enable the counter-current contact of reagents.

The obtained catalysts contain 5.34% of TiO_2 in the form of anatase and 2.35 – 3.51% of Mo with the total surface area in the range 59.3 – 70.3 m^2/g or 3.14 – 4.82% of V with the total surface area in the range 59.4 – 71.3 m^2/g (Table 1). The most active catalysts in phenol and formaldehyde removal were $\text{V-TiO}_2/\text{Al}_2\text{O}_3$ (Fig.2) and

enable at least 75% COD reduction in the photocatalytic oxidation. The best results for wastewater treatment were obtained using the H_2O_2 addition with the UV irradiation but the results were close to those obtained for the oxidation with only H_2O_2 , which may indicate that these catalysts are more sensitive to the presence of H_2O_2 than the UV light.

A significant decrease in the efficiency of the photocatalytic methods in the HCHO removal was observed over V catalysts; Mo addition has a various effect. During the photocatalytic oxidation of HCHO H_2O_2 causes deeper COD reduction, especially in the case of the $\text{V-TiO}_2/\text{Al}_2\text{O}_3$ catalysts. Over the catalysts demonstrating a small amount of V the oxidation proceeds over TiO_2 . Mo addition to the catalyst affects the oxidation positively. During the aeration of the wastes the presence of Mo has a detrimental effect. The $\text{Mo-TiO}_2/\text{Al}_2\text{O}_3$ catalysts are more sensitive to the H_2O_2 presence than the UV. With increasing the amount of V in the catalysts, the efficiency of oxidation with H_2O_2 is higher, but the efficiency of the photocatalytic oxidation is decreased.

CONCLUSION

The main advantage of the reactor was the counter-current contact of reagents and uniform access of the light to the catalyst. The obtained min. 60% of the COD reduction of the highly concentrated wastewaters (having COD 3000 mg/dm^3) is enough to sustain the law requirements. The most active catalysts in phenol and formaldehyde removal were $\text{V-TiO}_2/\text{Al}_2\text{O}_3$. The effect of oxidant addition is dependent on the type of the catalysts, the modifier and the pollutant. The obtained results, which may indicate that the catalysts are more sensitive to the presence of H_2O_2 than that of the UV light.

LITERATURE CITED

- (1) Zarzycki R. (Editor): Zaawansowane techniki utleniania w ochronie środowiska, PAN, Oddział w Łodzi, Komisja Ochrony Środowiska, Łódź, 2002.
- (2) Herrmann J.-M.: Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants, *Catalysis Today*, 1999, 53, 115.
- (3) Ertl G., Knözinger H., Weitkamp J. (Eds.): Handbook of Heterogeneous Catalysis, Vol. 4, VCH Wiley, Weinheim, 1997.
- (4) Centi G., Ciambelli P., Perathorner S., Russo P.: Environmental catalysis: trends and outlook, *Catalysis Today*, 2002, 75, 3.
- (5) Courty P. R., Chauvel A.: Catalysis, the turntable for a clean future, *Catalysis Today*, 1996, 29, 3.
- (6) Pelizzetti E.: Concluding remarks on heterogeneous solar photocatalysis, *Solar Energy Materials and Solar Cells*, 1995, 38, 453.

Table 1. The physicochemical properties of the catalysts

Catalyst		TiO_2 content [%wt.]	Metal content [%wt.]	Total surface area, S [m^2/g]
$\text{Mo-TiO}_2/\text{Al}_2\text{O}_3$	Mo-1	5.34	2.35	62.6
	Mo-2	5.34	2.53	59.3
	Mo-4	5.34	3.02	63.8
	Mo-8	5.34	3.38	66.1
	Mo-16	5.34	3.51	70.3
$\text{V-TiO}_2/\text{Al}_2\text{O}_3$	V-1	5.34	3.45	69.2
	V-2	5.34	3.74	66.4
	V-4	5.34	4.82	59.4
	V-8	5.34	4.40	71.3
	V-16	5.34	3.14	65.0

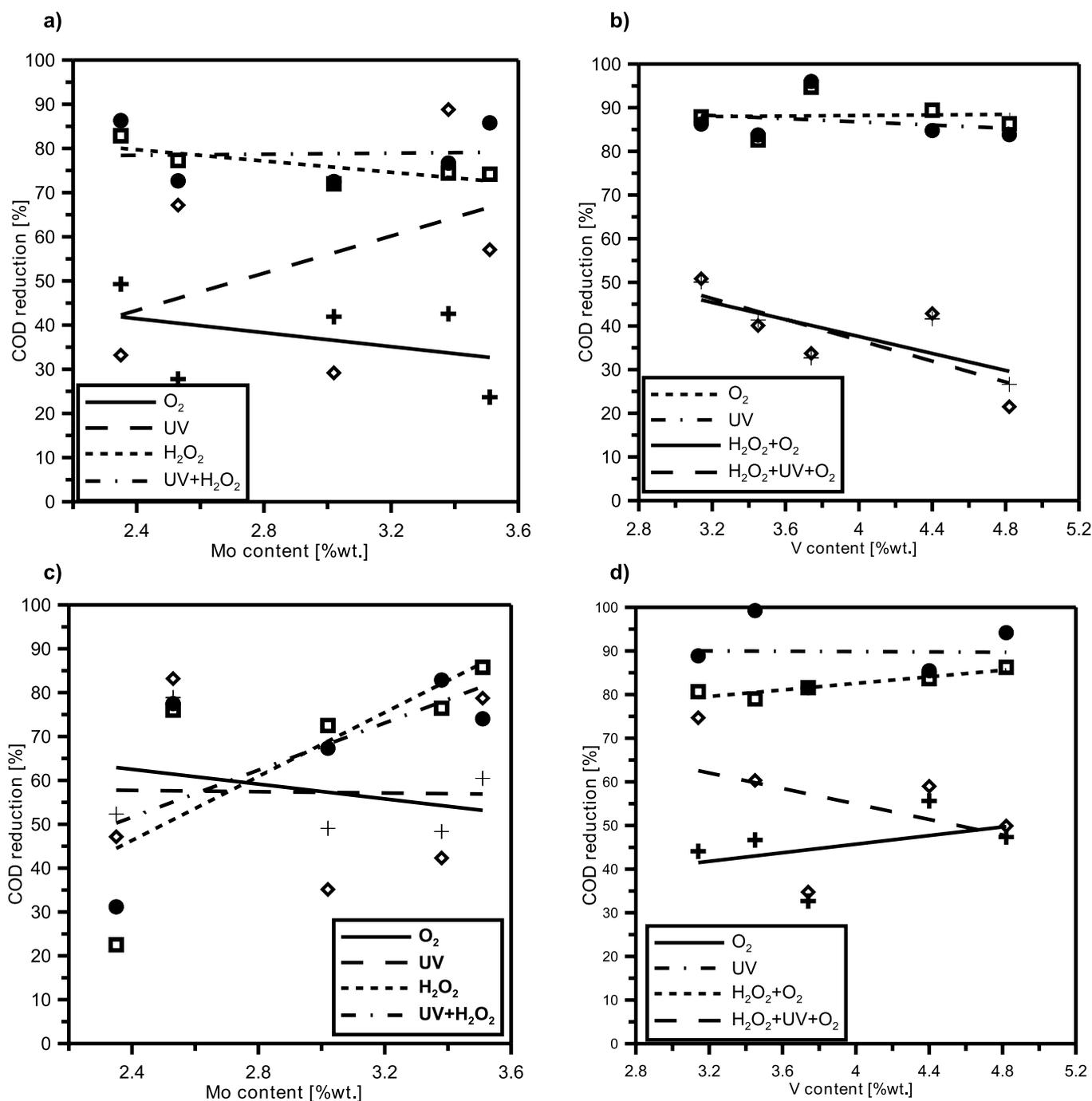


Figure 2. The COD changes of wastewaters containing formaldehyde (a and b) and phenol (c and d) over Mo- $\text{TiO}_2/\text{Al}_2\text{O}_3$ (a and c) and V- $\text{TiO}_2/\text{Al}_2\text{O}_3$ (b and d)

(7) Inui T.: Recent advance in catalysis for solving energy and environmental problems, *Catalysis Today*, **1999**, 51, 361.

(8) Mills A., Le Hunte S.: An overview of semiconductor photocatalysis, *Journal of Photochemistry Photobiology A: Chemistry*, **1997**, 108, 1.

(9) Gogate P. R., Pandit A. B.: A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, *Advances in Environmental Research*, **2004**, 8, 501.

(10) Czech B., Nazimek D.: Zastosowanie zaawansowanych procesów utleniania do oczyszczania wód i ścieków, *Przemysł Chemiczny*, **2006**, 8 – 9, 1005.

(11) Chen J., Ollis D. F., Rulkens W. H., Bruning H.: Photocatalyzed oxidation of alcohols and organochlorides in the presence of native TiO_2 and metallized TiO_2 suspensions. Part (I): photocatalytic activity and pH influence, *Water Research*, **1999**, 33, 661.

(12) Polish Norm PN-74/C-04578/03.

(13) Ray A. K.: A new photocatalytic reactor for destruction of toxic water pollutants by advanced oxidation process, *Catalysis Today*, **1998**, 44, 357.

(14) Morawski A. W., Radyno-Książkiewicz K., Grzechulska J.: Fotokatalityczny labiryntowy reaktor przepływowy do usuwania fenolu z wody; *Gaz, woda i technika sanitarna*, **2002**, 6, 216.

(15) Gupta H., Tanaka S.: Photocatalytic mineralisation of perchloroethylene using titanium dioxide, *Water Science and Technology*, **1995**, 31 (1995) 47.

(16) Czech B.: Photocatalytical reduction of organic water pollutants over K- $\text{TiO}_2/\text{Al}_2\text{O}_3$ and Fe- $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalysts, XXXVII Ogólnopolskie Kolokwium Katalityczne, Kraków 15 – 18 marca **2005**, 32.

(17) Sakthivel S., Shankar M. V., Palanichamy M., Arabindoo B., Murugesan V.: *J. Photochemistry, Photobiology A: Chemistry*, **2002**, 148, 153.