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Preparation and properties of a photocatalyst with TiO_2 nanoparticles

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This topic refers to obtaining advanced materials for the removal of toxic compounds from wastewater. The study presents a procedure for the preparation of a photocatalyst using TiO_2 nanoparticles and fiberglass as precursors. The incorporation of titanium species in the structure of photocatalyst was performed using the wet impregnation method. The photocatalytic properties of the product were evaluated through testing the degradation of the phenol from wastewater. A new photocatalyst was obtained and the results denote a good stability and higher photocatalytic activity, properties that can be exploited in the development of advanced materials with successful applications in water treatment.

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1. Introduction

A very promising method for solving problems concerning the degradation of toxic compounds from wastewaters is photocatalysis.

The detailed mechanism of the photocatalytic oxidation of organic compounds in water has been widely discussed in literature. In general, the process can be divided into the following steps:

1. Diffusion of reactants from the bulk liquid through a boundary layer to the solution-catalyst interface (external mass transfer).
2. Inter- and/or intra-particle diffusion of reactants to the active surface sites of the catalyst (internal mass transfer).
3. Adsorption of at least one of the reactants.
4. Reactions in the adsorbed phase.
5. Desorption of the product(s).
6. Removal of the products from the interface of the bulk solution.

The properties of a photocatalyst must be in agreement with the followings: (I) high activity, (II) resistance to poisoning and stability for prolonged time at elevated temperatures, (III) mechanical stability and resistance to attrition, (IV) non-selectivity in most cases, and (V) physical and chemical stability under various conditions, (VI) to be able to use not only UV, but also visible light and (VII) to be inexpensive.

Membrane processes are separation techniques which are widely applied in various sectors of industry including food, chemical-petrochemical, pharmaceutical, cosmetics and electronic industries [1], water desalination, water and wastewater treatment and many others. The main advantages of membrane processes are: low energy consumption; low chemicals consumption; production of water of stable quality almost independent on the quality of the treated water; automatic control and steady operation allowing performance of a continuous operation; low maintenance costs; easy scale up by simple connecting of additional membrane modules.

Many studies have been published on the use of TiO_2 as a photocatalyst for the decomposition of organic compounds. TiO_2 is active under UV light. Photocatalytic activity means the ability of a material to create an electron-hole pair as a result of exposure to ultraviolet radiation. The resulting free-radicals are very efficient oxidizers of an organic matter. The photocatalytic activity in TiO_2 has been extensively studied because of its potential use in sterilization, sanitation, and remediation applications. The ability to control the photocatalytic activity is important in many other applications utilizing TiO_2 including paint pigments and cosmetics that require low photocatalytic activity.

The photocatalytic detoxification of wastewater is a process that combines heterogeneous catalysis with solar technologies [2].

Semiconductor photocatalysis, with a primary focus on TiO_2, has been applied to a variety of problems of environmental interest in addition to water and air purification. The application of illuminated semiconductors for degrading undesirable organics dissolved in air or water is well documented and has been successful for a wide variety of compounds [3].

The immobilization of TiO_2 on different supporting materials has largely been carried out via a physical or chemical route: dip coating, porous material impregnation, sol-gel method, reactive thermal deposition, chemical

vapor deposition, electron beam evaporation, spray pyrolysis, electrophoresis, electro-deposition [4-8].

In chemistry, photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalyzed photolysis, light is absorbed by an adsorbed substrate. In photogenerated catalysis, the photocatalytic activity depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (hydroxyl radicals •OH) able to undergo secondary reactions.

Its practical application was made possible by the discovery of water electrolysis by means of titanium dioxide. The commercially used process is called the advanced oxidation process (AOP). There are several ways the AOP can be carried out; these may (but do not necessarily) involve TiO_2 or even the use of UV light. Generally the defining factor is the production and use of the hydroxyl radical.

The hydroxyl radicals [9] are very oxidative in nature and non selective with redox potential of +3.06 V.

Among the processes employed in water treatment, heterogeneous semiconductor photocatalysis shows great importance due to its ability to destroy a wide range of organic pollutants at ambient temperature and pressure, without generation of harmful products.

The study of the photodegradation for a large series of substances such as halogenated hydrocarbons, aromatics, nitrogenated heterocycles, hydrogen sulfide, surfactants and herbicides, and toxic metallicions, among others has clearly shown that the majority of organic pollutants present in waters can be mineralized or at least partially destroyed. The photocatalytic treatment of many organic compounds has been successfully achieved. The photocatalytic activity is dependent on the surface and structural properties of the semiconductor such as crystal composition, surface area, particle size distribution, porosity, band gap and surface hydroxyl density [10].

Phenolic compounds are one kind of priority pollutants, and are often present in the aquatic environment. Phenols, even at concentrations below 1 µg/L, can affect the taste and odor of water [11]. Hence, the identification and monitoring of these compounds at trace level in drinking water and surface waters are imperative.

Phenols and their derivatives exist in the environment. These compounds are used as components of dyes, polymers, drugs and other organic substances. The presence of phenols in the ecosystems is also related with the production and degradation of numerous pesticides and the generation of industrial and municipal sewages. Some phenols are also formed during natural processes. These compounds could be substituted with chlorine atoms, or could be nitrated, methylated or alkylated.

Phenol (hydroxybenzene) is a colorless, crystalline substance of characteristic odor, soluble in water and organic solvents. Phenol was one of the first compounds inscribed in the List of Priority Pollutants by the US Environmental Protection Agency (US EPA).

Phenols of anthropogenic origin exist in the environment due to the activity of the chemical, petrol or pharmaceutical industries. The compounds penetrate ecosystems as the result of drainage off the municipal or industrial sewage to surface water [12].

The presence of phenols in water induces a high pollutant potential due to their toxicity to aquatic life and carcinogenic and mutagenic effects to humans [10]. Based on their high efficiency, the AOPs (Advanced Oxidation Processes) can be successfully used in wastewater treatment to degrade the persistent organic pollutants, resistant to biological and classical physico-chemical processes [14-19].

Photocatalysis, also called the "green" technology, represents one of the main challenges in the field of treatment and decontamination systems, especially for water and air. Its operating principle is based on the simultaneous action of the light and a catalyst (semiconductor), which allows for pollutant molecules to be destroyed without damaging the surrounding environment.

The photocatalytic processes can operate using a catalyst suspended in the solution or immobilized on various supports: buoyant glass beads, fiberglass cloth, optical fibers, glass vessels of various shapes and sizes, silica, glass pellets and sheets [20, 21].

In this work, we present the results related to the preparation of a photocatalyst with TiO_2 nanoparticles, through the wet impregnation method and the evaluation of its performance to remove toxic compounds (such as the phenol) from wastewater.

2. Experimental part

Materials

The materials used for the membrane synthesis are: titanium dioxide (TiO_2), P25 type, Degussa, Germany; sodium silicate (Na_2SiO_3), solution, Chimforex, Romania; fiberglass Chopped Strand Mat EMC300 E, Vesta Intracon bv, Netherlands; boric acid (H_3BO_3) and fluorhidric acid (HF) from Merck; phenol analytical reagent grade Merck; freshly prepared with double-distilled water.

Methods

• *Photocatalyst synthesizes*

The precursor of fiberglass prepared in cylindrical shape was first washed in distilled water, dried for 1 h at 105°C and immersed at room temperature (30±2°C) for half hour into suspension (TiO_2/sodium silicate) under continuous stirring. Deposition of TiO_2 on fiberglass essentially complied with the following conditions: sodium silicate dilution ratio 1/5 (v/v); TiO_2/sodium silicate solution ratio 1/10 (w/w). TiO_2 nanoparticles were supersaturated in HF solution 5%. The sodium silicate glass after dilution with double distilled water was added over the supersaturated solution. The two precursor solutions were mixed perfectly at room temperature (30±2°C) by adding H_3BO_3 solution, 0.05 mol/dm^3. After impregnation, the samples were exposed to air for 10 minutes to drain the excess solution. Calcinations of deposited film were carried out at various temperatures: 1

hour at 105°C and 2 hours at 180°C. The sample was taken out from the treatment solution, washed with distilled water and dried at room temperature.

• *Characterization of deposited films*

The crystalline structure of the precursors and the photocatalytic membrane system were measured by X-Ray diffraction (XRD) using a PANalytical X'PertPRO MPD Diffractometer with Cu tube.

Scanning electron microscopy (SEM) using the Inspect S PANalytical model coupled with the energy dispersive X-ray analysis detector (EDAX) was used to characterize the external surface of the precursor materials and of the final product obtained by TiO_2 immobilization on fiberglass using sodium silicate solution as a binder agent.

For further analysis of transmission electron microscopy (TEM) we used a transmission electron microscope with high resolution (HRTEM) FEI Tecnai F30 type G2STWIN. Samples were prepared by grinding, dispersing by sonication in alcohol, and collecting the copper grid covered with amorphous carbon film with holes.

• *Photocatalytic degradation of phenol*

The laboratory experiments were achieved using a laboratory installation (Fig. 1). The photocatalytic reactor is a continuous recirculation one (reaction volume 1.5 L, total solution volume 2.0 L and recirculation flow rate 1 L/min), equipped with a photocatalyst (cylindrical shape, diameter of 65 mm, height of 300 mm) and a high pressure mercury lamp, of 120 W power, centrally and coaxially positioned.

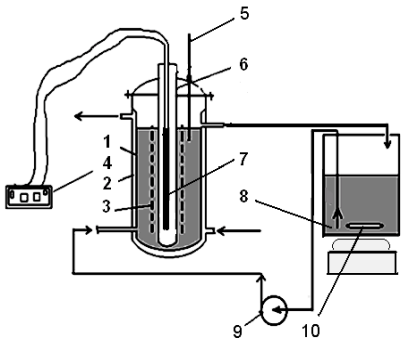

Fig. 1. Installation diagram of working (Laboratory photocatalytic reactor with continuous recirculation). 1-photocatalytic reactor; 2-cooling jacket; 3-photocatalyst, cylindrical shape; 4-UV lamp source; 5-thermometer; 6-quartz tube; 7-UV lamp; 8-recirculation reservoir; 9-recirculation pump; 10-magnetic stirrer.

Before being tested, the fiberglass support and the photocatalyst were washed in distilled water and activated for 2 h in a photocatalytic reactor with continuous recirculation, in the presence of hydrogen peroxide and UV radiation.

After activation, both cylindrical shape samples were finally washed in distilled water. The experiments were performed at 30±2°C using synthetic solutions of phenol with initial concentration equivalent chemical oxygen demand value of 300 mg O_2/L. The amount of hydrogen peroxide used was calculated at 1.5 stoichiometric ratio: H_2O_2/4-chlorophenol.

The oxidation process was studied by monitoring the organic substrate concentration changes using chemical oxygen demand (COD) analysis against reaction time. Chemical oxygen demand analyses were performed through a standard method (SR ISO 6060/1996) using a Digestor DK6.

3. Result and discussions

Photocatalyst characterization

A spectrum from TiO_2 samples (Figure 2a) shows the diffraction peaks of anatase TiO_2 corresponding to the angle diffraction (2θ): 25.3, 37, 37.8, 38.6, 48, 54 and 56 degree.

The diffraction pattern for the photocatalyst (Figure 2b) reveals the presence of TiO_2 anatase crystalline phase type.

The comparative data obtained by X-ray diffraction (XRD) confirm the crystallization of titanium dioxide in anatase form nanocrystals both initial and resulting photocatalyst samples obtained through the impregnation method.

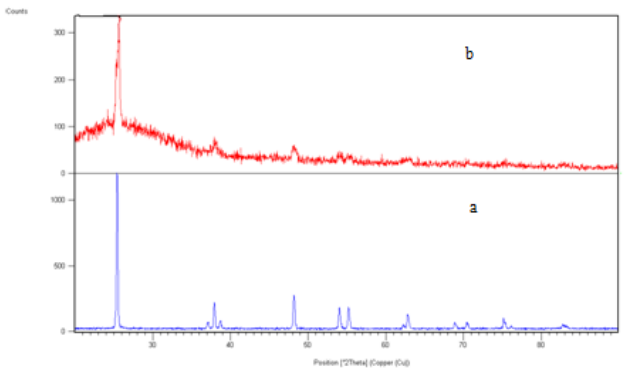

Fig. 2. XRD spectra (a)TiO_2 nanoparticles, (b) powder deposition on the photocatalyst.

The photocatalyst morphology is shown by of the SEM images – Fig. 3. The SEM images obtained through scanning electron microscopy show the formation of a TiO_2 layer on the external surface of the fiberglass substrate. Increasing the magnitude of SEM images indicates that the TiO_2 layer is quite relatively uniform and the crystallite size is in the range of 80-180 nm.

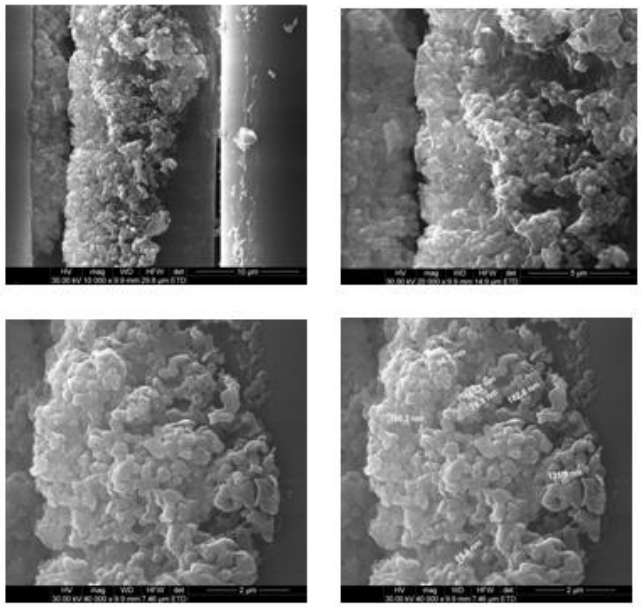

Fig. 3. SEM analysis of the photocatalyst.

EDAX analysis (Fig. 4) made on the morphology and structure of the photocatalyst indicates the elementary photocatalyst obtained.

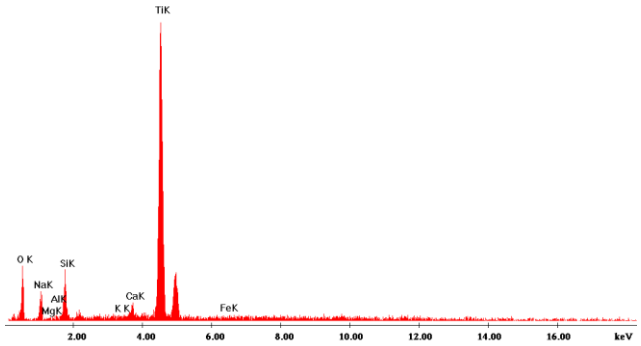

Fig. 4. EDAX analysis of the photocatalyst.

The presence of specific chemical elements of the fiberglass support (O, Si, Al, Ca, Mg and Na) is noted, but also the presence of Ti, certifying the TiO_2 layer formation. It was observed that the TiO_2 film deposition on fiberglass was found to be mechanically stable/robust and cannot be easily removed by rubbing.

Low resolution TEM images were obtained for the photocatalyst with TiO_2.

In general, the advantages of this analysis are: a high efficiency to collect signal (approx. 100%); high spatial resolution (in the limit of the beam size); high energy resolution (in the limit of the incident beam energy dispersion and the instrumental instabilities).

TEM analysis was used to deeply examine the particle size, the crystallinity and the morphology of some samples from the prepared photocatalytic systems.

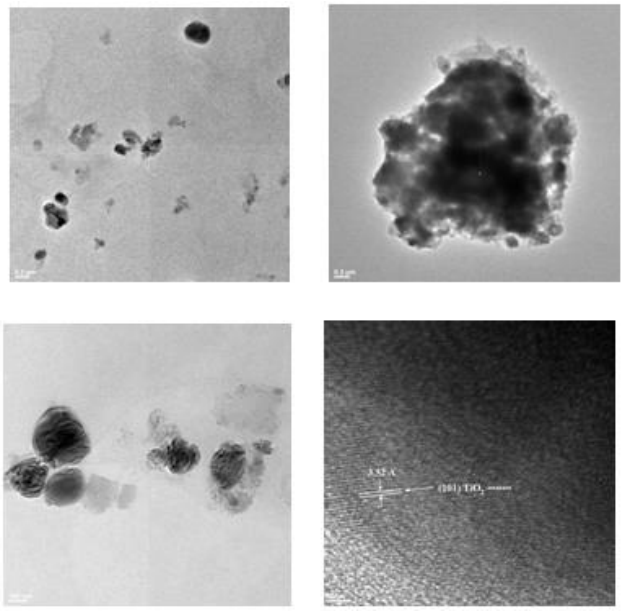

Fig. 5. TEM analysis of the photocatalyst.

In Fig. 5 it can be seen that the photocatalyst prepared through the present method shows clustered, easily aggregated nanoparticles with different shapes.

Photocatalytic activity tests

In the Figs. 6 and 7 is shown the phenol oxidative degradation, in the presence of fiberglass support and the use of photocatalyst with TiO_2 in 4 successive cycles.

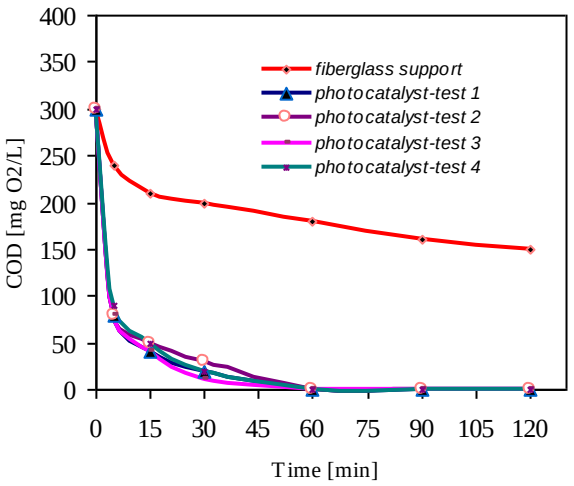

Fig. 6. Photocatalytic oxidation using fiberglass support and the photocatalyst with TiO_2.

In the presence of UV radiation, hydrogen peroxide decomposition occurs by direct photolysis with the

formation of HO • radicals, which play a decisive role in the oxidation process. The rate of decrease in the oxidation reaction time is associated with a higher consumption of hydrogen peroxide in the reaction medium.

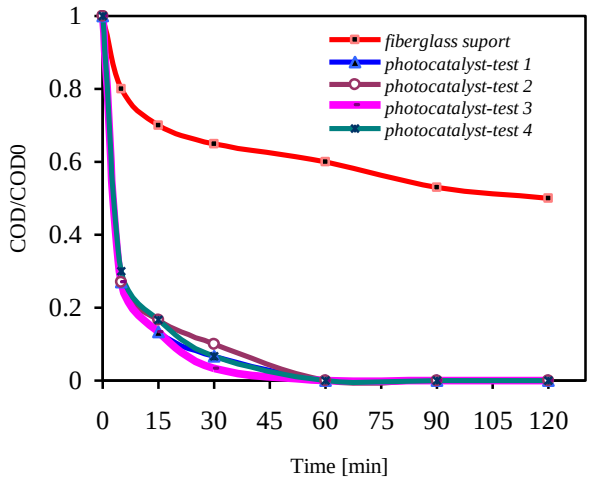

Fig. 7. COD/COD_0 values profile in time.

The COD/COD_0 values, determined at the same reaction time, indicate an insignificant variation for 4 successive tests.

It was observed that there is a clear distinction between the four sets COD/COD_0 values obtained in the presence of the photocatalyst as compared to those obtained when only fiberglass support was used. .

The experimental data, obtained by performing four oxidation successive cycles of phenol indicate a stability of the photocatalyst with TiO_2. The examination of the photocatalyst after several successive tests does not indicate any mechanical deterioration of fiberglass support or TiO_2 layer, the shape and general appearance remaining the same as the original sample.

4. Conclusions

Our work proved that a new photocalyst can be prepared through the wet impregnation method.

The procedure for obtaining the TiO_2 photocatalyst aimed at observing the main conditions that determine the characteristics of a photocatalyst (mechanical strength, chemical stability, TiO_2 adhesion on fiberglass support and high photocatalytic activity) when the photocatalyst is tested in the advanced degradation processes applied to organic compounds, hardly biodegradable in wastewater.

The deposition of titanium dioxide powder through the method presented above gives rise to the formation of stable films. In the processes for advanced wastewater treatment, specifically in photocatalysis, the properties of TiO_2 films deposited on fiberglass-type support materials simplify technology by eliminating the separation (filtering) and powder recovery stages.

The results obtained through the characterization of the photocatalyst indicate the good deposition; the TiO_2 deposition through the use of the method presented in this paper offers a new overview of how to obtain advanced materials for environmental applications such as removing phenol from wastewater.

Therefore, obtaining a new type of photocatalyst by immobilizing TiO_2 powder on a fiberglass substrate is viable and has resulted in deriving outstanding results both in terms of mechanical properties and the photocatalytic activity.

The advantage of this method derives from the fact that it is a simple and inexpensive procedure, by using commercial raw materials. The cost of using heterogeneous photocatalysis decreases and essentially allows a wide scale implementation of the process.

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