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TiO_2_W MATERIAL USED AS ADSORBENT AND/OR PHOTOCATALYST IN WATER DEPOLLUTION

BY

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Abstract. This work highlights the performance of TiO_2_W material as adsorbent and photocatalyst. The titanium dioxide was synthesized by sol-gel method from titanium (IV) butoxide (TIBT) in presence of cetyl-trimethyl-ammonium bromide (CTAB). The TiO_2_W composite was obtained by doping the titanium dioxide using Na_2WO_4 as precursor. The UV-DR and BET analysis were used for the characterization of the obtained materials. Their adsorption and photocatalytic efficiencies were investigated in a series of laboratory tests performed with and without UV-A irradiation. The target molecule was Rhodamine 6G (R6G). Experimental results clearly demonstrated that the presence of WO_3 strongly enhances the dye uptake from diluted aqueous solutions. It was found that the sample doped with W posed high performance in adsorption (after 30 min, the adsorption efficiency is over 80%), while the undoped TiO_2 exhibits higher photocatalytic activity for R6G. The experimental data suggested the superiority of combined adsorption-photocatalysis in the persistent organic compounds removal. The obtained materials can be successfully used for future applications in advanced wastewater treatment.

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Keywords: adsorption; wolfram doping; photocatalysis; Rhodamine 6G; titanium dioxide.

1. Introduction

Nowadays, nanotechnology seems to be one of the most attractive research domains due to its high potential for various applications, such as medicine (Saxena *et al.*, 2020), environmental science (Sescu *et al*., 2019; Sescu *et al*., 2020), food industry (Thiruvengadam *et al*., 2018), electronics (Eid *et al*., 2018), gas sensors (Zhang *et al*., 2017), etc. Nanotechnology is an advanced technology which deals with synthesis, characterization and applications of nanoscaled materials.

The synthesis method and doping procedure of materials represent a key factor for obtaining materials with different structural properties. Numerous studies shown that the performance of nanomaterials can be increased by doping with different ions (Harja *et al*., 2020).

The use of TiO_2 nanomaterials in water treatment processes has attracted significant attention due toits advantages, such as low price, availability, chemical stability, non-toxicity and high performance (Harja *et al*., 2018). TiO_2 nanoparticles can be obtained by various methods, such as sol-gel (Mousavi *et al*., 2018), solvothermal (Ramakrishnan *et al*., 2018), hydrothermal (Abdelraheem *et al*., 2019), sonochemical method (Bhagwat *et al*., 2017), coprecipitation (Sanchez-Martinez *et al*., 2018), etc.

The sol-gel method is the most commonly used preparation approach for the obtaining of TiO_2 nanomaterials because of its simplicity, effectiveness, homogeneity and the purity of the final product (Pant *et al*., 2019).

The water pollution with organic compounds became a great concern in the last decades because of their harmful effects on human health and aquatic life. The sources of these contaminants includes pharmaceuticals, detergents, dyes, pesticides and personal care products. Most of them are highly toxic for living organisms and their complete removal can be very limited (Di Marcantonio *et al*., 2020). Therefore, the scientific and practical interest for finding better ways for the elimination of water pollutants is increasing.

In this context, the aim of this work was to synthesize TiO_2 and W-doped TiO_2 nanoparticles and testing their performance in water treatment processes for the removal of R6G, a xanthene dye used in biotechnology applications (Terdale and Tantray, 2017).

2. Materials and Methods

Titanium(IV) butoxide (TIBT) used as a precursor for TiO_2 was purchased from Merck. Cetyl-trimethyl-ammonium bromide (CTAB) and ethyl alcohol (EtOH) were acquired from Sigma-Aldrich. HCl (37%) was purchased from Silal-Trading. Na_2WO_4used as precursor for the metal doping was purchased from Reactivul Bucureşti. Rhodamine 6G (Rh6G), used as target pollutant was procured from Sigma-Aldrich. The chemicals used for this study were used as received.

The sol-gel method was used for the synthesis of porous TiO_2. An overall initial gel composition is described as: 1 Ti(iBuO)4:0.16 CTAB: 1.4 HCl: 17H2O: 20 EtOH. CTAB was dissolved in half of the due amount of EtOH, then water was added and the mixture was stirred for 30 min at 40°C. Afterwards, HCl was added under continuous stirring. In another beaker, TIBT was dissolved and the other half of EtOH dnd stirred for 30 min. Finally, CTAB solution was added dropwise into TIBT solution under ultrasound treatment (Sonics VCX-750 Vibra Cell Ultra Sonic Processor device, using pulse/pause cycles 2/2, for 3h). The solid product was recovered by centrifugation, washed several times with distilled water and dried at 60°C overnight. The removal of the surfactant was made by slow calcination (1^o/min) at 650°C for 6h. The schematic representation of the preparation setup is displayed in Fig. 1.

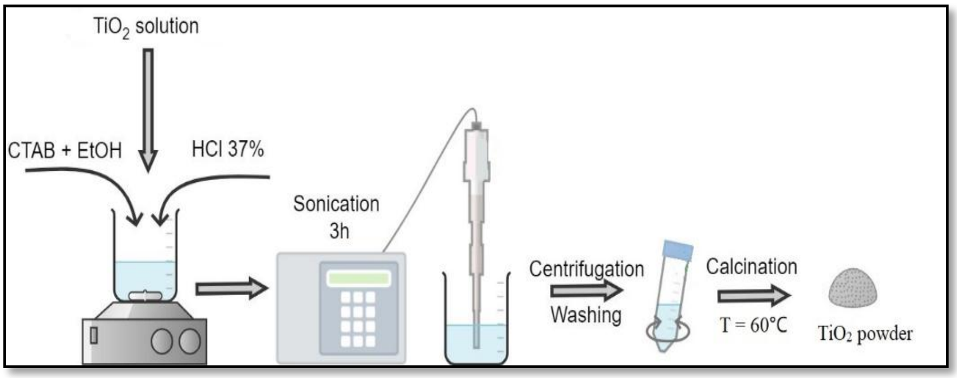

Fig. 1 – Schematic representation of TiO_2 synthesis.

The doped catalysts were obtained by a similar procedure, by adding thedue amount of Na_2WO_4 (in order to reach a 10% mole ratio of WO_3 with regard to TiO_2) dissolved in the water used for the CTAB solution.

The obtained materials were characterized by UV-DR, using Shimadzu 1700 system and BET, using a Quantachrome machine Nova 2200e.

The adsorptive and/or photocatalytic performance of the materials was tested for the R6G removal; this dye is a persistent organic pollutant, hard to destroy by classical methods. The adsorption and photocatalytic tests were carried out in a cylindrical reactor of 250 mL, magnetically stirred, with internal irradiation. The experiments were carried out at room temperature, at a catalyst loading of 1 g/L and for an initial pollutant concentration of 20 mg/L. Samples were withdraw at specific reaction times and the residual R6G concentration was measured by spectrophotometry using Shimadzu 1700.

3. Results and Discussions

3.1. Materials Characterization

The UV-DR spectra were used to calculate the band gap values of the two samples (Fig. 2). Surprisingly, the band gap value did not change by doping TiO_2 with WO_3; for both materials a 3.25 eV bang gap value was calculated.

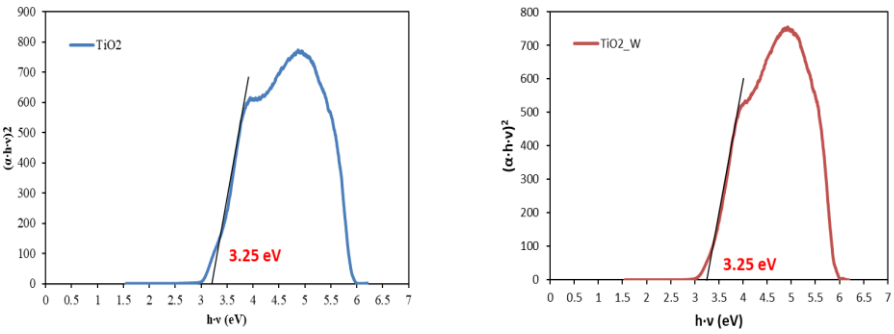

Fig. 2 − Band gap of the obtained catalysts.

The BET adsorption of pure nitrogen at 77 K was used to investigate the porous structure of the solids. The cylindrical pores of TiO_2 revealed by the type IV isotherm with a hysteresis loop having almost parallel branches are highly modified when WO_3 is incorporated in the lattice. In this later case, the type II isotherm contains a H_2 loop type, indicating a strong pore opening narrowing while wolfram oxide is included in the material (Fig. 3).

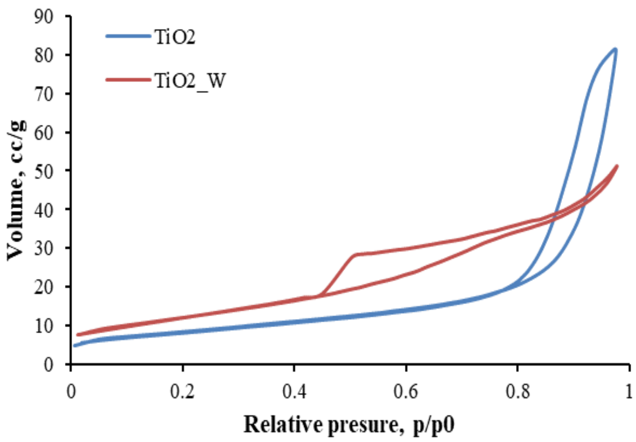

Fig. 3 − BET isotherms for TiO_2 and TiO_2_W.

In the cylindrical pores of pure TiO_2, the relative pressure where the capillary condensation occurs is around 0.8, indicating the existence of straight pores with uniform diameters. The mesoporous structure of TiO_2_W sample is dramatically changed: the hysteresis loop closes at a relative pressure of 0.43, indicating a disordered mesoporous structure, with irregular shaped pores. However, the doping of TiO_2 with W, led to an increase in the surface area for the TiO_2_W sample (44 m^2/g) compared to 30 m^2/g for the bare TiO_2. This behaviour suggests the extra formation of "ink bottle" shaped pores, which could act as pockets for the adsorption.

3.2. Materials Performance

The adsorption tests performed by contacting in the dark the solids with a R6G solution, under stirring, for time durations long enough to let settling the adsorption-desorption equilibrium, showed that when TiO_2_W sample was used, an elimination of 80% of the dye from the solution was reached. For comparison, in the case of pure TiO_2, but only 8% of the dye was retained from the solution (Fig. 4).

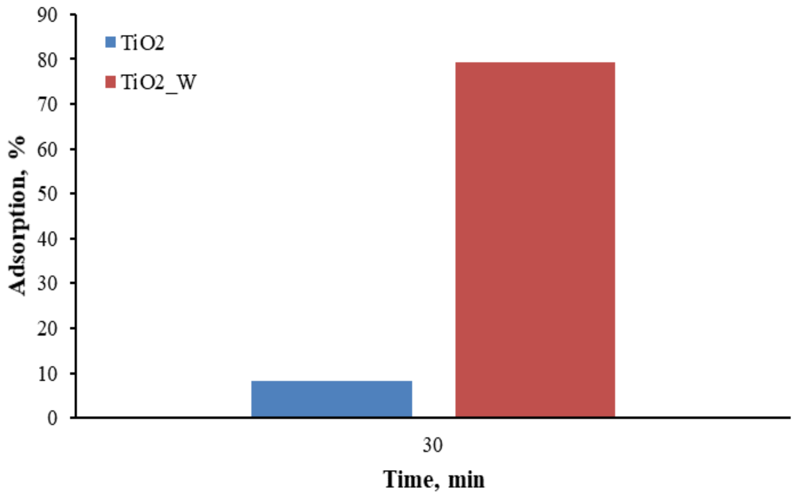

Fig. 4 − Adsorption of R6G on the obtained materials.

The performance of the WO_3-doped material for the elimination of R6Gby adsorption is quite high. The important difference in comparison with pure TiO_2 seems to be in connection with the higher porosity of the material and to the performant adsorption sites associated with the presence of WO_3.

In what concerns the efficiency of R6G elimination from solutions under UV irradiation by a photocatalytic process, Fig. 5, the results indicate that the undoped TiO_2 showed much better result in the photocatalytic degradation of Rh6G, achieving a performance of 67% in 120 min, compared to only 23% obtained in the case of TiO_2_W sample.

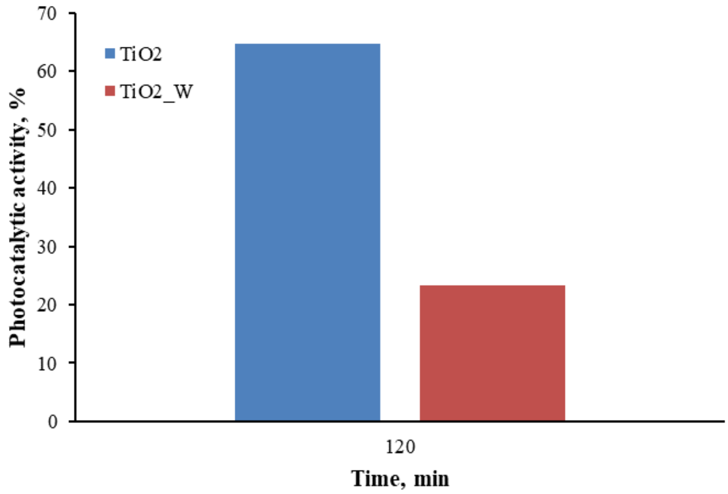

Fig. 5 − The photocatalytic activity of the obtained materials for the degradation of Rh6G.

This kind of behaviour can be explained by the fact that the WO_3 arrangement in the material structure does not deliver an energetic level to keep the electron-hole pair formed by TiO_2 activation, as we assumed when planned this doping procedure, but rather acts as a screen, hindering the UV light absorption on TiO_2 and thus, lowering the production of oxidizing and reducing species resulting in the formation of HO radicals, responsible for the dye degradation.

4. Conclusions

In this work, TiO_2 and W doped TiO_2 were obtained by a modified sol-gel method, using the ultrasound energy. The materials were characterized by UV-DR spectroscopy and BET nitrogen adsorption and their performances were evaluated in the adsorption and the heterogeneous photocatalysis processes for the removal of rhodamin 6G dye (R6G) from aqueous solutions.

The obtained results shown that by doping TiO_2 with W ions, the band gap did not change, but the surface area increased, improving the materials adsorptive capacity. Thus, in the adsorption process, TiO_2_W led to a R6G removal of 80% after 30 min, compared with only 8% in the case of TiO_2.

On the other hand, in the photocatalytic process, bare TiO_2 exhibited better results: a 67% elimination yield was found after 120 min, compared with only 23% on the doped sample.

The present study suggests that the activity of these nanomaterials in adsorption or photocatalytic processes depends on both surface area and structural characteristics, as well as on the nature of doping.

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MATERIALE PE BAZĂ DE TiO_2_W UTILIZATE CA ADSORBANȚI ȘI/SAU FOTOCATALIZATORI ÎN PROCESE DE DEPOLUARE A APELOR

(Rezumat)

Această lucrare evidențiază performanța materialului TiO_2_W ca adsorbant și fotocatalizator. Dioxidul de titan a fost sintetizat prin metoda sol-gel modificată, utilizând butoxidul de titan (TIBT), în prezența bromurii de cetil-trimetil-amoniu, sub tratament ultrasonic. Compozitul TiO_2_W a fost obținut prin introducerea precursorului Na_2WO_4 în rețeta de sinteză.

Materialele obținute au fost caracterizate prin UV-DR și BET, iar activitatea lor în procesele de adsorbție și fotocataliză au fost investigate într-o serie de teste de laborator cu și fără iradiere UV. Molecula țintă pentru aceste teste a fost rodamina 6G (R6G), un colorat foarte stabil, utilizat în aplicații ale biotehnologiei.

Rezultatele experimentale au demonstrat că prezența wolframului ca oxid în structura dioxidului de titan afectează performanța de eliminare a poluantului. S-a observat că proba dopată cu W prezintă activitate excelentă în procesul de adsorbție (80% după 30 min), în timp ce proba de TiO_2 nedopată prezintă caracteristici de adsorbție inferioare, dar are activitate considerabil mai bună în procesul de eliminare a R6G prin fotocataliză eterogenă.

Datele obținute sugerează că materialele sintetizate pot fi utilizate cu succes în procesele de tratare a apelor uzate.