Investigation of Photocatalytic Activities of Bi_2S_3 Nanoparticles Synthesized by Ethylene Glycol Assisted Hydrothermal Synthesis Method in Dyestuff Removal from Wastewater

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Abstract – The high photocatalytic activity of semiconductor nanomaterials in the photocatalytic removal of organic pollutants in wastewater increases the interest in these materials day by day. One of the most widely used semiconductor photocatalysts as a photocatalyst is Bismuth sulfide (Bi_2S_3). In this study, Bismuth sulfide (Bi_2S_3) nanomaterials, which is a widely used semiconductor type, were synthesized by ethylene glycol-assisted hydrothermal synthesis method. Then, the structural and morphological properties of the synthesized nanoparticles were defined by analysis techniques such as XRD, TEM, and BET. After confirming that the synthesized particles were Bi_2S_3, it was used it as a photocatalyst in the photocatalytic removal of Procion Yellow HE-3G, a diazo group textile dye, from synthetic wastewater. In these trials, trials were carried out with 4 different catalyst dosages, namely 0.010 g/L, 0.025 g/L, 0.050 g/L, and 0.10 g/L. The obtained results showed that the produced Bi_2S_3 nanoparticles were quite good photocatalysts. In the experiment with a catalyst concentration of 0.10 g/L, the dye in the solution was completely removed within 60 minutes. However, very close results were observed in photocatalysis experiments made with all catalyst dosages.

Keywords – Bi2S3, Hydrothermal Synthesis, Ethylene Glycol, Removal, Photocatalysis

I. INTRODUCTION

Control of environmental pollution and removal of existing pollutants is one of the most critical challenges of the 21st century. Although dozens of wastewater treatment methods are in use today, too much wastewater is generated due to developing technologies, increasing human population and pollution load, and increasing industrial activities. To overcome this situation, known treatment methods should be developed harmoniously with evolving technologies. Photocatalytic oxidation processes with artificial or natural ultraviolet (UV) light are accepted as a revolutionary treatment method in water and wastewater treatment with their potential to provide rapid and complete mineralization of organic pollutants in wastewater without leaving any harmful residues. Until recently, only metal oxides such as TiO_2 and ZnO were used as photocatalysts, but today it is known that many semiconductors exhibit excellent photocatalytic performances [1-3].

In photocatalysis processes, photo-generated electrons and holes are formed in the material when any semiconductor with a suitable band structure absorbs energy higher than the band gap under ultraviolet light radiation. These particles are

transferred to the catalyst surface, forming various active radicals, and these radicals decompose the organic pollutant [4].

An essential type of semiconductor materials used as photocatalysts is metal sulfides. Metal sulfide-type semiconductors show high efficiency in the photodegradation of organic pollutants. In this study, an economical and environmentally friendly synthesis method was proposed for the synthesis of Bi_2S_3 nanostructures, which is an essential member of metal sulfides, and then Bi_2S_3 synthesized by this method was used as a photocatalyst for dye removal from wastewater.

II. Materials and Method

A. Preparation of Materials

Bismuth nitrate, ethylene glycol, and thiourea were precursor chemicals in synthesis studies. All of these materials were purchased from Sigma-Aldrich. These materials are of analytical purity, and no additional purification has been applied. All other substances, such as H_2O_2 solution and ethyl alcohol used, were also supplied from Sigma Aldrich company. Procion Yellow HE-3G textile dye was purchased from Fluka. Pen-Ray type UV lamp (254 nm) purchased from Cole-Parmer was used as the UV light source in the experiments.

B. Synthesis of Bi_2S_3 Nanoparticles

Bismuth sulfide (Bi_2S_3) nanoparticles were synthesized by hydrothermal synthesis method. In this study, ethylene glycol was used as the surfactant. Specific volumes of bismuth nitrate and thiourea solutions determined by reaction stoichiometry were measured and combined in a beaker. 20 mL of ethylene glycol was added to the mixture and mixed effectively with a magnetic stirrer for approximately ten minutes. Meanwhile, the pH value of the mixture was increased to 11 by adding concentrated NaOH solution. The final mixture obtained was taken into a steel reactor with an inner surface coated with Teflon, and the tightly closed reactor was kept in an oven at 200°C for 24 hours. At the end of this period, the reactor removed from the furnace was cooled to room temperature, and the reactor contents were centrifuged. The solid particles obtained were washed twice with water and ethyl alcohol. The final product was dried at 100°C for 24 hours.

C. Characterization of Bi_2S_3 Nanoparticles

XRD analysis of the obtained Bi_2S_3 nanoparticles was performed with Bruker D8 Discover model device. In this study, FEI Talos F200S (200 kV) system was used for TEM analysis. BET analyses were performed with the Micromeritics Gemini VI model surface analyzer. To monitor the change in dye concentration in the solution, samples were taken at specific time intervals and, colour changes of the solution were measured with a Merck Spectroquant Prove 300 model UV-Vis spectrophotometer.

III. Results

Results X-ray diffraction analysis is the most widely used technique for identifying the phases of nanoparticles produced in powder form in the laboratory. With XRD analysis, while defining the phases of the material, very important data about its microstructural structure can be obtained at the same time. Accordingly, XRD analysis was performed on the powder sample obtained to define the phases of the nanoparticles produced in this study. The X-ray diffractogram obtained as a result of this analysis is given in Figure 1 below.

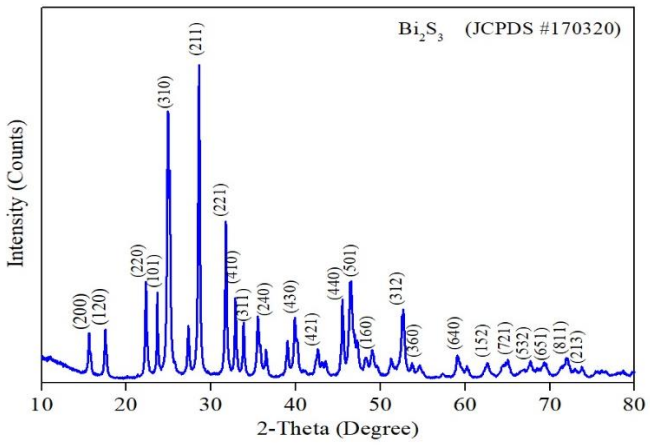


Fig. 1. X-ray diffractogram of the Bi_2S_3 sample prepared with the hydrothermal synthesis method

The X-ray diffractogram presented in Figure 1 was compared with the library of standard diffraction cards. It was determined that this diffractogram is fully compatible with JCPS#170320, defined for bismuth sulfide. No other formations were observed. This result shows that the obtained powder sample consists of a single phase. XRD analysis confirmed that the chemical structure of the received product was pure Bi_2S_3, as expected [5].

Accordingly, TEM imaging was performed to obtain information about the size and morphology of the powder sample. Acquired TEM images are given in Figure 2 below.

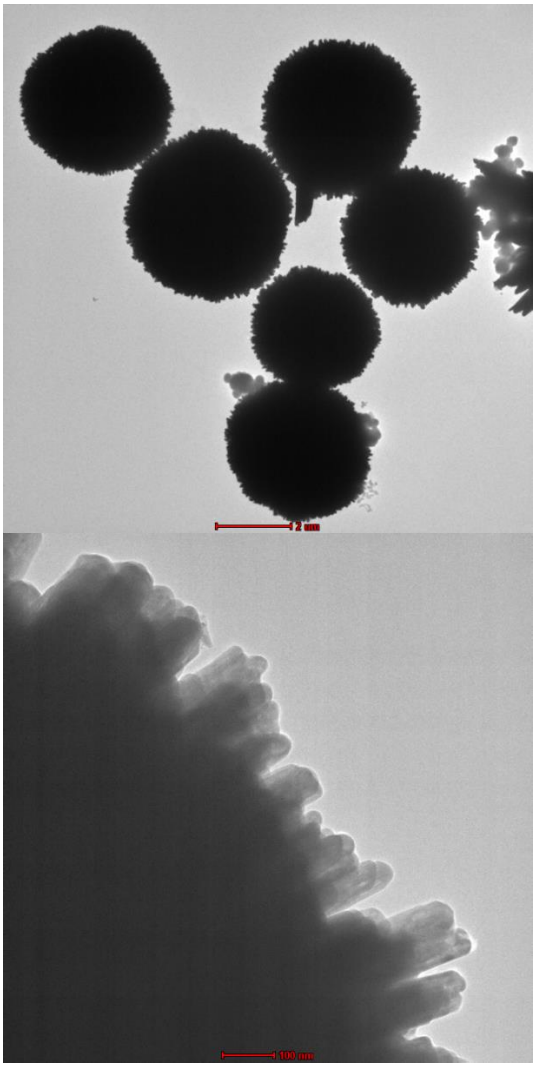


Fig. 2. The TEM images of the Bi_2S_3 sample prepared with hydrothermal synthesis method

In the TEM images presented in Figure 2, it is seen that the bismuth sulfide product obtained is morphologically spherical and flower-like, and the particle size is almost 1 micrometer. TEM images demonstrated that many nano-sized rod-like structures are formed on the surface of the particles.

Another essential characteristic of the particles used for catalysis is the surface area. BET analysis was performed to determine the surface area of the product bismuth sulfide particles. Before this analysis, degas treatment was carried out at 100 °C in an inert gas atmosphere (N_2) in order to remove the impurities on the sample. The adsorption desorption isotherm obtained as a result of this analysis is given in Figure 3.

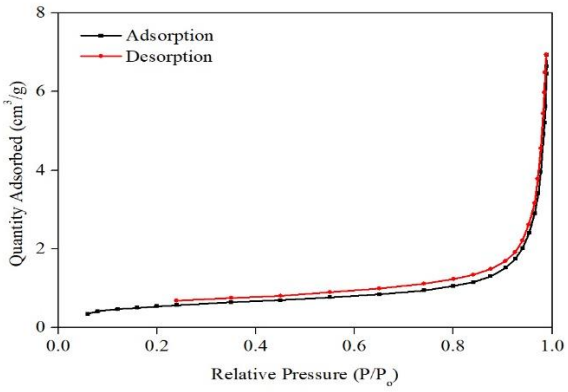
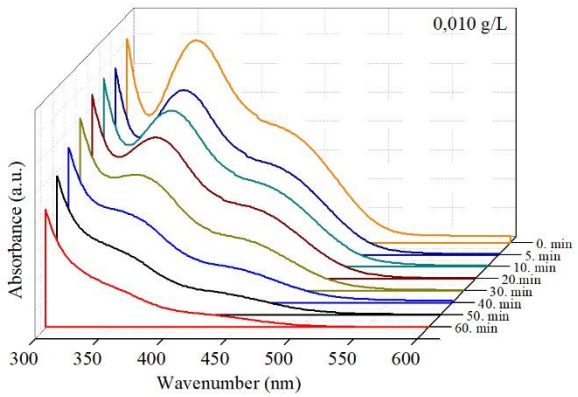


Figure 2. The Adsorption-Desorption isotherms of the Bi_2S_3 sample prepared with hydrothermal synthesis method

While the BET surface area of the synthesized nanoparticles in the BET analysis was measured as 2.1 m^2/g, the Langmuir surface area was measured as 3.01 m^2/g. These surface area values and the obtained adsorption desorption isotherms indicate that the produced samples have a microporous structure.

A.Photocatalytic activity tests

The photocatalytic activities of the synthesized Bi_2S_3 nanoparticles were tested in the removal of the dyestuff in a dye solution by photocatalytic oxidation. In these tests, catalyst was added to the solution containing 100 ppm dye, with catalyst concentrations of 0.010 g/L, 0.025 g/L, 0.050 g/L, and 0.10 g/L, respectively, and the mixture was exposed to UV radiation. No pH adjustment was made in the solutions and all experiments were performed at the natural pH of the solution.



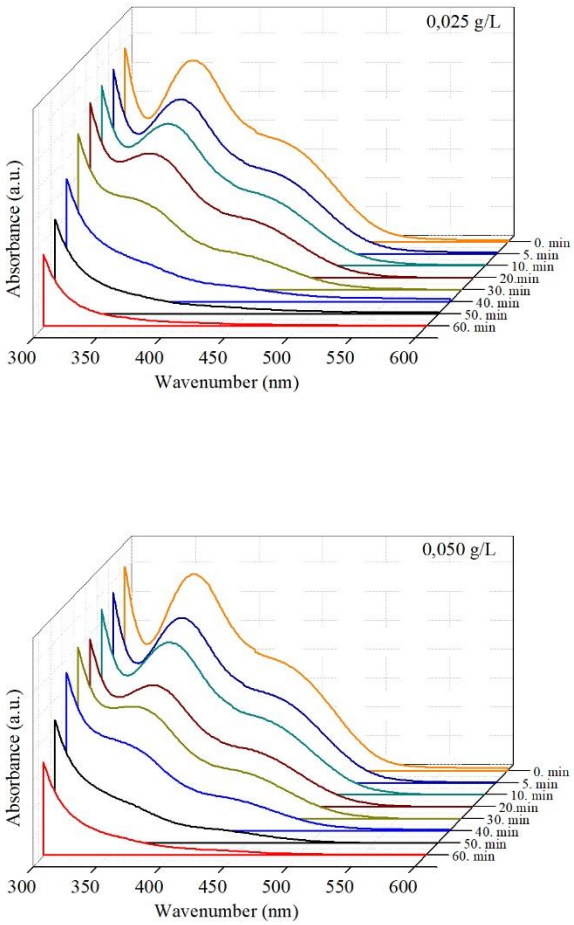


Figure 4. Time dependent absorbance graphs showing the concentration change in the dye solution

In these experiments, the time dependent absorbance graph showing the concentration change in the dye solution is given in Figure 4.

It is seen from the absorbance changes that there is a significant decrease in dye concentration over time. Color removal in the dye solution indicates degradation of the dye. In these analyses, the entire spectrum was scanned in the visible region (300-800nm), and it was also monitored whether the decayed dye transformed into another material. However, no other formation was observed. Removal efficiencies calculated concerning dye concentrations are presented in Figure 5.

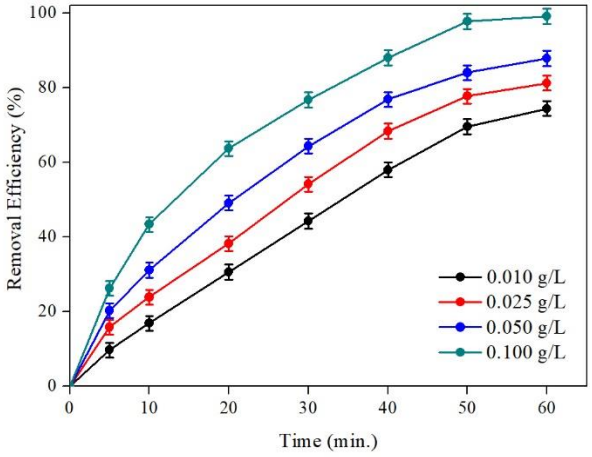


Figure 5. Time-dependent changes of removal efficiencies calculated from the change in dye concentration in photocatalysis experiments

When the experimental data given in Figure 5 are examined, it is seen that there is an increase in the removal efficiency with the increase in the catalysis concentration. This increase is an expected result as the amount of active surfaces increases with increasing catalysis concentration. Although there are significant differences in amount between the catalyst concentrations, no significant difference was observed in the resulting removal efficiencies.

IV. CONCLUSION

Bi_2S_3 nanoparticles were produced by ethylene glycol assisted hydrothermal synthesis technique. It was determined that the particles were on average 1 micron in size. In photocatalysis trials, it was observed that almost all of the dye in the solution could be removed in about 60 minutes. No significant change was observed in the removal efficiencies with the change in catalyst concentrations. It is estimated that the removal efficiencies can be further increased by optimizing

parameters such as temperature, light intensity, mixing speed, and exposure time.

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