



Photocatalytic TiO₂-catalyzed degradation of bromophenol blue-mediated Mo(VI)-peroxo complexes in the presence of SDS

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ABSTRACT

In the present study, the photocatalytic TiO₂-catalyzed degradation of bromophenol blue (BPB)-mediated Mo(VI)-peroxo complexes in the presence of sodium dodecyl sulfate (SDS) under UV irradiation was investigated. The analytical variables, such as pH, TiO₂ catalyst dosage, initial concentration of the dye, concentrations of H₂O₂, Mo(VI), and SDS influencing the photocatalytic degradation of BPB, were studied in detail. The obtained optimum conditions were as follows: pH 5.0, 0.5 mL of 11.0 mol L⁻¹ H₂O₂, 200 µg L⁻¹ Mo, 0.02 mmol L⁻¹ SDS, 5 mg L⁻¹ dye, 1.0 g L⁻¹ TiO₂. Under the optimized conditions, the percent removals have been 85.4 and 75.3% for TiO₂-UV-H₂O₂-Mo(VI) system with and without SDS, while they are 65.2 and 59.4% for TiO₂-UV system with and without H₂O₂. As a result, it has been observed that the maximum removal rate is obtained for TiO₂-UV-H₂O₂-Mo(VI) in presence of SDS at premicellar concentration with a value of 85.4%. The removal rate of the dye was spectrophotometrically monitored at 590 nm during the analysis.

Keywords: Dye; Photocatalytic degradation; Micellar effect; Titanium dioxide; Bromophenol blue

1. Introduction

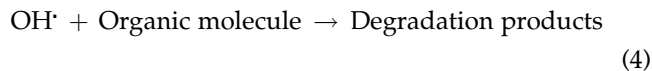
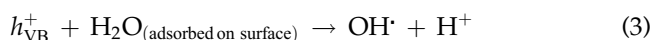
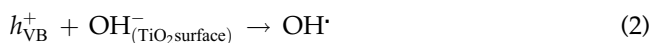
The wastewater containing organic dyes at high concentrations, which are extensively used in the textile, is a major problem for threat to the environment [1]. Their discharges into water as nontreatment are threatening for humans, animals, and plants health [2,3]. The conventional treatment methods are ineffective for degradation of the dyes due to the high concentration and stability of organic types [4,5]. Advanced oxidation processes (AOPs) are quite

appropriate for the remediation of wastewater as a pre or post-treatment step. They are mainly able to generate the hydroxyl radical (OH[•]), which has a great oxidation power, and are able to oxidize almost all organic compounds to carbon dioxide and water [6]. Heterogeneous photocatalysis through the irradiation of UV on semiconductor surface is an attractive AOP [7]. The AOPs involving Fenton and photo-Fenton processes, ozonation, electrochemical oxidation, photolysis with H₂O₂ and O₃, high-voltage electrical discharge process, photocatalysis, radiolysis, water solution treatment by electronic or beams and various combinations of these methods [8] and [9] are often

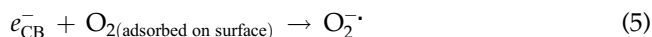
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used in the literature [8–10]. The common homogeneous Fenton systems are the cost-effective sources of hydroxyl radicals, but have some following major drawbacks that limit the industrial applications of this technology: (i) the tight range of pH in which the reaction precedes, (ii) the need for recovering the precipitated catalyst after treatment and (iii) deactivation by some ion-complexing agents like phosphate anions. The resulting sludge may also contain organic substances as well as heavy metals and has to be treated further, thus increasing the overall cost [11]. Among the various AOP techniques, semiconductor mediated photocatalysis like ZnO, TiO₂, Fe₂O₃, In₂O₃, SrTiO₃, SnO₂, and WO₃ as well as metal sulfides like ZnS and CdS, has recently been accorded great importance due to its potential to destroy a wide range of organic and inorganic pollutants at ambient conditions, without the production of harmful products [12–16]. However, the remained semiconductors except for ZnO did not show a photoactivity as much as those of TiO₂. Semiconductor photocatalyst generates electron and hole pairs (e^-/h^+) upon irradiation of light energy that could be utilized in initiating oxidation and reduction reactions [17,18]. Among the above-mentioned semiconductors, TiO₂ and ZnO have successfully been used as effective, inexpensive and nontoxic semiconductors for producing of photocatalysts for the degradation of a wide range of different pollutants in recent years [19,20].

Titanium dioxide (TiO₂), which is selected as semiconductor in the present study, has widely been used for the treatment of waters contaminated with many environmental pollutants, which can be degraded by oxidation and reduction processes on its surface [21,22]. Besides, TiO₂ is a chemically stable, nontoxic, highly efficient, and relatively inexpensive photocatalyst. Photocatalytic oxidation processes are taken place among AOPs. When a photon with an energy, which matches or exceeds the band gap energy of the semiconductor, is incident on a semiconductor surface, a conductive band electron will jump to its valence band leaving a positively charged hole behind. The initial step in this type of photo-oxidation process is believed to be the formation of free hydroxyl radicals [23–25]. Hydroxyl radicals are generated as a result of reaction of water (OH⁻ ions) with reactive positively charged holes produced by interaction of photon with TiO₂. The processes proceed according to the following proposed mechanism:



On the other hand, the dissolved O₂ molecules are transformed to anionic superoxide (O₂^{-•}) radicals via electrons from conductive band.



In the present study, the photocatalytic removal efficiency of bromophenol blue (BPB), which is a highly water-soluble anionic triphenylmethane group dye, chosen as a model compound in the UV/TiO₂ method was improved, and the effect of the parameters, such as pH, H₂O₂, Mo(VI), sodium dodecyl sulfate (SDS), initial concentration of the dye, TiO₂ dosage were investigated. With this purpose, TiO₂ was generally preferred as photocatalyst since it has non-toxic, inexpensive, reusability and highly reactive nature.

In the present study, the photocatalytic TiO₂-catalyzed degradation of BPB was investigated under UV irradiation at pH 5.0. The experimental factors, such as pH, initial concentration of the dye, concentrations of H₂O₂, Mo(VI) and SDS, TiO₂ dosage influencing the photocatalytic degradation of BPB, have been optimized in detail. The degradation rate was greatly improved by the activation of Mo(VI) in the presence of H₂O₂ as both hydroxyl radical generator and chelating ligand and SDS as micellar catalysis at TiO₂ catalyst–water interface. The removal rate of the dye was spectrophotometrically monitored at 590 nm during the analysis.

2. Materials and methods

The dye, BPB was purchased from Merck (Darmstadt, Germany). The stock solution of BPB was prepared in deionized water in all experiments. Titanium dioxide (anatase, 99.9% (w/w)) with a surface area of 9.35 m² g⁻¹ was supplied by Sigma–Aldrich (St. Louis, MO). The diluted HCl and NaOH solutions at 1.0 mol L⁻¹ were used to adjust the pH of the studied dye samples via pH meter. Hundred milliliters of an aqueous dye solution and 0.1 g TiO₂ (neat TiO₂) were initially placed into a 500-mL Pyrex flask (which is covered with aluminum foil) with a condenser. The pH of BPB sample solution was adjusted with diluted HCl and NaOH solutions. Suspension was stirred by magnetic bar after additions of reagents and was irradiated by means of an OSRAM-Ultra Vitalux 300 W low-pressure mercury lamp (no cutoff filters) with a

flux output of approximately 5.8 W near the 254 nm for 1 h. At specific time intervals, 5.0 mL of aliquots of irradiated sample was withdrawn and analyzed the residual dye's amount after centrifugation twice at 4,000 rpm for 10 min to separate TiO₂. The concentrations of the residual dye were spectrophotometrically measured at maximum absorption wavelength of 590 nm for time of 60 min. The degradation extent was determined using the following equation:

$$\text{Degradation \%} = \left(\frac{A_0 - A_t}{A_0} \right) \times 100 \quad (6)$$

where A_0 are the initial absorbance of BPB, and A_t are the final absorbance of at time t . Additionally, after the H₂O₂, Mo(VI), SDS at suitable doses were added into the photocatalytic system, their effects on the photocatalytic degradation were investigated.

3. Results and discussion

3.1. Prior studies

A series of experiments using BPB (Fig. 1) was carried out under three different conditions: in the presence of TiO₂ without UV light, in the presence of UV light without TiO₂, and in the presence of both TiO₂ and UV light. From the results obtained, it can be clearly seen in Fig. 8 that degradation of the dye in the absence of UV light is very slow and is similar to those in the absence of TiO₂ (in dark). As can be seen from the Fig. 8, the degradation of BPB has been significantly increased when the process is conducted with both TiO₂ and UV irradiation. It is clear that the process with UV irradiation in the absence of TiO₂ (or process with TiO₂ in the absence of UV irradiation) only causes to lower dye removal than 20%.

3.2. Effect of pH

The effect of pH on the degradation of dye has been investigated because wastewater contaminated with dyes has various pH values and it may be needed to a specific method for the treatment of the wastewater

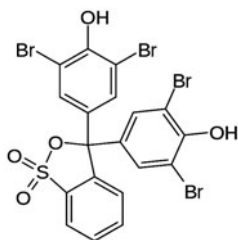


Fig. 1. The open molecular structure of BPB.

having specific pH. Experiments were repeated three times in the pH range of 3.0–10.0, and the results were shown in Fig. 2. As can be seen from Fig. 2, degradation yield increases in the acidic conditions and raises to a maximum value at pH 5.0. At higher pHs than 5.0, according to Lair et al. [26], degradation yield decreases, photocatalytic degradation increases in the near the zero point of charge conditions of TiO₂, then degradation yield decreases in the alkaline regions. At optimal pH 5.0, surface charge of TiO₂ is relatively positive because it has a pH_{pzc} ranging from 5.6 to 6.2 [27], while dye has a negative surface charge due to have a pK_a of 4.0. This decrease may be due to the nucleophilic attack of hydroxyl ions into unsaturated π -bonding of triphenylmethane dye, so as to cause colorless carbinol form of dye. The adsorption is an important factor in the photocatalytic reactions in acidic and alkaline conditions [28]. Based on the zero point charge of the TiO₂, it is clear that the surface charge will be positive in the acidic region, $\text{pH} < 5.6$ [29] and negative in the alkaline region, $\text{pH} > 6.2$ [30]. Since the BPB is an anionic dye having negative charge in a wide pH range of 5.0–9.0 and the TiO₂ has positive surface charge at lower pHs than 6.2, there will be an electrostatic interaction between molecules of negatively charged BPB and positively charged TiO₂ in the acidic conditions [28,31].

3.3. Effect of TiO₂ amount

The effect of photocatalyst amount on the rate of decolorization of the BPB was carried out by using different amounts of TiO₂ in range of 0.5–10.0 g L⁻¹ at pH 5.0. The degradation of dye on the surface of TiO₂ is

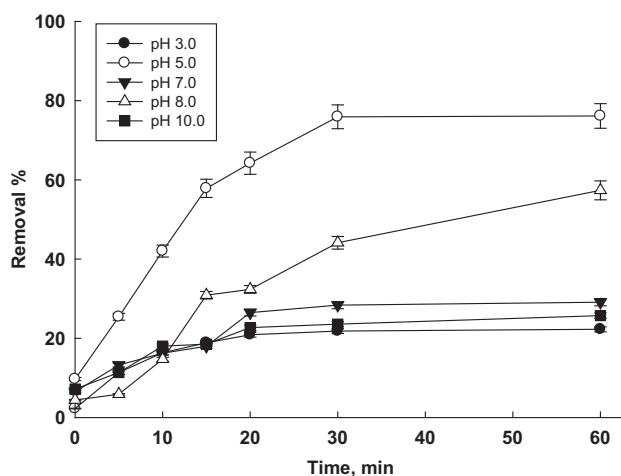


Fig. 2. Effect of pH on the photocatalytic degradation of BPB. Conditions: TiO₂ amount of 1.0 g L⁻¹, initial dye concentration of 5.0 mg L⁻¹, 0.5 mL of 11.0 mol L⁻¹ H₂O₂, 2.0 mL of 0.2 mg L⁻¹ Mo(VI), 2.0 mL of 1.0 mmol L⁻¹ SDS.

based on the electrostatic and hydrophobic interactions at solid-liquid interface. By the same mechanism, the degradation rate of dye is greatly improved by using Mo (VI) at trace levels as activator and/or promoter in presence of H_2O_2 and SDS as kinetically rate enhancement agent in pre-micellar region. As can be seen from Fig. 3, degradation rate increases with increasing TiO_2 amount from 0.5 to 1.0 g L^{-1} ; however, degradation rate has been almost unchanged while photocatalyst amount increases. It is known that the total active surface also will increase while photocatalyst amount increases [32]. The similar results have also been explained for the photocatalyst dosage on the photocatalytic degradation of other studies [28,32,33]. With increasing photocatalyst amount, the surface area that can be adsorbed, increases and more pollutant molecules interact with increasing hydroxyl and superoxide radicals in the catalyst surface [34]. However, the increase in the amount of catalyst has caused a negative effect [35]. Also, the cause of this negative effect may be the fact that when the concentration of the catalyst rises, the solid particles increasingly block the penetration of the UV photons when consideration of slopes of degradation curves in initial rate region of first 30 min. Hence, the overall number of the photons reaching to the catalyst particles and the production of OH radicals decreases [36]. Another reason may be the aggregation of solid particles when a large amount of catalyst is used [37].

3.4. Effect of H_2O_2 concentration

According to Zang and Farnood [38], in the photocatalytic system, the recombination of electrons and

holes exists. In order to avoid this recombination, the inorganic oxidants (electron acceptors) such as H_2O_2 [39,40], BrO_3^- [1,41], Ag^+ ions [36,42], and $\text{S}_2\text{O}_8^{2-}$ [43,44] may efficiently be used. Hydrogen peroxide is a powerful and eco-friendly oxidant that has been used in the treatment of wastewater, drinking water, and soil containing unhealthy contaminants. It can be used in the degradation of dye either directly in the presence of a catalyst and UV light or both [45]. As a result of the decomposition of hydrogen peroxide, hydroxyl radicals are formed. As can be seen from Fig. 4, the degradation rate of BPB increases with increasing H_2O_2 amount, but as amount of H_2O_2 further more increases, the degradation rate decreases. The similar results have been reported for photocatalytic oxidation of a dye selected in the literature [46]. Shortly, the enhanced degradation of dye in the presence of H_2O_2 can be due to the trapping of electrons with hydrogen peroxide, thereby reducing the recombination of $e_{\text{CB}}^- - h_{\text{VB}}^+$ pairs under UV photolysis, and thus increasing the chances of formation of O_2^- , HOO^- and OH^- on the catalyst surface. However, when considered initial slopes of degradation curves of the first 30 min at lower and higher volumes than optimal 0.5 mL in the presence of Mo(VI) and SDS [37], the high doses of H_2O_2 may absorb UV light and hence, degradation rate decreases [39].

3.5. Effect of SDS concentration

The effect of SDS concentration on the rate of degradation of the BPB was studied for different concentrations of SDS as a rate enhancement surfactant in range of (0.02–0.2 mmol L^{-1} at pH 5.0. As can be seen

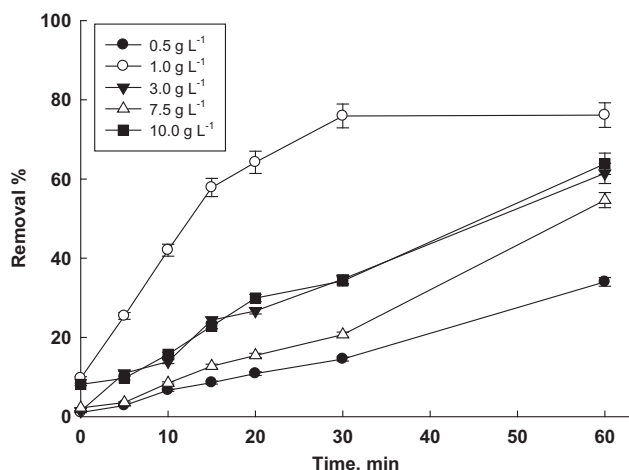


Fig. 3. Effect of TiO_2 amount on the photocatalytic degradation of BPB. Conditions: pH 5.0, initial dye concentration of 5.0 mg L^{-1} , 0.5 mL of 11.0 mol L^{-1} H_2O_2 , 2.0 mL of 0.2 mg L^{-1} Mo(VI), 2.0 mL of 1.0 mmol L^{-1} SDS.

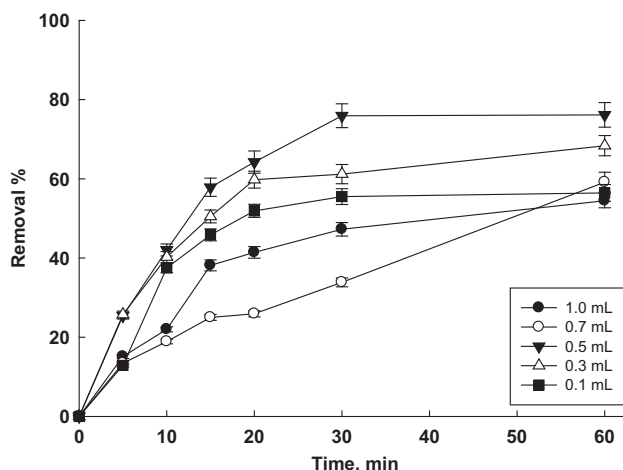


Fig. 4. Effect of 11.0 mol L^{-1} H_2O_2 volume on the photocatalytic degradation of BPB. Conditions: TiO_2 amount of 1.0 g L^{-1} , pH 5.0, initial dye concentration of 5.0 mg L^{-1} , 2.0 mL of 0.2 mg L^{-1} Mo(VI), 2.0 mL of 1.0 mmol L^{-1} SDS.

from Fig. 5, it has been observed that the catalytic effect in premicellar region is efficient at lower concentrations (0.02 mmol L^{-1}) than critical micelle concentration (CMC: 8.2 mmol L^{-1}). At higher concentrations than 0.02 mmol L^{-1} , the percent removal of dye significantly decreases with a decrease in slopes of initial linear parts of degradation curves. The cause of this decrease at higher concentrations than 0.02 mmol L^{-1} may be inhibitory effect of SDS as a consequence of competitive reaction with anionic dye molecules [47]. Therefore, a concentration of 0.02 mmol L^{-1} at final volume of 100 mL was selected as optimal value for further studies.

3.6. Effect of Mo(VI) concentration

The effect of Mo(VI) concentration on the rate of degradation of the BPB was studied for different concentrations of Mo(VI) as activator in range of $60\text{--}300 \mu\text{g L}^{-1}$ at pH 5.0. As can be seen in Fig. 6, it is clear that activation effect is efficient at low concentrations. At higher concentrations than $60 \mu\text{g L}^{-1}$, the percent removal of dye significantly decreases with a decrease in slopes of linear parts of degradation curves. Therefore, a concentration of $200 \mu\text{g L}^{-1}$ at final volume of 100 mL was adopted and selected as optimal value for further studies. It is known that Mo(VI) forms stable peroxo complexes, $\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})_2$ and $\text{MoO}(\text{O}_2)_2(\text{OH})^-$ depending on pH of reaction medium at pH 5.0. Moreover, it is implied that oxidation rate of bromide in presence of oxalate ions significantly increased at pH 5.0 as a result of anionic complex formation, MoO

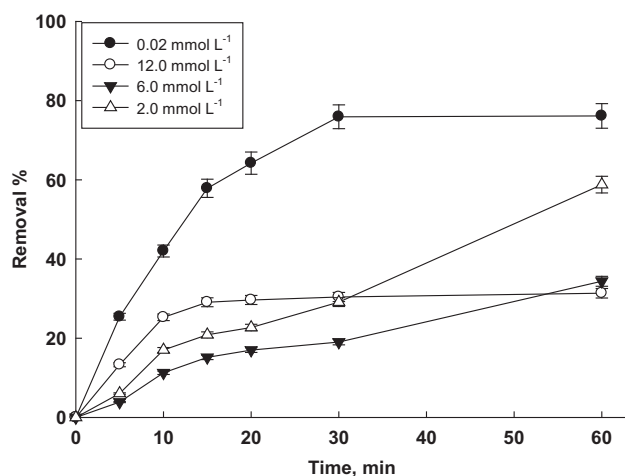


Fig. 5. Effect of SDS amount on the photocatalytic degradation of BPB. Conditions: TiO_2 amount of 1.0 g L^{-1} , pH 5.0, initial dye concentration of 5.0 mg L^{-1} , 0.5 mL of $11.0 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$, 2.0 mL of $0.2 \text{ mmol L}^{-1} \text{ Mo(VI)}$.

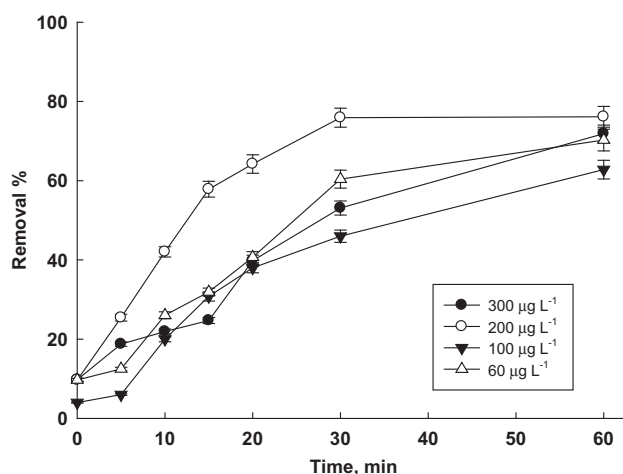
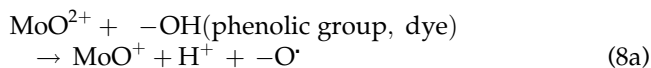
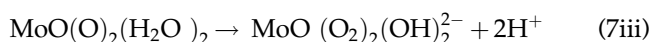
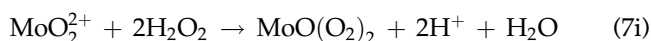
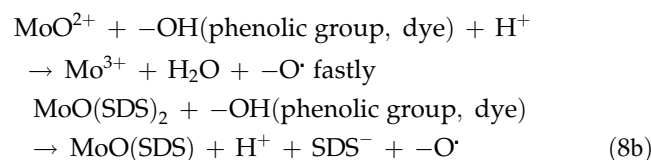


Fig. 6. Effect of Mo(VI) concentration on the photocatalytic degradation of BPB. Conditions: pH 5.0, TiO_2 amount of 1.0 g L^{-1} , initial dye concentration of 5.0 mg L^{-1} , 0.5 mL of $11.0 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$, 2.0 mL of $1.0 \text{ mmol L}^{-1} \text{ SDS}$.

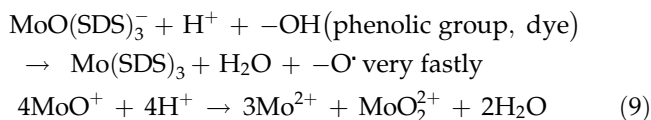
$(\text{O}_2)_2(\text{C}_2\text{O}_4)^{2-}$, in a similar way of anionic SDS molecules at hydrophobic character [48]. It is possible that hydrophobic ionic peroxo complexes of molybdenum species in the presence of SDS similarly will be formed at pH 5.0, so as to increase the Mo-catalyzed reaction rate in aqueous surfactant medium. The catalytic cycle depending upon SDS concentration in premicellar region will be completed by disproportionation of reduced-Mo species produced by the interaction of Mo(VI) with H_2O_2 and dye at the first two reaction steps. As a result, it is supposed that the catalytic mechanism on active surface of TiO_2 in aqueous surfactant medium proceeds at pH 5.0 as follows:



or



or



3.7. Effect of initial dye concentration

BPB generally is used in many industrial sectors such as textile, veterinary medicine, dermatological agent and biological stain [49]. It is a well-known acid-base indicator in the pH range 3.0–4.6 and is yellow at pH 3.0 and purple at pH 4.6 [28]. The effect of initial dye concentration on the rate of degradation of the BPB was studied in range of 0.5–10.0 mg L⁻¹ at pH 5.0. The effect of the initial BPB concentration on the photocatalytic degradation is shown in Fig. 8. As can be seen from Fig. 7, the most effective optimal concentration for degradation of BPB is 5.0 mg L⁻¹. As the initial dye concentration increases in range of 5.0–10.0 mg L⁻¹, the degradation rate of the dye interacting with the available photocatalyst has decreased in the presence of H₂O₂, Mo(VI) and SDS at fixed concentrations. Thus, the available photocatalyst amount may be insufficient for degradation of dye at higher concentrations. Also, since lifetime of hydroxyl radicals is too short, they can especially react as soon as they are formed on the catalyst–water interface [31,50,51]. In the case of increasing dye concentration, the dye molecules can absorb the UV light, and thus, fewer photons are attracted into the photocatalyst

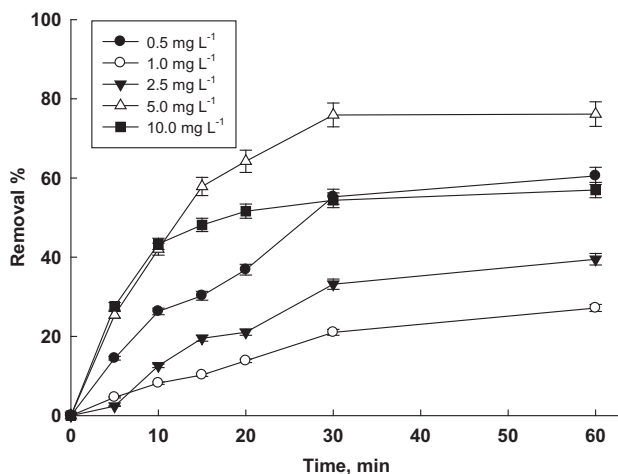


Fig. 7. Effect of initial dye concentration on the photocatalytic degradation of BPB. Conditions: pH 5.0, TiO₂ amount of 1.0 g L⁻¹, 2.0 mL of 0.2 mg L⁻¹ Mo(VI), 0.5 mL of 11.0 mol L⁻¹ H₂O₂, 2.0 mL of 1.0 mmol L⁻¹ SDS.

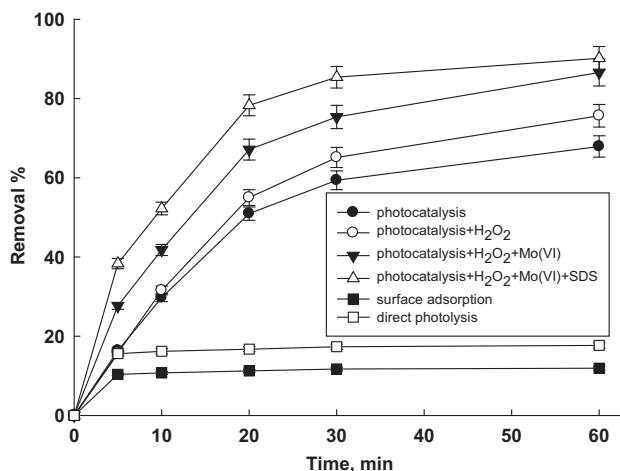


Fig. 8. Effect of Mo(VI) in presence of H₂O₂ and SDS on the photocatalytic degradation of BPB. Conditions: pH 5.0, TiO₂ amount of 1.0 g L⁻¹, initial dye concentration of 5.0 mg L⁻¹, 0.5 mL of 11.0 mol L⁻¹ H₂O₂, 2.0 mL of 0.2 mg L⁻¹ Mo(VI), 2.0 mL of 1.0 mmol L⁻¹ SDS.

surface, consequently, the removal rate of the dye is decreased [41,52].

As can be seen from Fig. 8, when the initial rates, k_c : dR/dt , in time intervals of first 20 min, are considered, the catalytic effect of molybdenum in the presence of H₂O₂ and SDS is very clear with increasing slope. Moreover, the removal rate in time of $t: 0$ significantly has confirmed and supported this increase in rate.

4. Conclusions

The catalytic performance of Mo(VI) in the presence of H₂O₂ and SDS was indicated for the photocatalytic degradation of BPB under visible irradiation with different intervals of time. Furthermore, the effect of H₂O₂, Mo(VI) and SDS concentrations on the photocatalytic activity was also investigated and compared in terms of percent removal rates. Among all additives, it was observed that UV-TiO₂-H₂O₂-Mo(VI)-SDS system, according to other selected systems, exhibited best catalytic performance with the removal rate of 85.4% owing to its low activation energy, high surface area of TiO₂ as a consequence of possible electrostatic interactions on solid–liquid interface depending on zero-point charge pH of TiO₂ and acidity constant of dye in premicellar region. Consequently, the results obtained by using TiO₂ based semiconductor depict profound potential for the photocatalytic degradation of wastewater containing environmental hazardous substances.

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