INFLUENCE OF GRAPHENE OXIDE ON PHOTOCATALYTIC PROPERTIES OF TITAN (IV) OXIDE

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ABSTRACT
Pollution of the environment, especially on water causes increasing pressure on mankind. The use of pharmaceuticals, cleaning agents and pesticides appears to have caused the emergence of new types of pollution in the environment, called micropollutants. Micropollutant cause major changes in plants and animals living in the aquatic environment. Classical wastewater treatment methods do not purify water from this type of pollution and new methods of purification need to be developed. One of the processes that cause the total degradation of this type of pollution is photocatalysis. For the process of photocatalysis photocatalyst such as titanium (IV) dioxide (TiO₂) is required. The efficiency of using TiO₂ on a daily sun light is limited due to the high energy banned zone (3-3.2 eV) so only UV-A light, which makes up 5% of solar radiation, activates the photocatalyst. In order to overcome the problem of prohibited zones and to shift the light response threshold of TiO₂ into the visible part of the spectrum, different photocatalysts can be used. One of the methods showing the potential is the use of graphene oxide (GO). In this paper a TiO₂/GO composites with various concentrations of GO were prepared. The concentrations of GO ranged from 5, 10 and 25 wt. % GO relative to the mass of TiO₂. It was observed that the concentration of GO affects the photocatalytic activity of the obtained composite. Photocatalytic activity was followed by a degradation of salicylic acid in prepared modal solution, in a pilot reactor followed by UV-VIS spectrometry. The prepared catalysts were characterized by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX).

MATERIALS AND METHODS
Graphene oxide (GO) and TiO₂, Aerosol® P25, Evonik, Germany, tetraethoxysilane (TEOS), VWR Chemical, USA, acetic acid from VWR Chemicals, France, salicylic acid (SA), Kemika Croatia and ethanol, GramMol, Croatia used as received. As a carrier the glass mesh from Keltex, Croatia (CM 300/300, p = 610 g/m²) was purchased. For the preparation of the immobilized layer TiO₂ and GO were added to the glass mesh using sol-gel method. Glass mesh was cut into the reactor’s dimension and weighed. The suspension from which TiO₂ and GO were applied to the glass mesh was prepared by mixing TiO₂ and MWCNT with distilled water and ethanol (water: ethanol = 1:1) on a magnetic stirrer. Three different solutions with different concentrations of GO were prepared. The concentrations of GO ranged from 5, 10 and 25 wt.% GO relative to the mass of TiO₂. The pH of the suspension was adjusted by adding acetic acid with stirring to pH 1.5-2. After achieving the desired pH, the suspension was mixed for 15 minutes, after which the homogenization was performed with ultrasound for 6 minutes (ultrasonic bath 120W, frequency 40 kHz). After homogenization, TEOS was added and further stirred over a period of 60 minutes at a temperature of 50 °C. Glass mesh is immersed in the prepared suspension and dried. Drying was carried out in a 70 °C drier for 20 minutes. The immersion and drying procedure was repeated 4 times. The prepared glass mesh were left in air for 7 days, after which they were washed with distilled water, dried and weighed to determine the mass of the applied layer. Clean meshes and meshes with TiO₂ / GO obtained by the described procedure were recorded by scanning electron microscope (SEM, FEG QUANTA 250) operated at 20kV. The presence of TiO₂ and/or GO on fiber glass mesh was determined by using energy dispersive spectroscopy (EDX) mapping analysis. For mapping analysis SEM microscope was operating at 20 kV while working distance was set at 20 mm. Mesh for SEM / EDX analysis were previously fixed to the carrier using double-sided self-adhesive carbon-guided strips and a gold-palladium layer. The photocatalytic properties of the catalyst were investigated through the degradation of salicylic acid in the prepared 0.2 mmol / dm³ model solution. The UV-VIS spectrophotometer (Perkin Elmer LAMBDA 35, 200-700 nm with a recording speed of 480 nm / min) was used to monitor the photocatalytic degradation reaction. Tests for photocatalytic properties were carried out in batch pilot photoreactor of rectangular geometry (size 4.5 x 17.5 cm) with recirculation by peristaltic pumps with a flow rate of 48 cm³ / min. The source of the simulated solar radiation (UV-B 2.5 / 26 W) is placed 7 cm above the surface of the solution reaction and is covered with a shadow / reflective surface of Al-sheet in order to evenly illuminate the reactor space. The immobilized photocatalyst was placed at the bottom of the reactor and a model solution of SA 100 cm³ was added. At the beginning of the procedure, a sample of SA 2 cm³ was taken, after which the reactor was left in the dark for 30 minutes and the sampling was repeated. At the end of the phase in the dark, the source of the simulated solar radiation was included, and the samples were taken periodically 15, 30, 60, 90, 120 minutes.

RESULTS

Figure 1. a) Clean glass mesh, b) mesh with immobilized TiO₂, c) mesh with immobilized TiO₂ / GO.

Figure 2. EDX analysis of the immobilized TiO₂ / GO layer.

Figure 3. Degradation results of salicylic acid with different concentrations of GO in the TiO₂ / GO photocatalyst.

Figure 4. Comparison of salicylic acid degradation with photocatalyst TiO₂ and TiO₂ / GO.

CONCLUSIONS
In this paper two types of photocatalysts were prepared by sol-gel method, glass meshes with immobilized TiO₂ and TiO₂ / GO with various concentrations of GO. The concentrations of GO ranged from 5, 10 and 25 wt.% GO relative to the mass of TiO₂. After preparation, photocatalytic property was investigated through the degradation of salicylic acid in pilot reactor. Comparing the results of the photocatalysis it was concluded that the best result is achieved using the clean TiO₂. After photocatalysis, SEM and EDX analysis of prepared photocatalysts demonstrated the presence of TiO₂ and GO on glass meshes that confirm the stabilization of immobilized TiO₂ and TiO₂ / GO.

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