

Investigation of photocatalytic degradation of methylene blue by titanium dioxide composites

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In this study, titanium dioxide (TiO₂) nanoparticles were prepared from titanium powder by a simple flame transfer method. Hydroxyapatite (HAp) and barium sulfate (BaSO₄) were used to prepare titanium dioxide nanocomposites and their characterization was performed by using X-ray diffraction, Fourier transform infrared resonance (FT-IR) and BET surface area analysis techniques. The effect of HAp/TiO₂ and BaSO₄/TiO₂ nanocomposites on the degradation of methylene blue was investigated. It was observed that the photocatalytic properties of nanocomposites with hydroxyapatite and barium sulfate were slightly better when compared to pure titanium dioxide.

Keywords: Titanium dioxide, Nanocomposites, Photocatalytic, Hydroxyapatite, Barium sulfate.

INTRODUCTION

Nanocomposite materials are widely used in many fields due to their superior performance [1, 2]. Various nanoparticle materials with a diameter of less than about 100 nanometers are used in industrial applications such as electronics, optics, cosmetics, pharmaceuticals, etc. [3-5]. As the particle size gets smaller, the solid particles tend to show different properties from the bulk material. Even physical properties such as melting point and dielectric constant can change when the particle reaches a size of a few nanometers [6]. The optical property of the nanoparticle varies greatly depending on whether the nanoparticle is an insulator, semiconductor or metal. [7]. Titanium dioxide is considered a more promising catalyst compared to all other semiconductor photocatalytic materials due to its good inertness, eco-friendliness, low cost, non-toxicity, high photocatalytic activity, strong oxidizing power and long-term stability against photo and chemical corrosion [8-12]. TiO₂ is a wide-bandgap metal oxide semiconductor widely recognized with photocatalytic properties for pollution removal from polluted water and gases. Most photocatalysts are metal oxide pure semiconductors and their doped forms. Among various photocatalytic-based metal oxides such as ZnO, Nb₂O₃, SnO₂, Al₂O₃, nano TiO₂ stands out with its superior photocatalytic properties [13].

In this study, synthesis of titanium dioxide nanocomposites with hydroxyapatite and barium sulfate and investigation of their photocatalytic properties were aimed.

EXPERIMENTAL

Preparation and Characterization of Nanocomposites

Titanium powder (-325 mesh, 99.5 %) was provided by Alfa Aesar. Barium chloride (BaCl₂) was purchased from J. T. Baker. Sodium sulfate (Na₂SO₄) and hydroxyapatite (HAp) were from Sigma-Aldrich. TiO₂ synthesis procedure was reported previously in detail [14]. Synthesis of BaSO₄ nanocrystals was carried out by a previously described chemical precipitation method [15, 16]. Briefly, crystal growth of barium sulfate was achieved by slow mixing of equal volumes (0.1 M) of barium chloride and sodium sulfate solutions in presence of additives.

Particle size of the produced TiO₂ was investigated using laser diffraction (Micromeritics Saturn DigiSizer 5200 VI.10.). TiO₂ particles had a size between 200 and 400 nm. Characterization of functional groups present in the composites was performed by FT-IR spectroscopy (PerkinElmer Spectrum 100). The XRD patterns of the pure TiO₂ and composites of TiO₂ were recorded on a diffractometer (Panalytical X'Pert Pro PW 3040/60) with nickel filtered CuK ($\lambda = 1.54 \text{ \AA}$) as a radiation source and at a 2θ scan speed of $1^\circ/\text{min}$ at 30 kV and 20 mA.

The surface areas of the TiO₂ composites were analyzed by the Brunauer-Emmett-Teller (BET) method. Nitrogen sorption isotherms according to the multiple-point BET (Brunauer, Emmett and Teller- COSTECH Kelvin Sorptometer 1042) method were used to determine the specific surface area of the samples.

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To evaluate the degradation rate of methylene blue, samples were collected at different times and analyzed by UV-Visible spectroscopy (Perkin Elmer), considering the main peak of this dye located at 665 nm.

RESULTS AND DISCUSSION

Characterization

Figure 1 shows the FT-IR spectra of neat TiO_2 and of the prepared nanocomposites. The presence of BaSO_4 and HAp was confirmed by FT-IR analysis. X-ray diffraction patterns of bulk TiO_2 (a), HAp/ TiO_2 nanocomposites (b) and $\text{BaSO}_4/\text{TiO}_2$ nanocomposites (c) are seen in Figure 2, respectively. A rutile structure is seen with the 2θ peak at 27.6° . The pattern reveals the successful formation of HAp and conforms to the HAp standard (Joint Committee on Powder Diffraction Standards) JCPDS pattern 01-072-1243) shown in Figure 2 (b). All the diffraction peaks in Fig. 2 (c) matched with the reference of the barite structure (JCPDS No:01-080-0512).

BET surface area and total pore volume of the samples are given in Table 1. The BET surface area of the prepared TiO_2 particles was $0.1754 \text{ m}^2/\text{g}$, the BET surface area of HAp/ TiO_2 composite was $1.1162 \text{ m}^2/\text{g}$ and the BET surface area of $\text{BaSO}_4/\text{TiO}_2$ was $1.9913 \text{ m}^2/\text{g}$. BET analysis showed that the addition of BaSO_4 and HAp increased both surface area and pore ratio. The surface area increased more than 10 times in the presence of barium sulfate.

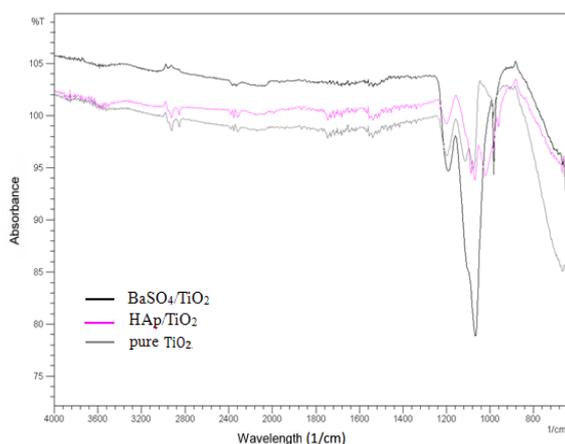


Figure 1. FT-IR analysis of titanium dioxide composites

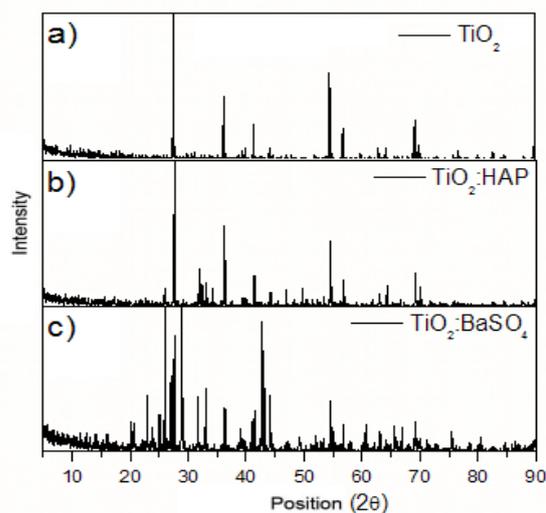


Figure 2. X-ray diffraction patterns of TiO_2 composites

Table 1. BET surface area of TiO_2 composites

Samples	BET Surface Area (m^2/g)	Total Pure Volume (cm^3/g)
Pure TiO_2	0.1754	0.0403
HAp/ TiO_2	1.1162	0.2564
$\text{BaSO}_4/\text{TiO}_2$	1.9913	0.4574

Photocatalytic Decomposition of Methylene Blue

Photocatalytic decomposition graphs of methylene blue are shown in Figure 3. Experiments were carried out for 8 hours. It was observed that the variation of the concentration values with time is not linear. Figure 3 (a) shows the concentration-time plot of the degradation of methylene blue with neat TiO_2 .

It can be seen from this graph that the concentration decreased from 0.0173 mmol/L to 0.0157 mmol/L over 8 hours. Figure 3 (b) shows the degradation of methylene blue with a sample of $\text{BaSO}_4/\text{TiO}_2$. The concentration decreased from 0.0165 mmol/L to 0.0158 mmol/L over time. In this graph, the concentration values are relatively linear after the sixth hour. Decomposition test data of methylene blue with HAp/ TiO_2 sample is shown in Figure 3 (c). It was observed that the concentration decreased from 0.0173 mmol/L to 0.0155 mmol/L within 8 hours. In the present work, it was observed that the addition of HAp and BaSO_4 does not significantly modify the physicochemical properties of sulfated TiO_2 , as can be seen in Fig. 3. Thus, as expected, the photocatalytic degradation efficiency of methylene blue in the presence of all the samples is very similar to each other within 8 hours of reaction time. No deactivation of the photocatalysts was observed even after 18 hours of reaction time.

CONCLUSIONS

In the present study, HAp/TiO₂ and BaSO₄/TiO₂ nanocomposites were successfully synthesized and their effects on photocatalytic degradation of methylene blue were examined. In the degradation experiments of methylene blue with all three samples, it was observed that the degradation

values obtained after 8 hours were very close to each other. When compared according to the amount of absorption in studies with methylene blue, it was observed that HAp/TiO₂ > BaSO₄/TiO₂ > pure TiO₂.

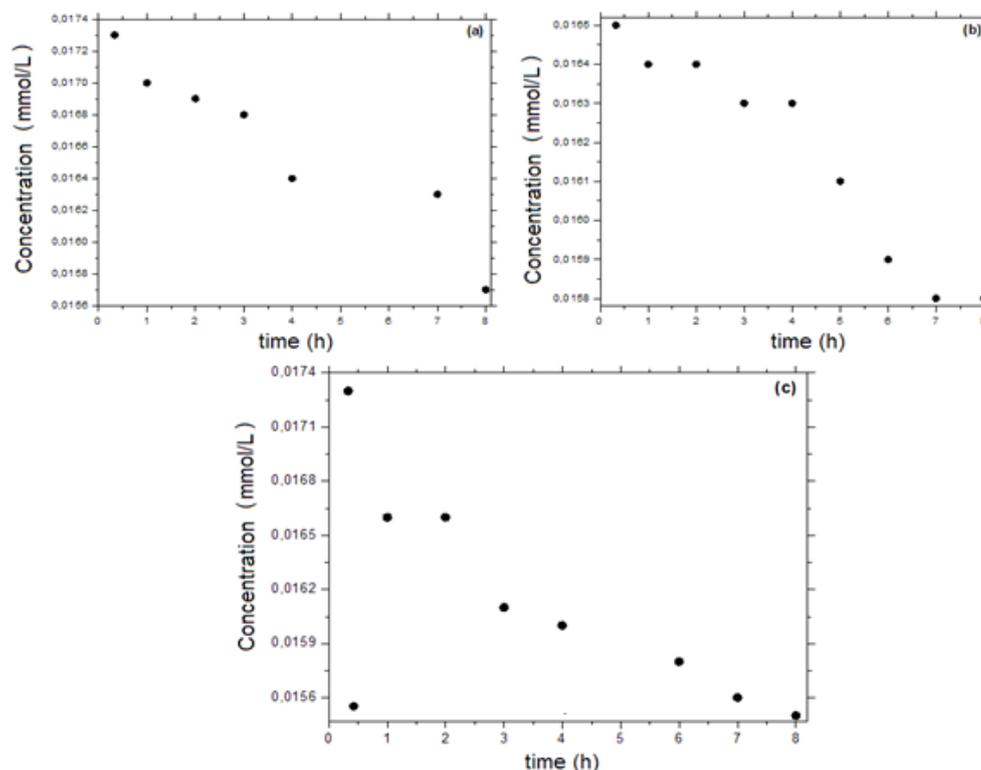


Figure 3. Methylene blue degradation over 8 h using a) TiO₂, b) BaSO₄/TiO₂, c) HAp/TiO₂

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