

Removal of Antibiotics from Wastewater Using Photocatalytic Membranes

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This paper presents a method with a photocatalytic membrane for the disposal of organic compounds from synthetic solutions of antibiotics (ampicillin, erythromycin and tetracycline). The hybrid process for the removal of antibiotics from aqueous solutions combines the selectivity of the membranes with the high efficiency of the photocatalytic process. The variable parameters of the process are: the type of membrane used, the type and the initial concentration of antibiotics. The degradation process was studied by monitoring the organic substrate concentration changes function of reaction time using chemical oxygen demand analysis (COD) and total organic carbon analysis (TOC).

Keywords: hybrid method, photocatalytic membrane, ampicillin, erythromycin, tetracycline

The removal of organic compounds in wastewater is a very important subject of research in the field of environmental chemistry [1-5]. Although for human nature, antibiotics have renowned therapeutic effects, the properties of antibiotics are often detrimental to the environment. Data monitoring the concentrations of certain antibiotics in the aquatic environment indicate a significant increase, even in the sewage. Also, high concentrations of antibiotics have been identified in effluents resulting from hospitals or veterinary clinics in surface and ground waters [6, 7].

Sometimes, impermissible levels of pollution have been reached, leading to environmental contamination. In this case, the natural resources cannot be used for certain purposes because their characteristics have changed [8]. Antimicrobial agents such as sulfonamides, macrolides, trimethoprim, cephalosporins or fluoroquinolones can be found at potentially active concentrations in activated sludge treatment, and the antibiotic load along the year correlates with the variation in annual consumption data [9]. Tetracycline is frequently detected in wastewater [10]. Erythromycin is a bacteriostatic antibiotic becoming the first choice in treating infections in patients allergic to penicillin. Ampicillin is one of the most widely used antibiotics.

The diversity of the sources of pollution, of the nature and the concentration of organic pollutants and wastewater flows to be treated, has led to the development and implementation of a large number of decontamination processes, whose efficiency is correlated with the above-mentioned factors and with the specific features of each process of treatment/purification [11-12].

This paper describes a hybrid method using a photocatalytic membrane for the disposal of organic compounds from synthetic solutions of antibiotics (ampicillin, erythromycin and tetracycline). The efficiency of the proposed method has been evaluated in correlation with the initial concentration of the antibiotics.

Results and discussions

Materials and methods

The materials used in this study are: chopped type sisal fiber, higher-grade fibre, made in Turkey; TiO₂, P25 type, Degussa, Germany; sodium silicate solution, Chimforex, Romania.

The TiO₂ deposition on the sisal fiber materials (support) was developed in order to obtain the photocatalytic membrane, in accordance with an experimental program which took into account: the concentration of the sodium silicate solution as a binder agent; the ratio of TiO₂/sodium silicate solution; the manner of contact between the sisal fiber and the suspension TiO₂-sodium silicate. The deposition was performed layer upon layer, by impregnating the support material in the suspension mentioned. After impregnation, the sisal fiber precursor was exposed to air for two days, to remove the excess slurry and to dry completely. In this way, there resulted the membrane type 1. Another part of the sisal type material was prepared in similar conditions, but drying was performed in a controlled manner, for 10 h at 105 °C. In this way, there resulted the membrane type 2. Practically, the photocatalytic membranes were produced through the layer-by-layer technique. Finally, the impregnated sisal fibers (photocatalytic membranes) were rolled in a cylindrical shape and then washed in distilled water.

The antibiotics used in this work (table 1) were ampicillin (AMP), erythromycin (ERY) and tetracycline (TET), crystalline powder of pharmaceutical grade.

For the evaluation of the efficiency of the photocatalytic membranes, the experiments were achieved with synthetic solutions of antibiotics (ampicillin, erythromycin and tetracycline) using a reactor with continuous recirculation (reaction volume 1.5 L, total solution volume of antibiotic 2.0 L and the recirculation flow rate of synthetic solution of antibiotic 1 L/min), equipped with photocatalytic membranes and a high pressure mercury lamp (120 W), centrally and coaxially positioned. The initial concentration of the antibiotics was equivalent to a chemical oxygen

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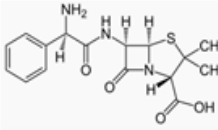
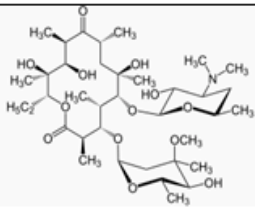
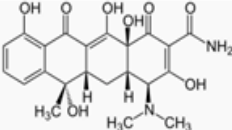
Antibiotics	Ampicillin (AMP)	Erythromycin (ERY)	Tetracycline (TET)
Chemical formula	$C_{16}H_{19}N_3O_4S$	$C_{37}H_{67}NO_{13}$	$C_{22}H_{24}N_2O_8$
Molecular mass	349.41 g/mol	733.93 g/mol	444.44 g/mol
Structure			

Table 1
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demand value of 300 mg O_2/L and 600 mg O_2/L . The degradation process was studied by monitoring the changes in the concentration of antibiotics as organic substrate, function of reaction time using chemical oxygen demand analysis (COD) and total organic carbon analysis (TOC). The amount of hydrogen peroxide used was calculated at 1.5 times H_2O_2 /antibiotic stoichiometric ratio. The hydrogen peroxide (Comchim, Romania) solution stock of 30% (w/w) was an analytical reagent. All experimental sets were performed at pH 3. The samples collected from the reactor at different reaction times were stabilized through MnO_2 addition for a quick decomposition of the unreacted H_2O_2 . The samples were then filtered and analyzed through the Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) standard methods. Chemical Oxygen Demand was performed using a Digester DK6 through a standard method (SR ISO 6060:1996). For the Total Organic Carbon, a Multi N/C 2100 (Analytik Jena) TOC analyzer (SR ISO 14235:2000) was used. The pH was measured using a Jenway 370 pH-meter.

Results and discussions

In the first set of measurements the possible photocatalytic properties of the sisal fiber (precursor) only were investigated using a photocatalytic installation with continuous recirculation [12]. Figure 1 shows that there is not a clear distinction between the experimental sets of COD/COD₀ values (in the presence of sisal fiber and the absence of sisal fiber-support). This situation indicates that the oxidation process is due to the hydrogen peroxide from the solution rather than to the photocatalytic activity of the sisal fiber substrate.

In figure 2 experimental data are shown with reference to the photocatalytic activity of TiO_2 on sisal fiber (hereinafter-membrane) compared with only the sisal fiber (hereinafter-support). There is a clear distinction between the COD/COD₀ values in accordance with the reaction time, obtained in the case of the photocatalyst and in the case of

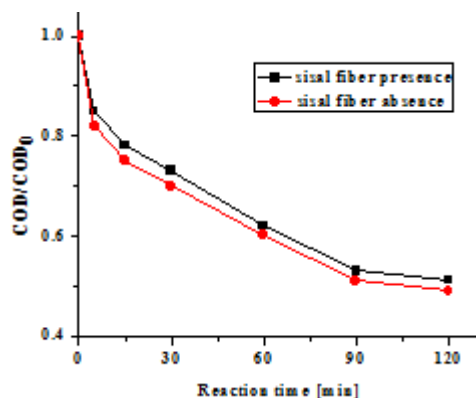


Fig. 1. Evaluation of the photocatalytic properties-support

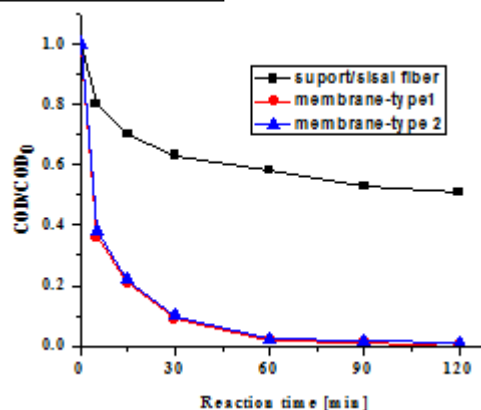


Fig. 2. Photocatalytic activity of the membranes

the support. It is to be added that here, in all experimental tests shown until now, ampicillin (COD₀ equivalent at 300 mg O_2/L) was used as a test substance. In the test with the photocatalytic membranes, the oxidation process takes place at a higher reaction rate than in the case of the support, which confirms the photocatalytic role of the TiO_2 deposited on the sisal fiber. The oxidation process of ampicillin may be attributed to the hydroxyl radicals generated by the direct photolysis of H_2O_2 , but especially to the hydroxyl radicals generated by the photocatalytic mechanism that occurs on the TiO_2 surface layer in the presence of UV radiation.

The comparative analysis of the results related to the photocatalytic membranes indicates that there are no significant differences in relation to the degree of oxidation of the organic substances in the sample analyzed (the test substance, ampicillin). The COD/COD₀ experimental data at the set reaction times are close, which indicates that both types of membranes resulting from the deposition of TiO_2 on the chopped type sisal fiber with a sodium silicate solution as a binder and drying in the air or through controlled thermal treatment lead to feasible results in terms of the efficiency of the antibiotics oxidation. Most likely, the small differences can be attributed to a partial degradation of the sisal fiber through forced drying.

Further on, in the tests for a comparative degradation of the antibiotics we worked with membrane-type 1 because the data in figure 2 show some preference for this type of photocatalytic membrane. The experimental data regarding the type of antibiotic and the influence of the initial concentration of the antibiotic in the working solution (equivalent COD₀ with 300 mg O_2/L or 600 mg O_2/L) are shown in figures 3 and 4 as COD/COD₀ and TOC/TOC₀ values. Due to a much higher number of hydroxyl radicals generated in the reaction medium through the photocatalytic effect of the TiO_2 , the oxidation process takes place with a high rate, a complete mineralization of the organic substrate being possible in a relatively short time.

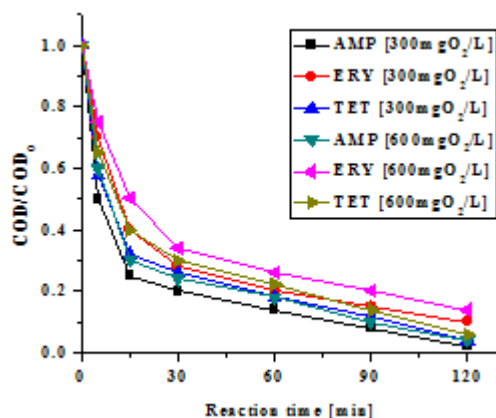


Fig. 3. COD/COD₀ versus time

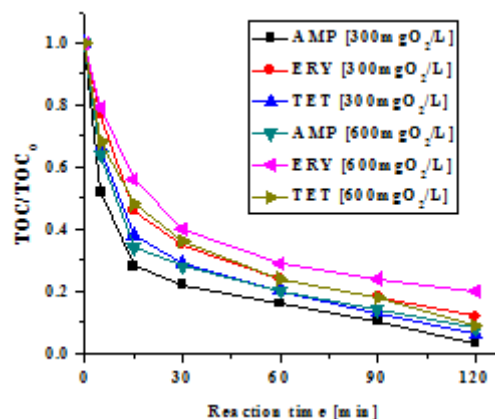


Fig. 4. TOC/TOC₀ versus time

The COD/COD₀ (fig. 3) and the TOC/TOC₀ (fig. 4) variations of reaction time show that the overall oxidation process follows two successive stages. In the first stage (0-15 min reaction time) the oxidation of the antibiotics takes place with a high reaction rate, being minimum in the case of erythromycin: 90 and 86% oxidation degree, respectively, function of the initial concentration of the antibiotics in the working solution. In the second stage (15-120 min reaction time) the reaction rate is much lower. These oxidation degrees can be attributed to organic intermediates formed as a result of the oxidation, which are more resistant, especially in the final phase of the oxidation process.

The breakdown of antibiotics is complex. During the experiment, antibiotics were transformed into other organic intermediates. Under the study conditions, a constant stability of degradation in the case of erythromycin can be seen. Erythromycin shows a higher resistance towards the oxidation process than do tetracycline and ampicillin. The degree of oxidation decreases in the order: ampicillin > tetracycline > erythromycin. This behaviour can be explained by the fact that the latter has a more complex structure and a molecular mass (table 1). The examination of the membrane after the tests indicates a small deterioration of the sisal fiber substrate or the TiO₂ layer, the shape and general appearance remaining largely the same as the original support.

Conclusions

This work proposes a new procedure for obtaining photocatalytic membranes through the direct deposition of TiO₂ powder on sisal fiber using a binding agent-the sodium silicate solution. The novelty derived from that the sisal fiber not been investigated in similar applications. The method used for the preparation of the photocatalytic membranes starting from sisal fiber is relatively simple and not expensive. The degradation of antibiotics (ampicillin, erythromycin and tetracycline) using the photocatalytic membrane synthesized was evaluated in a

photocatalytic process using a reactor with a special construction. The photocatalytic membranes obtained through TiO₂ immobilization on the sisal fiber substrate using a sodium silicate solution as a binding agent show a reasonable stability in the process of antibiotics oxidation and a good photocatalytic activity. This photocatalytic membranes are feasible for applications such as removal of antibiotics from wastewater.

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