ADVANCED CATALYTIC MATERIALS OBTAINED FROM WASTE FOR WASTEWATER TREATMENT APPLICATIONS

Iasmina- Florina BURLACU[1], György DEÁK[2], Lidia FAVIER[3], Ingrid Proriol SERRE[4], David BALLOY[4]

In the present work is presented a reusable support material based on waste, photo catalytically functionalized with zinc oxide film. The obtained immobilized catalyst was structurally characterized using SEM equipment and successfully used in the photocatalytic degradation of an organic compound present in aqueous solutions with yields of over 97%. The proposed catalytic material is important in the context of the circular economy and sustainable development by restoration in the economic circuit of some waste into functional products with wastewater treatment applications, thus contributing to the preservation of water resources and to the smart waste management.

Keywords: reusable catalytic material, waste, circular economy, wastewater treatment, heterogeneous photo catalysis

1. Introduction

Clean and safe water, free of toxic materials, carcinogens and harmful bacteria, is necessary for human health. According to the United Nations World Water Development Report from 2018, the demand for clean water will increase by almost a third by 2050 [1]. Clean water is an elementary primary requirement in a variety of crucial industries, for example electronics, food and pharmaceuticals. A rapidly growing population and a constantly improving industrialization have made the wastewater problem vital in recent years and have therefore led to the need to develop research on Advanced Oxidation Processes (AOPs). There are many researches into the development of sustainable water treatment techniques that can improve water quality, thus the unavailability of drinking water is a crucial problem especially in regions where conventional drinking water treatment systems failed to degrade emerging pollutants, toxic metal ions and industrial waste present in the aquatic environment. Research and development in this field have given rise to a new class of processes called AOPs,

[1] Eng. PhD. Student, Faculty of Material Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: iassminaa@yahoo.com
[2] Eng. PhD. Habil., National Institute for Research & Development in Environmental Protection-Bucharest, Romania, e-mail: dkrcontrol@yahoo.com
[3] Prof., Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France, e-mail: lidia.favier@ensc-rennes.fr
[4] Prof., Univ. Lille, Unité Matériaux et Transformations- UMET, CNRS, INRAE, UMR 8207 - F-59000 Lille, France, e-mail: ingrid.proriol-serre@univ-lille.fr, david.balloy@univ-lille.fr

especially heterogeneous photo catalysis, which converts photonic energy into chemical energy. Advances in technology in this area have improved the ability to specifically develop and adapt the properties of photocatalytic materials used in this area. Therefore, in order to meet the demand for water supply, more and more efforts are being made to develop new methods and materials for wastewater treatment. The need for continuous development of new support materials for the immobilization of photocatalytic semiconductors used in the degradation of organic pollutants in wastewater, has gained an important place in the last decade, due to the many advantages they have compared to suspended catalytic powders [2, 3, 4, 5, 6, 7]. This paper objective was to obtain some new oxide support materials by waste recovery, in order to use them in the removal of emerging compounds from wastewater [8], especially pharmaceutical compounds through Advanced Oxidation Processes (AOPs) -heterogeneous photo catalysis. This material is important in the context of the circular economy and sustainable development by restoration in the economic circuit of some waste [9].

2. Experimental. Materials and methods

The catalyst materials were obtained in two technological steps as it follows- first step consisting in the accomplishment of the support materials from Waste from Electrical and Electronic Equipment (WEEA), waste glass from end-of-life fluorescent lamps, agricultural fertilizer Epsom salt ($MgSO_4$) as binder and eggshells as foaming agent. The material consists of a backing material with the following composition expressed in mass percentages: 86 ... 94 % glass waste, 5 ... 10% waste eggshells added as a foaming agent and 1….4 % anhydrous Epsom salt added as a binder, and on the surface of the obtained support material is deposited and stabilized Zn oxide powder in a mass ratio between 1/1000 ... 5/1000. The procedure of work has the following steps:

1. obtaining the support material by washing and drying glass and eggshells, grinding them, along with Epsom salt in a planetary mill with balls, until the entire amount of powder passes through 63 μm mesh sieve, cold powder pressing under capsule form, drying the capsules at a temperature between 100 ... 150 ° C for 24 h and then synthesized at a temperature of 750 ° C with a level of 1 ... 3 h;
2. ZnO deposition on the surface of the material spongy support by orbital shaking of the oxide powder previously dispersed in ultrapure water, in mass ratio between 1/1000 ... 5/1000 and subsequently fixed by autoclaving at a temperature between 110 ... 150 ° C, for up to 1 hour, and finally the composite material SpongeMat/ZnO is dried at a temperature between 90 ... 150 ° C for 1 ... 2 h.

The resulted catalytic materials were studied to investigate the microstructural development with back scattered electron imaging (BSE) mode in a scanning electron microscope (model FLEXSEM 1000). In order to reduce

electrical charging of non- conducting specimens that could be induced by the incident electron beam, all sample surfaces were sputter coated with chromium.

Clofibric Acid (CA) has been employed in this study as the pollutant. CA is the bioactive metabolite of the lipid regulators clofibrate, etofibrate, and etofyllinclofibrate and is considered as a potential endocrine disruptor, since it interferes with the synthesis of cholesterol [10, 11].

3. Results and Discussions

3.1. Scanning electron microscopy characterization of the spongy catalytic material (SpongeMat/ZnO)

The spongy- like architecture microstructure of the synthetized materials is different on the top view compared with the bottom view. In the below figures are presented the scanning electron microscopy (SEM) images for the top layer (*Fig. 1*) and respectively lower layer (*Fig. 2*) of the support materials coated with 17.5 % and 10 % of ZnO.

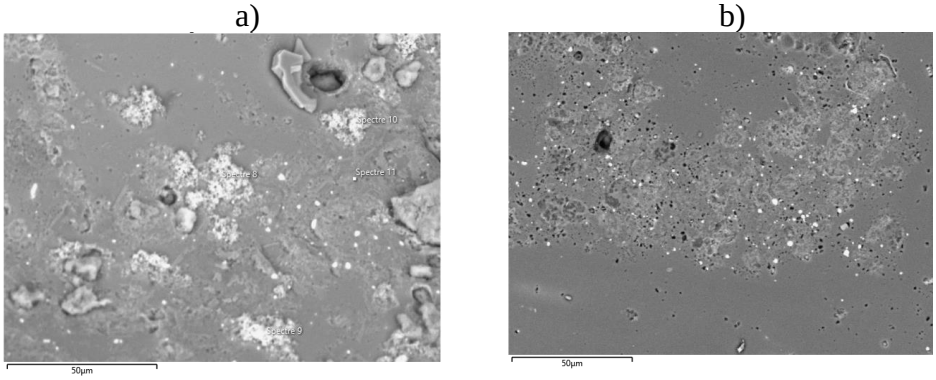

Fig. 1. Top layer SEM images of the SpongeMat/ZnO a) 17.5 % and b) 10 % ZnO

At the macroscopic scale, the surface of the ZnO coating observed in top layer view (*Fig. 1*) shows an inhomogeneous distribution of the ZnO particles on the surface of the support materials. It appears as some white agglomerations of ZnO particles in different parts of the analysed surfaces.

The SEM micrographs of the two presented Figs., confirmed a quite homogeneous distribution of components in the support materials microstructure. The phases were differentiated by SEM analysis, using the BSE detector that captures the retro-scattered electrons from the analysed sample, so that the specific phase of the glass is highlighted by the light grey colour. Homogeneity of the support materials is particularly important for the stabilization of ZnO oxide films coatings on the surfaces.

Comparing the *Fig. 1* and the *Fig. 2*, we can observe that, for the same analysed samples, the lower layer analysis of the SpongeMat/ZnO materials presents a higher surface coated with ZnO than the top layer analysis, these could

be explained by the higher spongious structure of the bottom of the sample than the top part, which allows to the thin film of ZnO solution to adhere better on the sample surfaces.

a) b)

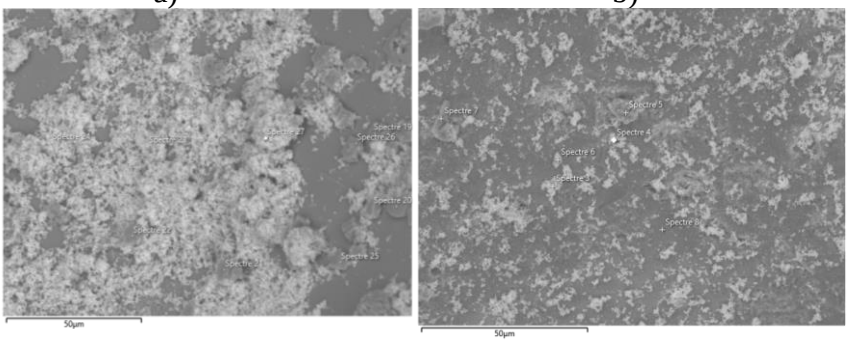

Fig. 2. Lower layer SEM images of the SpongeMat/ZnO a) 17.5 % and b) 10 % ZnO

3.2. Wastewater treatment applications

In order to evaluate the potential applicability of obtained catalytic material for environmental protection field in wastewater treatment, degradation efficiency tests through heterogeneous photo catalysis were carried out. In this context 200 mL of ultrapure water with neutral pH (~7) was enriched with 5 mg/L of CA organic compound and placed in contact with SpongeMat/ZnO of 17.5 % ZnO concentration (CA and ZnO concentrations used in experiments were arbitrarily chosen) in UV-A and VISIBLE spectrum. The photocatalytic degradation efficiency of SpongeMat/ZnO material was tested for 1 to 8 h and 24 hours of light exposure in the UV-A and VISIBLE spectrum, after that samples of filtered water were collected. The CA concentrations were determined by High Performance Liquid Chromatography - HPLC WATERS 600. In the catalytic efficiency experiments, the stability of the zinc oxide film deposited on the surface of the synthesized support materials was investigated in 5 consecutive experiments using CA solution of 5 mg/L concentration in a volume of ultrapure water of 200 mL, pH of the solution being the natural one, measured at the beginning of the experiments as 7.4 and ZnO deposited on the support material having a concentration of 17.5 %. Thus, according to *Fig. 3*, the degradation efficiency of Clofibric Acid is over 97% in UV-A spectrum. After a number of 5 cycles, the degradation efficiency is kept at high values of over 92%.

The latest researches in the field of heterogeneous photo catalysis in the advanced oxidation processes used in wastewater treatment, focuses on the convergence to the VISIBLE light spectrum, in order to be able to transpose the process on a real scale. In this context, the SpongeMat/ZnO oxide material obtained was tested for the degradation yield of organic compounds in the VISIBLE light spectrum.

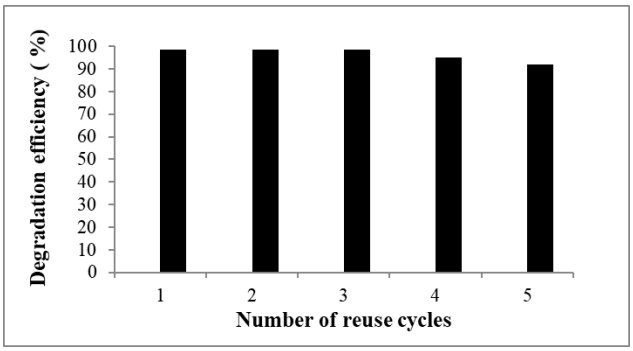

Fig. 3. Photocatalytic degradation efficiency of Clofibric Acid = 5 mg/L depending on 5 cycles of reuse of the synthesized catalytic oxide material (24h). SpongeMat /ZnO / 17.5%, maximum UV irradiation flux of 8.17 mW/cm^2, ambient temperature, pH 7.4

Fig. 4 shows the degradation percentage as a function of irradiation time in terms of SpongeMat/ZnO efficiency of Clofibric Acid degradation in the VISIBLE spectrum.

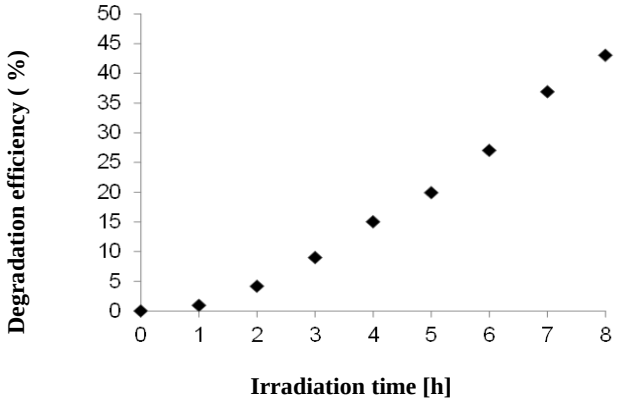

Fig. 4. Degradation efficiency of Clofibric Acid = 5mg/L using SpongeMat/ZnO/17.5%, in the VISIBLE spectrum

From the analysis of the data presented in *Fig. 4*, we can see that, after 8 hours of irradiation in the VISIBLE light spectrum, the Clofibric Acid degradation efficiency follows an ascending slope reaching at the end of the 8 hours of irradiation over 43% of degradation.

4. Conclusions

SpongeMat/ZnO synthesized catalytic material has potential for application in the field of environmental protection mainly in wastewater treatment, resulting from tests that the efficiency of degradation of Acid Clofibric, in the presence of light and SpongeMat/ZnO synthesized catalytic material, is over 97 % after 24 hours in the UV-A light, and 43% after 8 hours in the

VISIBLE light. For a good comparison, similar conditions must be used. At the same time, SpongeMat/ZnO presents the advantage of the fact that, being a catalyst immobilized on a fixed support, it is no longer necessary to perform an additional step of recovery of particles from the post-experiment suspension. In conclusion, the results presented in this paper confirmed that obtaining the oxide material SpongeMat/ZnO, represents a viable alternative to conventional catalysts that could be used for the efficient removal of toxic organic compounds from polluted waters.

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