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**Original Research Article**

# Photocatalytic degradation of methyl orange dye using bismuth oxide nanoparticles under visible radiation

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**ABSTRACT**

In this study, Bismuth oxide supported by copper nanoparticles were successfully synthesized by hydrothermal method and the effect of pH, catalyst dose of initial dye concentration was studied. It has shown excellent photocatalytic performance in the degradation of methyl orange dye under UV light, so that 93.76% degradation was obtained at acidic pH and color concentration of 20 mg/l with 0.04 g/l photocatalyst. The kinetic study reacted that the Pseudo-first-order model is the best model for the photocatalytic degradation of methyl orange. In addition, the reuse test showed that the nanocomposite, after 4 reuse periods maintained its stability in high colour removal. Therefore, it can be safely said that the nanocomposite due to its good photocatalytic performance can be used as a promising photocatalyst for the treatment of environmental pollutants on a large scale.

**Keywords:** Methyl orange, Hydrothermal center, Photocatalytic degradation, Reuse.

## Introduction

The presence of organic pollutants in water can cause environmental problems and adverse effects on the lives of humans and other living organisms. Among the different types of organic pollutants, dyes are widely used in the food and textile industries and are also highly stable in aquatic environments [1]. Consumption of these compounds in industrial processes leads to the production of large volumes of dye after containing organic and inorganic materials that the treatment of them is one of the environmental requirements [2]. Colours are often resistant to biodegradation due to their complex structure, and have been considered due to their carcinogenic effects, toxicity to living organisms, dysfunction of wastewater treatment systems, and aesthetics of the environment [3]. There are various methods for removing color compounds such as methyl orange from water and wastewater such as coagulation and flocculation, biological treatment, chemical oxidation, electrochemical treatment, ion exchange and adsorption process, but these methods are expensive and costly [4].

In recent years, advanced oxidation processes have been widely used to remove organic pollutants, especially dyes. The mechanism of these processes is based on the production of reactive active radicals such as OH and ultimately the decomposition of pollutants through the oxidation of pollutants [5,6]. At present, the use of efficient photocatalytic and the applications of metal oxide, sulfate, or nitride-based semiconductors and nanomaterials to remove contaminants are highly considered [7].

One of the most important metal oxide semiconductors that has been considered in recent years is bismuth oxide, which is a photocatalyst due to heat and electrical transfer, large area, non-toxicity in various processes including fuel cell, gas sensor. Under UV and sunlight has attracted a lot of attention [8,9].

One of the weaknesses of $Bi_2O_3$ is the rapid combination of electrons and pores, which limits the use of this semiconductor in photocatalytic processes. Thus, new $Bi_2O_3$-based photocatalysts are needed for further practical applications [8]. Since the conduction band edge for CuO semiconductors is much higher than $Bi_2O_3$ and facilitates the transfer of electrons from the conduction band, CuO to $Bi_2O_3$, the use of $Bi_2O_3$ and $Cu_2O$ to facilitate photocatalytic activity

may be a good solution. Therefore, in this study, the photocatalytic removal of methyl orange was investigated using a combination of $Bi_2O_3$/CuO semiconductor catalysts.

## Experimental

Production stages and physical and chemical properties of nanocomposites are presented in the supplementary material.

### Photocatalytic degradation tests of methyl orange dye

Photocatalytic experiments were performed in a 100 ml batch reactor containing 50 ml of dye solution at room temperature. UV-C lamp (6 watts) was used as the light source. A magnetic stirrer and an aeration pump were used to mix and supply dissolved oxygen. NaOH and HCl were used to adjust the pH. Before irradiation, the solution was stirred in the dark for 30 minutes to achieve an adsorption/desorption equilibrium. The solution was then exposed to light and the samples were taken from the solution at various reaction intervals (5, 15, 30, 45, 60, 90, 120 minutes). The effect of parameters such as pH, catalyst content and initial dye concentration in the presence of UV radiation was studied. Finally, the samples extracted from the reactor were then centrifuged for 15 minutes at 2000 rpm to separate the photocatalytic nanoparticles from the dye solution. The final concentration of methyl orange dye was determined using a spectrophotometer at 464 nm. Methyl orange paint degradation efficiency was calculated using the following equation [3, 10]:

$$\text{Photodegradation efficiency } (\%) = \frac{C_0 - C_t}{C_0} \times 100$$

In this regard, R: color degradation efficiency, $C_0$ and $C_t$ are the initial and final concentrations at time t.

## Results and discussion

### Photocatalytic degradation experiment

### Effect of pH on photodegradiation of methyl orange

One of the effective parameters in photocatalytic reactions is the initial pH of the solution. For this purpose, the effect of pH on different levels of 2, 3, 5, 7 and 9, concentration of 10 mg/l of color pollutant and catalyst dose of 0.02g/l were investigated.

Figure (1) shows the results of pH optimization. As can be seen, with increasing pH, the amount of color degradation decreases. Before starting the experiment, the solution was placed in the dark condition for 30 minutes for adsorption/desorption equilibrium, and then light color degradation tests were performed. The results showed that in dark conditions and only in the presence of nanoparticles, the removal was negligible but after light irradiation due to the production of hydroxyl radicals, the removal increases so that the most removal was obtained at pH 2. The reason for the increase in the degradation efficiency of methyl orange at pH 2 is that in an acidic environment the formation of hydroxyl radical (OH◦) is higher due to the high concentration of H ions and superoxide radicals. The mechanism is shown as the following reactions [3,11,12]:

$$2HO_2 \longrightarrow O_2^{\circ} + H_2O_2$$

$$H_2O_2 + O_2^{\circ-} \longrightarrow OH^{\circ} + OH^{-} + O_2$$

$$e^{-} + O_2 \longrightarrow O_2^{\circ-}$$

$$O_2^{\circ-} + H^{+} \longrightarrow 2HO^{\circ}_2$$

Also at low pH, the activity of the $CuO/Bi_2O_3$ photocatalyst increases due to the reduction of electron-hole recombination, which leads to further removal in these conditions. At alkaline pH, the rate of degradation is much lower due to the negative charge in the nanocomposite and the dye [13].

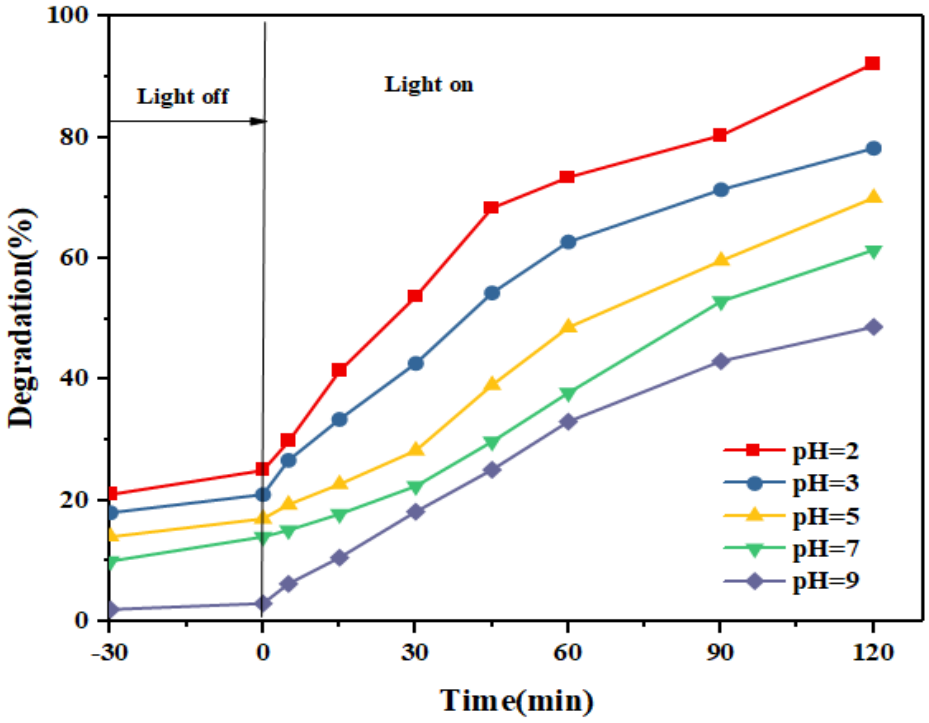


**Figure 1.** Effect of different pHs (2-9) on the removal of methyl orange (catalyst dose: 0.02 g/l, dye concentration: 10 mg/l)

**Effect of catalyst dose on photocatalytic degradation of methyl orange**

Figure (2) shows the effect of different concentrations of $CuO/Bi_2O_3$ nanoparticles (0.02-0.05 g/l) on the degradation of methyl orange dye. As can be seen, with increasing the amount of nanoparticles from 0.02 to 0.04 g/l, the number of absorbed photons increases, which increases the number of active sites available at the catalyst surface, which in turn produces the number of hydroxyl and superoxide radicals produced. As a result, the number of dye molecules adsorbed on the catalyst surface also increases, so the degradation increases [8,3]. Other researchers also showed that with increasing the concentration of photocatalyst, the amount of degradation increases to the optimal level and with increasing more than the optimum, the degradation decreases due to reduced light penetration [14, 15]. The solution turbidity increases the light scattering from the catalyst surface and reduces the degradation efficiency, which is consistent with the present study because the degradation efficiency decreased with increasing concentration of 0.05 g/l due to reduced light penetration and turbidity in the solution. In fact, when the dose of $CuO/Bi_2O_3$ nanoparticles increased more than a certain amount, due to the increase in turbidity in the solution and the decrease in light penetration as a result of increasing the scattering effect, the amount of dye degradation decreased. As a result, 0.04 g/l was considered optimal.

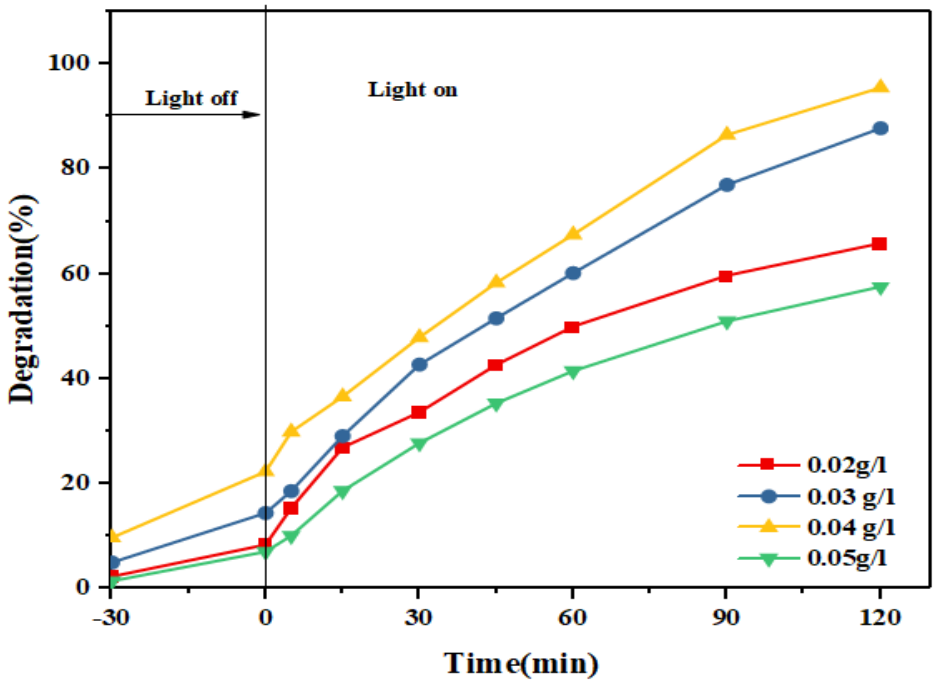


**Figure 2.** Effect of different doses of $CuO/Bi_2O_3$ catalyst (0.05-0.02 g/l) on photocatalytic degradation of methyl orange (pH=2 catalyst dose: 0.05-0.01 g/l, dye concentration: 10 mg/l)

**Effect of initial concentration of dye on photocatalytic degradation of methyl orange**

Experiments on the effect of initial concentration of methyl orange at pH = 2 and the optimal concentration of catalyst (0.04 g/l) showed that with increasing the initial concentration of the pollutant, the rate of photocatalytic decomposition decreases (Figure 3). The results of adsorption showed that the use of nanoparticles alone has little effect on removal if the amount of removal increases after light irradiation. The maximum degradation of methyl orange by $CuO/Bi_2O_3$ in 120min and the initial dye concentration of 20 mg/l was 93.76%. The maximum degradation of methyl orange was obtained in 120 min at a concentration of 20 mg/l methyl orange. The reason for the decrease in high concentrations of methyl orange is that in the photocatalytic process the concentration of radicals produced is the same in all solutions. Photocatalyst becomes more dye at low concentrations [3, 10, 16]. Also, during the decomposition of dye molecules, more reactive intermediate products are formed which react with these radicals and due to the competition between intermediate products, the amount of hydroxyl decreases, thus the degradation efficiency decreases at higher concentrations [6]. In a study by Vinoth and colleagues showed that at higher concentrations of dye molecules, part of the photons emitted into the adsorption medium are contaminated, thus reducing the penetration of light into the environment, resulting in less damage at higher concentrations [17].

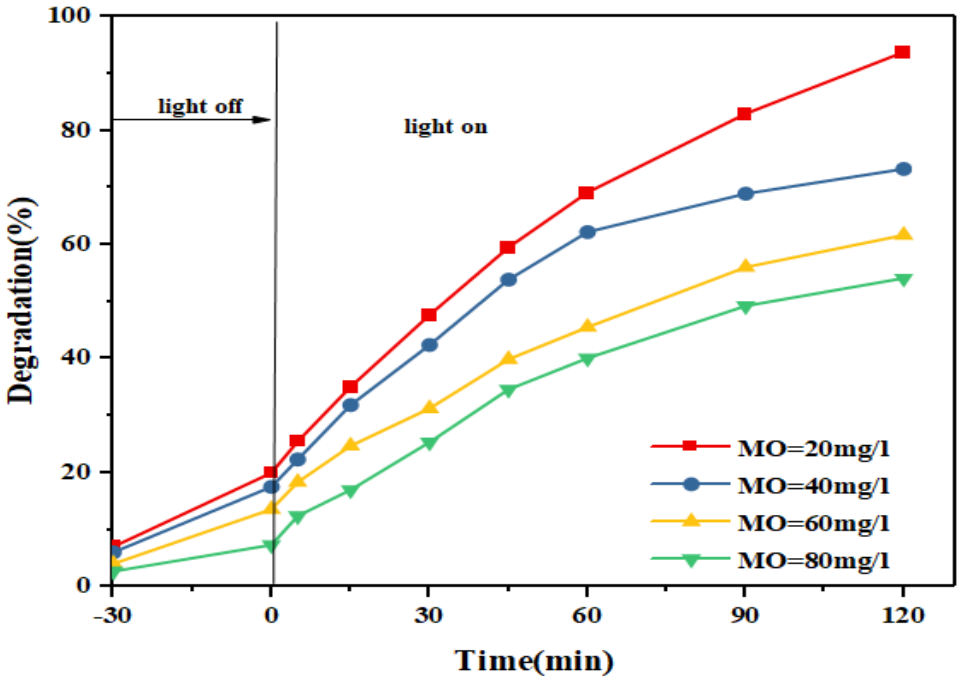


**Figure 3.** Effect of initial dye concentration (20-80 mg/l) on photocatalytic degradation of methyl orange (pH = 2 catalysts 0.04 g/l, dye concentration: 10-50 mg/l)

**Kinetic model of methyl orange photocatalytic degradation**

The photocatalytic oxidation kinetics of many organic compounds, including dyes, is expressed by the Langmuir-Hinslowwood equation, which covers the properties of the substrate at the catalyst level [6,18]. The photocatalytic degradation kinetics of methyl orange was tested under optimal conditions (pH = 2, concentration of methyl orange 20 mg/l, nanocomposite dose 0.4 g/l).

$$-\ln(\frac{C_t}{C_0}) = kt$$

Displays the velocity constant (k) for different photocatalysts by plotting ln ($C_t/C_0$) versus time t, from which the velocity constant (k) can be determined from the slope (Figure 4). This kinetic model is related to Pseudo-first-order model for low concentrations. The results of Pseudo-first-order model are shown in Table 1. According to the results, it was found that with increasing the concentration of methyl orange, the amount of k decreases. At high concentrations of pollutants, as previously mentioned, due to the production of intermediate products, the amount of hydroxyl produced decreases, which leads to a decrease in degradation efficiency [19].

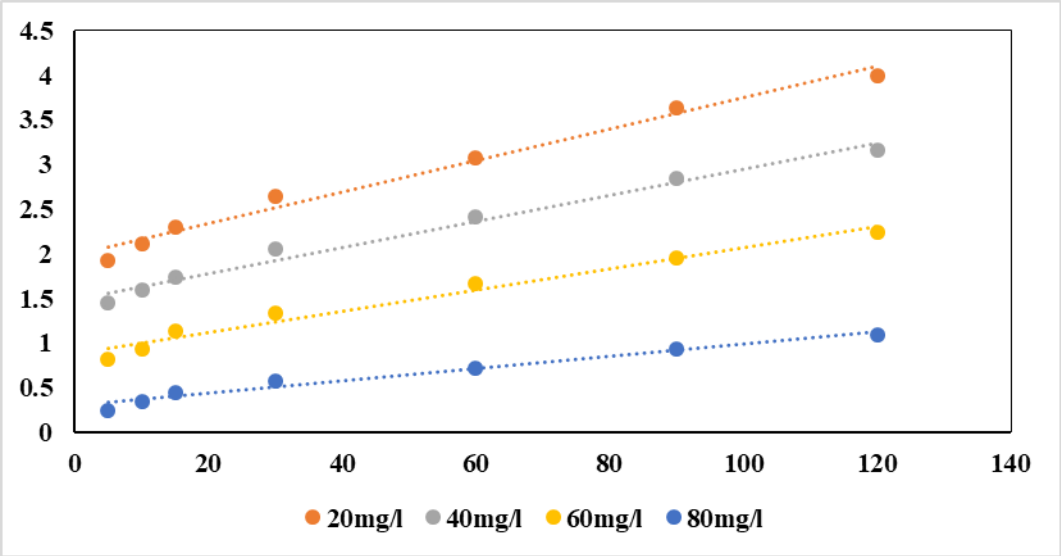


**Figure 4.** photodegradation kinetics of methyl orange dye (pH = 2 catalysts dose 0.04 g/l, dye concentration: 20-80 mg/l)

**Table 1:** Kinetic constant for MO dye adsorption

| $R^2$ | K0($min^{-1}$) | Equation | Concentration of MO(mg/l) |
|---|---|---|---|
| 0.9827 | 0.0176 | Y=0.0176x+1. 9821 | 20 |
| 0.9836 | 0.0146 | Y=0.0146x+1.4917 | 40 |
| 0.9725 | 0.0884 | Y=0.01118x+0.8837 | 60 |
| 0.9726 | 0.0069 | Y=0.0069x+0.2968 | 80 |

**Stability and reuse of photocatalysts**

Stability potential and reusability of the catalyst is one of the important parameters to determine its activity and stability. Therefore, the potential for reusability of $CuO/Bi_2O_3$ nanoparticles was investigated in 4 consecutive periods. The fourth has decreased by 82.45%. This slight decrease in $CuO/Bi_2O_3$ photocatalytic activity is probably due to the loss of stability during the washing and drying processes [8,11]. In addition, ICP-OES analysis of $CuO/Bi_2O_3$ nanoparticles after photocatalytic degradation process showed that only 2% of nanoparticles were lost after 4 reuse cycles, indicating very good stability of these nanoparticles during photocatalytic processes. Therefore, due to the good reusability of the present photocatalytic system, it can be used as a promising candidate for industrial applications on a larger scale.

**Mechanism of photocatalytic reaction for photodegradiation of methyl orange**

A mechanism for increasing photocatalytic activity for the $CuO/Bi_2O_3$ composite has been proposed. The synergistic effect between CuO and $Bi_2O_3$ nanoparticles leads to an increase in the high photocatalytic activity of $CuO/Bi_2O_3$ composite nanoparticles. Figure (5) shows the generation and conversion of electron holes and their $CuO/Bi_2O_3$ catalyst surface. Since $Bi_2O_3$ nanoparticles are the main catalyst and copper oxide coating facilitates charge separation and reduces the bond gap, electron transfer at the photocatalyst surface is facilitated. The optical electrons (e-) generated in the conduction band $Bi_2O_3$ are transferred to the surface layer of CuO. These electrons are rapidly absorbed by $O_2$ molecules in solution and form O radicals. The holes (h+) created in the $Bi_2O_3$ capacitance band react with $H_2O$ molecules to form hydroxyl radicals [3,4]. Therefore, the hydroxyl and superoxide radicals OH and O formed with the pollutant constantly react and cause photocatalytic degradation of methyl orange.

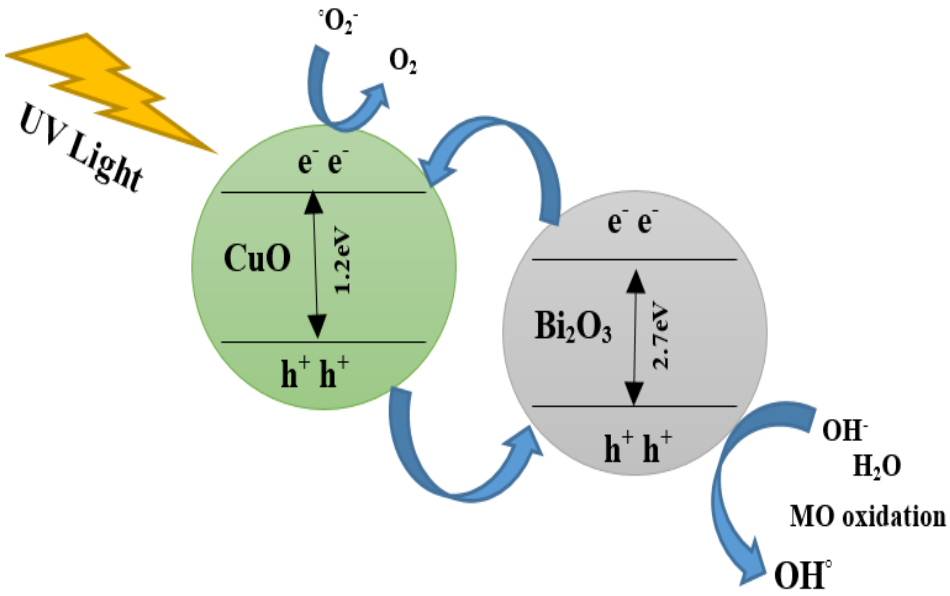


**Figure 4.** Mechanism of photocatalytic reaction

**Conclusion**

In this study, $CuO/Bi_2O_3$ nanocomposite was used to remove methyl orange dye from aqueous solutions. The results of this study showed that the percentage of photocatalytic degradation of methyl orange dye increased with increasing the catalyst load from 57.39 to 95.52%. Also, the percentage of dye removal decreased from 93.76 to 54.1% due to the increase in initial dye concentration. The results of pH optimization showed that in acidic environment the formation of hydroxyl radical (OH◦) is higher due to the high concentration of $H^+$ ions. The photocatalytic degradation kinetics follows a pseudo-first-order model. The catalyst was used for 4 reuse

periods without significant photocatalytic activity. According to the results of this study, it can be stated that CuO/ $Bi_2O_3$ photocatalyst due to its good photocatalytic performance can be used as a promising photocatalyst for the treatment of environmental pollutants.

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