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Toxicity assessment and degradation of benzoquinone by ZnO photocatalytic oxidation process

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ABSTRACT

This study aims in the photocatalytic degradation of a synthetic aqueous solution of 1,4-benzoquinone (BQ) in a batch slurry reactor in the presence of photocatalyst using ultraviolet light at 365 nm. The removal of intermediate products resulting from the degradation of BQ is also investigated by total organic carbon (TOC) analysis. The effects of various process variables such as initial pH (5–10), initial BQ concentration (50–500 mg/L), light intensity (12–36 W), catalyst type and loading (ZnO and TiO_2, 0.5–2.5 g/L), and reaction time (0–90 min) on the removal efficiency have been examined. The results show that the BQ and TOC removal efficiencies are both affected by the solution pH, and the maximum removal efficiencies are observed at pH 6 for BQ and pH 7 for TOC in the pH range of 5–10. Removal efficiencies are inversely related to the initial BQ concentration and directly related with light intensity. ZnO exhibits higher photocatalytic activity than TiO_2, and removal efficiencies increase with higher catalyst loading. As a result, maximum BQ and TOC removal efficiencies are obtained as 98% and 78%, respectively, at the experimental conditions (Co = 50 mg/L BQ and 32.7 mg/L TOC, pH 6–7, 2.5 g/L ZnO, >12 W, 90 min). In addition, a toxicity test was also carried out to evaluate the toxicity of the untreated and treated BQ solutions. Toxicity was measured with the luminescent bacteria *Vibrio fisheri* test. The results showed a decrease in toxicity as BQ degraded, and toxicity reduced to the 49% level of inhibition at the end of 90 min. This study demonstrated that the photocatalytic oxidation process has a satisfactory potential for the wastewater with a high organic content and toxicity purification.

Keywords: Toxicity, Advanced treatment technologies; Photocatalytic degradation; *p*-Benzoquinone; Zinc oxide; Titanium dioxide

1. Introduction

Treatment of industrial wastewater is a problem of major concern nowadays. More strict regulations are being imposed on the development and employment of the treatment technologies capable to deal with the hazardous pollutants present in many industrial waste streams [1]. *p*-Benzoquinone (BQ) is an important chemical which is used for the production of hydroquinone (HQ), various dyes, insecticides, and fungicides in the pharmaceutical and polymer industries, as a toner and intensifier in the photographic industry, and as a tanning agent in leather industry [2]. BQ is also one of the oxidation products of phenol [3]. When the BQ-containing wastewaters are discharged by the various industries, they cause some problems due to their high toxic characteristics. They also cause skin necrosis after prolonged contact, corneal ulcers after acute exposure, and corneal opacities after chronic exposure [2]. Therefore, this wastewater needs to be treated before discharging. However, conventionally physicochemical treatment processes such as coagulation, flocculation, reverse osmosis, membrane separation, and adsorption are not destructive and mainly concentrate the pollutants which need further processing before disposal [4–9]. On the other hand, biological processes do not work efficiently due to the high solubility and

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biological resistance of BQ. In recent years, advanced oxidation processes (AOPs) have led to new improvements in the oxidative degradation of the organic compounds.

AOPs are a subject of increasing interest as water treatment methodologies due to their ability to degrade bio-recalcitrant organic compounds by means of production of nonselective and highly reactive $OH^{\bullet}$ radical being a powerful oxidant [10–12]. They are capable of oxidizing many wastewater constituents indiscriminately. In the case of aromatic contaminants, the $OH^{\bullet}$ radical attack produces the hydroxylation of the benzene ring followed by ring opening and the carboxylic acid formation in the final steps of the degradation process [13,14]. This may sometimes inadvertently result in the formation of the oxidation by-products that may be more active and toxic. It is well known that during application of oxidative degradation processes in wastewater treatment, the achievement of toxicity reduction depends on the nature of the intermediates that appear during the mineralization process. To discharge treated wastewater safely, the toxicity of the wastewater samples before and after treatment needs to be analyzed. For this reason, biological toxicity tests are vital subject to determine the ecological effect of wastewater.

AOPs have been successfully used to treat various wastewaters such as textile dye [15,16], cellulose bleaching [17], insecticide [18], phenols [19–21], natural organic matter [22], and gas purification [23]. Photocatalytic oxidation process has also been successfully applied for phenol and its degradation intermediates [24].

The aim of this study is to investigate the photocatalytic degradation of an aqueous solution of a commercial BQ in a batch slurry reactor in the presence of ZnO and TiO_2 catalysts using ultraviolet (UV) light at 365 nm. The removal of intermediate products resulting from the degradation of BQ was also investigated by the total organic carbon (TOC) analysis. The effects of various process variables such as initial pH, BQ concentration, light intensity, catalyst type, catalyst loading, and reuse on the degradation performance of the process have been elucidated. Besides, the toxic effect was also studied on the luminescent bacteria *Vibrio fischeri*, determining the EC50 value to assess the cytotoxicity of BQ solutions.

2. Materials and methods

2.1. Materials

A commercially available BQ and HQ are obtained from Merck. The characteristics of BQ are summarized in Table 1, and the absorbance spectra of the BQ and HQ solutions are shown in Fig. 1. The photocatalyst ZnO is obtained from Merck (Brunauer-Emmett-Teller (BET) specific surface, <5 m^2/g) and TiO_2 is obtained from Degussa (p25, BET: 50 ± 15 m^2/g Rutile/Anatase: 85:15, particle size: 20 nm) and used as received.

Table 1
Typical properties of *p*-BQ

Parameter	Value
CAS number	123-31-9
Molecular formula	$C_6H_6O_2$
Molecular weight	110.11
Description	Color: white solid, Odor: not available. Taste: not available
Specific gravity at 20°C/4°C	1.320 g/cm^3
Flash point (closed cup)	165°C (329°F)
Water solubility at 15°C	5.9 g/100 mL
Categories of danger	Toxic, irritant, dangerous for the environment
Acute oral toxicity LD_{50} (mg/kg)	320
Acute dermal toxicity LD_{50} (mg/kg)	5,970
Fish toxicity (rainbow trout) $LC5_0$ (mg/L)	>0.097
pH (1% soln/water) 20°C	7 (neutral)
λ_{max} wavelength (nm)	245

2.2. Experimental apparatus

Schematic representation of the experimental setup of the batch slurry photocatalytic reactor is shown in Fig. 2. The laboratory-scale quartz photo reactor is designed as cylindrically shaped with 25 cm height and 4.5 cm diameter. The quartz reactor is surrounded by six UV lamps that predominantly emit at 365 nm (6 W, General Electric F6T5/BLB) and are positioned so as to ensure homogenous radiation field inside the reactor. Air is blown into the BQ solution by air pump at a flow rate of 150 mL/min to keep the solution saturated with oxygen during reaction. BQ solution is mixed thoroughly in the reactor with a stirrer at 600 rpm, ensuring the complete mixing of catalyst suspensions during the photoreaction. Heat generated by UV lamps is eliminated by blowing cool air between the lamp assembly and the quartz reactor to keep the temperature of the reaction medium at a constant value.

2.3. Experimental procedure and analysis

Photocatalytic oxidation experiments are carried out with 0.45 L of BQ solutions prepared in appropriate concentrations

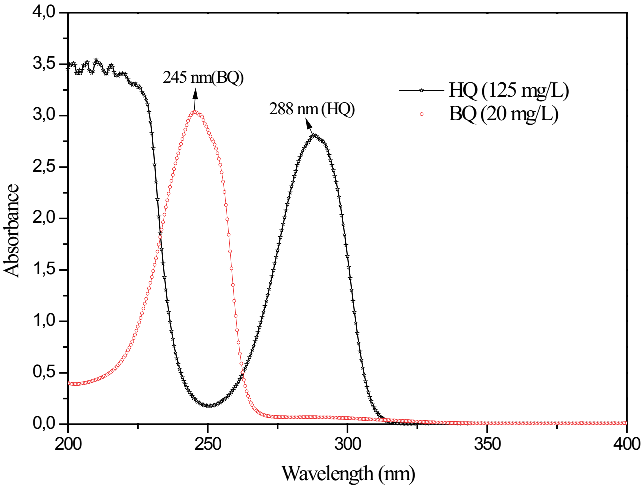


Fig. 1. The absorbance spectra of the HQ and BQ solutions.

using deionized water. The experiments are conducted at constant temperature of 25°C by cooling the reactor with air passing through the ice bath (Fig. 2). The pH of the BQ solution is adjusted by adding 0.01N NaOH or 0.01N H_2SO_4. The BQ solution is exposed to the UV light for 90 min, while the progress of the BQ oxidation is monitored by withdrawing 10 mL aliquots at regular intervals. After the catalysts have been added, the BQ solutions are stirred in the dark for 30 min. Experiments were run with different pH (5, 6, 7, 8, 9, and 10), initial BQ concentrations (50, 100, 150, and 200 mg/L), light intensity (12, 18, 24, 30, 36 W), and catalyst type and loading (ZnO, TiO_2 and 0.5, 1.0, 1.5, 2.0, 2.5 g/L). At the end of the run, catalysts are immediately separated by centrifugation at 3,500 rpm for 10 min. The absorbance is measured in UV-Vis spectrophotometer (PerkinElmer, Lambda 35) at the peak of λ_{max} = 245 nm.

2.4. Analytical method

UV/Vis spectrometer is used to estimate the BQ and HQ concentrations. The BQ removal efficiency, E, is calculated as

$$E = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where C_i is an initial BQ concentration (mg/L) and C_f is a final concentration (mg/L).

2.5. Toxicity study

The toxicities of untreated BQ samples and those treated with ZnO catalyst were assessed through the bioluminescence decay in the light-emitting bacteria *V. fischeri*. Dehydrated *V. fischeri* (strain NRRL-B-11177) was supplied by Modern Water Acute Reagent (Microtox). Basal media (BM) (Nutrient broth, 10 g; NaCl, 0.23% w/w; $Na_2HPO_4{\cdot}2H_2O$, 19.43 g; NaH_2PO_4, 2.516 g; pH, 7.0) was used as an optimum bioluminescence media.

An optimum bioluminescence value time and cell number of indicator bacteria were selected in culture media (BM) using 96-well white polypropylene microplates (Costar, Assay Plate, flat bottom). The microplate assay method was modified from the flash-plate assay and Microtox basic test assay according to ISO/CD 11348. Fresh bacterial culture was adjusted to 0.5 McFarland (about 108 cfu/mL), and then the bacterial suspension was diluted to 1/10 ratio using BM. The diluted bacterial suspension of 100 mL was transferred on a 96-well microplate.

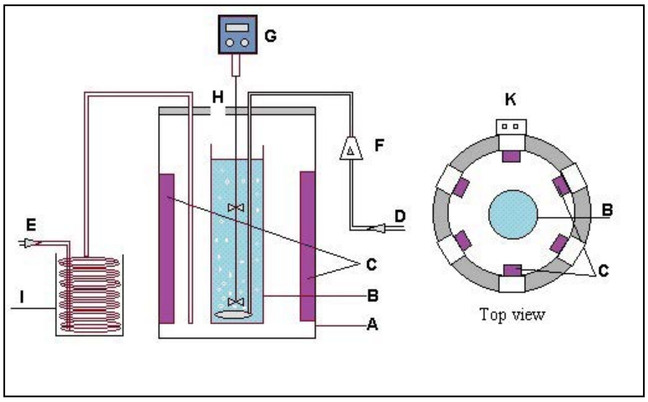


Fig. 2. Experimental setup in the photocatalytic experiments: A-Lamp assembly, B-Quartz batch reactor, C-UV lamps, D,E-Air inlet, F-Flowmeter, G-Stirrer, H-Sampling point, I-Ice bath, K-Switches for power supply.

Sample of treated BQ solutions (5, 15, 30 min) were tested by flash-plate assay using a FLUOstar Omega Microplate Reader (BMG LABTECH, USA). The pH and osmotic level of each sample were adjusted. The bacterial bioluminescence inhibition values were assessed at 15 min of exposure times as millivolts. Each assay was duplicated. Results were compared with changes in the light emission values of a positive control (nontreated BQ solutions, 50 mg/L) and a toxic-free control [*V. fischeri* cell suspension (0.5 McFarland) in BM, 2% NaCl] to give the percentage of inhibition. The EC50 value of raw BQ solution was determined with different concentrations of the BQ samples resulting in a 50% reduction of bioluminescence of *V. fischeri* [25].

3. Results and discussion

Wastewater containing industrial pollutants is one of the major pollution sources in many countries, and their degradations by AOP have attracted a lot of attention in academic and industrial communities. AOPs include photocatalysis system such as a combination of a semiconductor (ZnO, TiO_2, etc.) and UV light. Photocatalysis is a promising method in water treatment for removal and mineralization of organic pollutants [24]. Photocatalytic oxidation studies are based on the generation of very reactive species such as hydroxyl radicals ($^{\bullet}OH$) that oxidize a broad range of pollutants quickly and none selectively. In this process, organic pollutants can be mineralized into carbon dioxide (CO_2), water (H_2O), and mineral acids in the presence of ZnO particles and reactive oxidizing species, such as oxygen or air. The photocatalytic reactions are initiated when ZnO particles absorb photons from the illumination with energies greater than the gap energy [Eq. (2)]. In a photocatalytic process, photo-generated holes in the valence band will recombine with the photoexcited electrons in the conduction band and dissipate in the form of heat [Eq. (3)]. Therefore, the presence of oxygen as electron scavenger prolongs the recombination of electron–hole pair while forming the superoxide radicals (O_2^-) [Eq. (4)] . The reaction of h_{VB} with OH^- [Eq. (5)] may lead to the formation of hydroxyl radicals [26].

$$\mathrm{ZnO} + h\nu \rightarrow \mathrm{ZnO}\left(e_{CB}^{-} + h_{vb}^{+}\right) \tag{2}$$

$$e_{CB}^{-} + h_{vb}^{+} \rightarrow \text{heat} \tag{3}$$

$$e_{CB}^{-} + O_2 \rightarrow {}^{\bullet}O_2^{-} \tag{4}$$

$$h_{vb}^{+-} + OH^{-} \rightarrow {}^{\bullet}OH \tag{5}$$

$$^{\bullet}OH + R-H \rightarrow \acute{R}^{\bullet} + H_2O \tag{6}$$

3.1. Effect of initial pH

In the heterogeneous photocatalytic treatment process, pH is one of the most important operating parameters. The effect of pH on photocatalytic oxidation of organic compounds in water is associated mainly with (1) the ionization state of catalyst surface, (2) position of the valence and conduction bands of the photocatalyst, (3) agglomeration of catalyst particles, and (4) formation of hydroxyl radicals [27]. The isoelectric point (point of zero charge, pzc) of the used ZnO is at pH 9.0. Thus, the ZnO surface is positively charged in acidic media ($pH < 9.0$), whereas it is negatively charged under alkaline conditions ($pH > 9.0$) [16]. This means that at pH > pzc, the adsorption of positively charged contaminants, while at pH < pzc the adsorption of negatively charged contaminants, is favored.

It is well known from the chemistry of HQ and BQ that both compounds can be easily transformed into one another [28,29]. HQ and BQ are known as an active redox couple in equilibrium in an aqueous solution [30]. Their fractionation depends mainly on pH and other aquatic chemistry conditions [31]. In the solution with high pH, both compounds are unstable [32]. By considering these facts, the role of pH in the photocatalytic treatment process is very important.

As shown in Fig. 3, the BQ degradation increases in the acidic medium. The reason for the increase of degradation rate at low initial pH value is that the more H^+ ions are in the solution, the more conduction band electrons (e^-) can be transferred to the surface of catalyst to react with O_2 and to produce more hydroxyl radicals ($^{\bullet}OH$) [27]. The hydroxyl radicals are the dominant oxidizing species in the photocatalytic process.

The influence of initial pH on BQ and TOC removal efficiency is studied in the range of initial pH_i taken as 5–10 at the light intensity of 36 W, catalyst loading of 1.5 g/L, and operating time of 90 min. To avoid the dissolution and photo corrosion of the catalyst, strongly acidic or basic mediums were not investigated. As seen in Fig. 3, BQ and TOC removal efficiencies merely decreased from 90% to 88% and from 32% to 28%, respectively, with pH_i increasing from 5 to 9 during the first 30 min. However, there is an evident decrease in removal efficiencies for the BQ and TOC at pH_i 10, which are 73% and 11%, respectively. As can be seen from the above discussion, the charge of ZnO is negative under alkaline conditions ($pH_i > 9.0$) and has its zero point for pH_i 10. The maximum BQ and TOC removal efficiencies are found as 98% at pH_i 5 and 78% at pH_i 7, respectively. Moreover, BQ removal efficiency is slightly increasing in the interval of 30–90 min, whereas TOC removal efficiency is increasing during all 90 min.

The rest of photocatalytic treatment experiments are carried out at pH 6.05, which is the original pH of BQ. Therefore, the initial pH of BQ does not need to be adjusted since this pH falls into the optimum pH range that makes the photocatalytic treatment process more economical. It is observed that the final pH_f for this process does not change at the end of the experiment. On the other hand, final pH for original BQ solution falls into limits set by discharge standards of water pollution control regulations (pH 6–9). Therefore, no secondary treatment is required for BQ treated by the photocatalytic process.

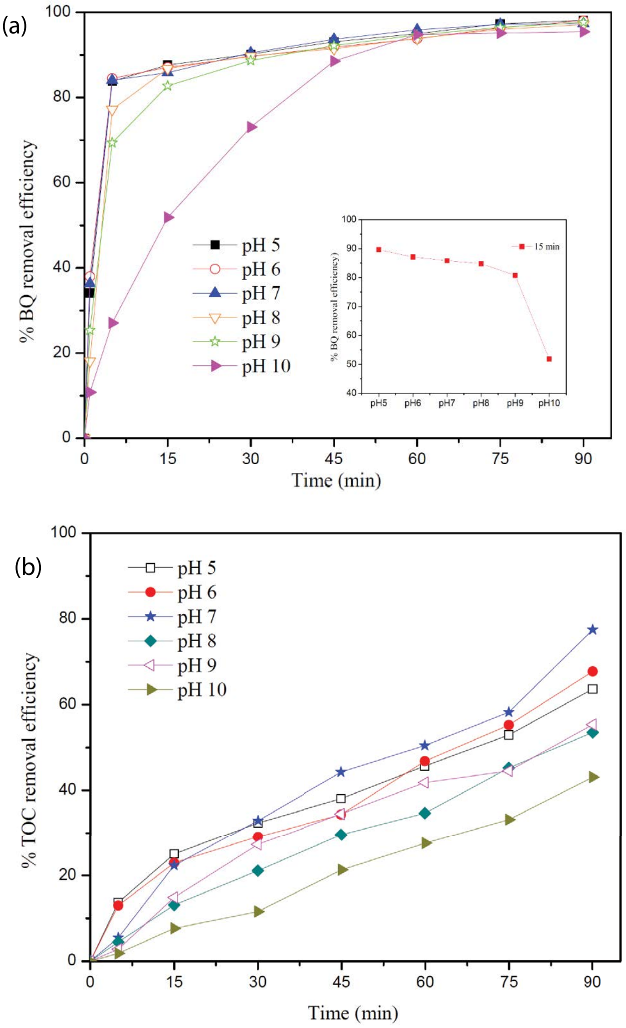


Fig. 3. Effect of pH on the (a) BQ and (b) TOC removal efficiency (conditions: catalyst loading: 1.5 g/L, BQ concentration: 50 mg/L, operating time: 90 min, light intensity: 24 W).

3.2. Effect of initial BQ concentration

The effects of different initial concentrations on the photocatalytic degradation of BQ are investigated. Initial concentration is an important operating factor influencing the performance of photocatalytic process, as observed also by other investigators [16,33]. It is also known that photocatalytic studies are very sensitive to light transmission. By considering these facts, the concentration of the BQ solution for the experiments is chosen in the range of 50–500 mg/L based on the previous work [2]. Fig. 4 shows the effect of initial concentration on BQ and TOC removal efficiencies. It is clear from Fig. 4 that complete BQ removal is not achieved on high concentrations of BQ at the same time conditions. The BQ and TOC removal efficiencies decrease at the end of 90 min from 98% to 14% and from 68% to 21%, respectively, with increase in concentration of the BQ from 50 to 500 mg/L. As is seen, the removal efficiencies of BQ and TOC are inversely affected by the BQ concentration. This negative effect can be commented as follows. As the BQ concentration

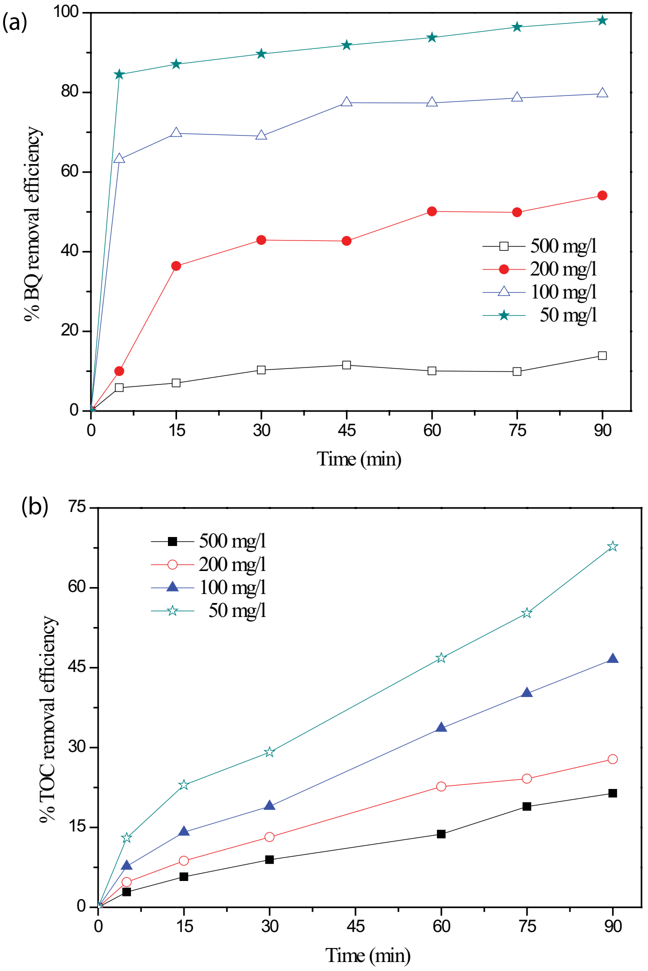


Fig. 4. Effect of initial BQ concentration on (a) BQ and (b) TOC removal efficiency (conditions: catalyst loading: 1.5 g/L, initial pH: 6.05, operating time: 90 min, light intensity: 24 W).

increases, the adsorption equilibrium of BQ on the catalyst surface active sites increases; hence, competitive adsorption of OH^- on the same sites decreases, which means a lower formation rate of $OH^\bullet$ radicals, which is the principal oxidant indispensable for a high degradation efficiency [16]. Fig. 4 proves that for the first 15 min, the photocatalytic reaction rate is comparatively faster for the reason that BQ has not been adsorbed on all active sites of the catalyst. Between 15 and 90 min, BQ adsorption on the ZnO catalyst surface increases that results in lower photon absorption on the catalyst particles and, consequently, in lower photocatalytic reaction rates.

As seen from Fig. 5, the low BQ concentration provided better removal efficiency in concordance with Beer-Lambert law (or Beer's law), which states the linear relationship between absorbance and concentration of absorbing species [17].

3.3. Effect of light intensity

Light intensity is one of the few parameters that affect the photocatalytic degradation of organic compounds. To achieve high photocatalytic degradation in wastewater treatment, a relatively high light intensity is needed to adequately provide the entire active site of the catalyst with sufficient photon energy [34]. The influence of light intensity on the degradation efficiency has been examined at a constant BQ concentration (50 mg/L), initial pH 6.05, catalyst loading (1.5 g/L), and operating time of 90 min. The light intensity is simply altered by varying nominal light power (12–24–36 W).

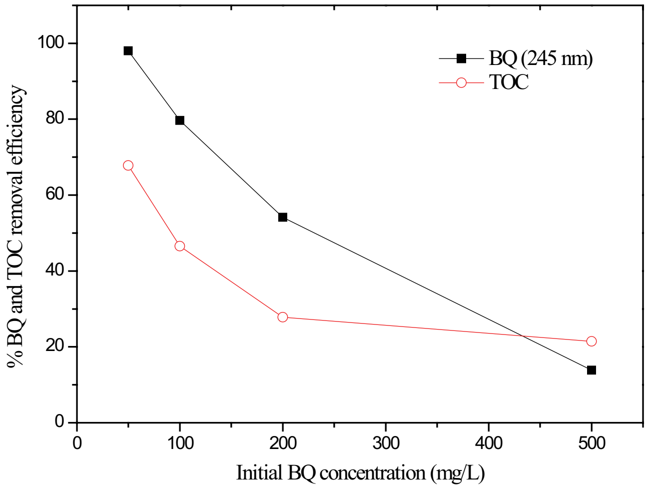


Fig. 5. The variation of BQ and TOC removal efficiencies with initial BQ concentration (conditions: catalyst loading: 1.5 g/L, initial pH: 6.05, operating time: 90 min, light intensity: 24 W).

As seen from Fig. 6(a), the efficiency increases slowly with increasing light power. The BQ removal efficiency increases from 69% to 85% with the increase of the light power from 12 to 36 W in 5 min. Maximum BQ removal efficiency is found as 98%, which is provided during 90 min treatment by the 36-W light power. In the case of no light, BQ cannot be highly removed under air feeding, where the BQ removal efficiency is lower than 3%. There is no expected effect as to the BQ removal, when the light power increases from 12 to 36 W. The photocatalytic degradation rate of BQ in the first 5 min is higher than this rate between 5–90 min of processing, as seen from Fig. 6(a). This can be explained in two ways. First, BQ is absorbed onto the catalyst surface, and saturated surface of the catalyst limits mass transfer in the process of adsorption and desorption. The second explanation is that the initial reaction during the first 5 min is characterized by the BQ oxidation, which might be its oxidation to a series of intermediate products with the aromatic ring opening. Fig. 7 shows that, while BQ is oxidized by hydroxyl radical, a part of BQ is also reduced by electrons (e^-) formed in the photocatalytic process to HQ. In the first 5 min, while the concentration of BQ decreases from 53 to 8.5 mg/L, the concentration of HQ increases up to 43 mg/L. Thus, the photocatalytic degradation rate of BQ decreases rapidly in the range of 5–90 min, and, obviously, the main reaction in this period might be the oxidation of the intermediates and HQ formed in the first 5 min. These compounds oxidize more difficult than BQ [27]. Eventually, both BQ and HQ organic compounds are nearly removed completely by oxidizing after 90 min of processing, as shown in Fig. 7.

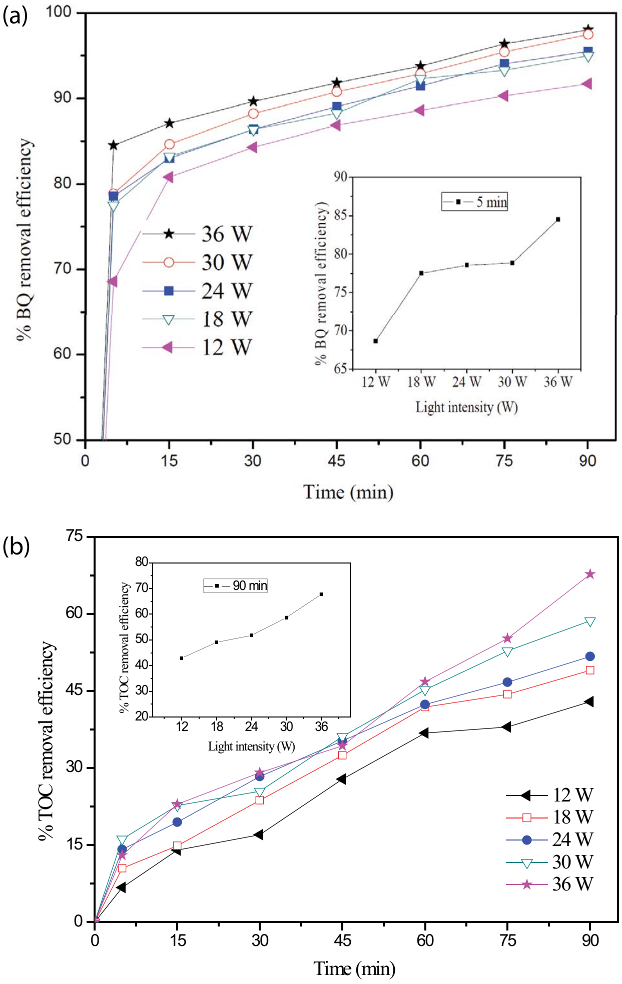


Fig. 6. Effect of light intensity on (a) BQ and (b) TOC removal efficiency (conditions: catalyst loading: 1.5 g/L, BQ concentration: 50 mg/L, initial pH: 6.05, operating time: 90 min).

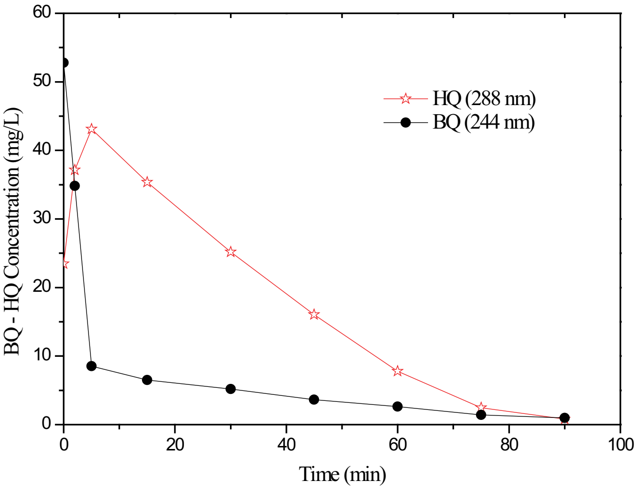


Fig. 7. Photocatalytic degradation of BQ at pH 5 (conditions: catalyst loading: 1.5 g/L, BQ concentration: 50 mg/L, operating time: 90 min, light intensity: 24 W).

The results support the fact that in the first 5 min, no sharp reduction of TOC is observed, compared with the BQ removal efficiency. TOC removal efficiency increases monotonically from 43% to 68% with light power increasing from 12 to 36 W as shown in Fig. 6(b). TOC could not be completely removed at the end of the 90-min interval, probably, because of the more difficult oxidation of intermediate products than BQ. Further oxidation of intermediates provides harmless end products CO_2 and H_2O [35]. A similar finding is reported in literature where the dye degradation rate is reported to increase with the radiation intensity [16].

Both efficiencies are nonlinearly dependent on the light power due to its complex effect on hole generation and electron–hole recombination processes. At low power, hole generation increases linearly with photonic flux, whereas at high power, excess photonic flux promotes the hole/electron recombination and, consequently, lowers the quantum yield [16].

3.4. Effect of catalyst type and catalysis loading

The effects of catalyst type and catalysis loading on photocatalytic degradation of BQ are studied. The ZnO and TiO_2 powder catalysts are mixed uniformly with the BQ solution prior to the introduction into the reactor system in the dark during 30 min. Similar runs carried out for comparison with two different catalyst samples, ZnO and TiO_2, revealed that approximately 5% higher BQ removal efficiency and 17% higher TOC removal efficiency are obtained with ZnO sample. The results show that ZnO exhibits higher photocatalytic activity than TiO_2 due to greater quantum efficiency of ZnO. The low cost is another important advantage of ZnO. Thus, subsequent experiments are carried out with ZnO. Concentration of catalyst in the photocatalytic system affects the overall photocatalytic reaction rate in a true heterogeneous catalytic regime, where the amount of catalyst is directly proportional to the overall photocatalytic reaction rate [36]. The effect of the catalyst loading on BQ removal efficiency is shown in Fig. 8(a), where the initial pH is fixed as 6.05, concentration of BQ is 50 mg/L, and light intensity is 36 W in the presence of air. It is found that the removal efficiency of BQ increases with the increase of catalyst loading. High catalyst loading produces inconsiderable increase in the removal efficiency from 96% at 0.5 g/L to 98% at 2.5 g/L in the 90-min interval. On the other hand, the BQ removal efficiencies for the catalyst loading of 2.5 g/L also increase sharply to 87% at the first 5 min and then reaches 98% at the end of these 90 min. This expected behavior could be explained so that with the increase of surface of the catalyst, more hydroxyl radicals are generated. As seen in Fig. 8(a), although BQ removal efficiency increases with the increase of concentration of ZnO in the first 75 min, at the end of 90 min it is nearly same, except for the catalyst loading of 0.5 g/L. Thus, high catalyst loading cannot be beneficial for ensuring efficient photon absorption. Fig. 8(b) shows that TOC removal efficiency also increases upon increasing catalyst loading from 0.5 to 2.5 g/L. As expected from the literature, both removal efficiencies do not show a maximum for the ZnO concentration [37–39]. Similarly, the continuous increase in photocatalytic degradation rate for textile dyes Reactive Black

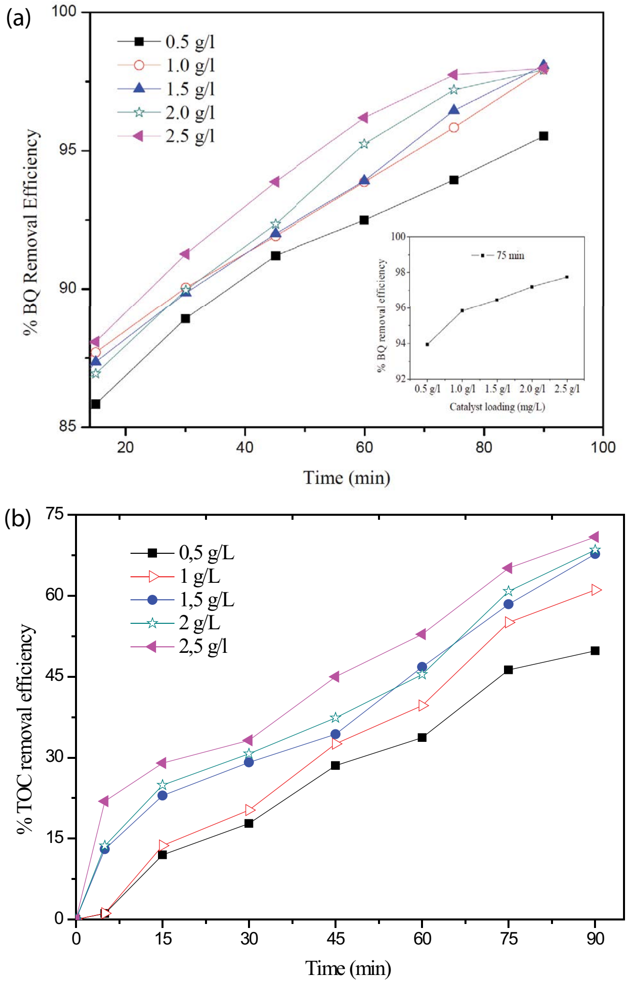


Fig. 8. Effect of catalyst loading on (a) BQ and (b) TOC removal efficiency (conditions: light intensity: 36 W, BQ concentration: 50 mg/L, initial pH: 6.05, operating time: 90 min).

5 and Reactive Red RR is observed by the catalyst loading up to 3,500 mg/L for TiO_2 and ZnO [16,40]. The crucial concentration depends on the geometry, working conditions of the photo reactor, and the type of UV lamp (power, wavelength) [27]. It is reported that the optimum catalyst loading for photodegradation is varied and depends mainly on the dimension of the photo reactor [34]. In general, an excessive increase of the catalyst loading above the optimum value causes the agglomeration of the catalyst particles. Hence, the part of active sites on the photocatalyst surface becomes unavailable for photon absorption, and degradation rate decreases [41]. The excess catalyst particles can also create a light screening effect, which masks a part of the photosensitive surface and reduces the photocatalytic efficiency. This extreme point results from the conflicting effects of this parameter on the photocatalytic process. At lower loading levels, such as 0.5 g/L, photonic adsorption controls the reaction extent because of the limited catalyst surface area. Increase in catalyst loading greatly enhances the process performance. Many studies have reported the effect of catalyst loadings on the process efficiency [36,42].

3.5. ZnO catalysis stability and reusing

The reuse of catalyst is a critical criterion for improvement of photocatalytic treatment, as this is a major factor contributing to the operating costs of the BQ treatment. In order to find the effect of the catalyst reuse on the BQ and TOC removal efficiencies, experiments have been carried out using the same ZnO catalyst at constant BQ concentration (50 mg/L), initial pH 6.05, catalyst loading of 1.5 g/L, light intensity of 36 W, and operating time of 90 min. At the end of the first run, the catalyst is dried and reused. As shown in Fig. 9, when the catalyst is reused, BQ and TOC removal efficiencies merely decrease from 98% to 97% and from 68% to 66%, respectively, in 90 min, as shown in a similar study [43]. In other words, the catalyst stability is monitored in terms of the dissolution of Zn^{2+} ions from ZnO catalysts under neutral pH. No traces of Zn^{2+} are found in solution at the end of the experiment. ZnO is resistant to photo corrosion in the range of initial pH 5–10. However, the activity of the ZnO catalyst is slightly reduced. These results can be explained by the agglomeration of the catalyst particles. Fig. 10(a) and (b) shows scanning electron microscopic (SEM) images of the nanosized ZnO catalyst powder before and after experiment. As seen, ZnO catalyst consists of particles with the size of 200–500 nm.

3.6. Effect of time

The progress in the absorbance spectrums of the BQ solution during the photocatalytic reaction is also monitored with initial 50 mg/L BQ concentration, 1.5 g/L catalyst loading, and 36 W light intensity at pH 6.05. Fig. 11 shows the reduction of integrated absorbance in the spectral range of 200–600 nm for the BQ and HQ photocatalytic oxidation processes. As seen in Fig. 11, the reductions in two absorbance peaks at 244 and 288 nm indicate the degradation of the BQ and HQ compounds, respectively. The intensity of the curves decreases with time after the BQ solution is treated by the

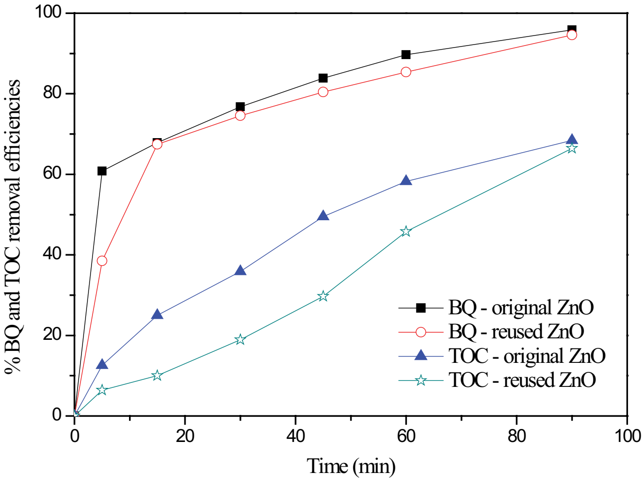
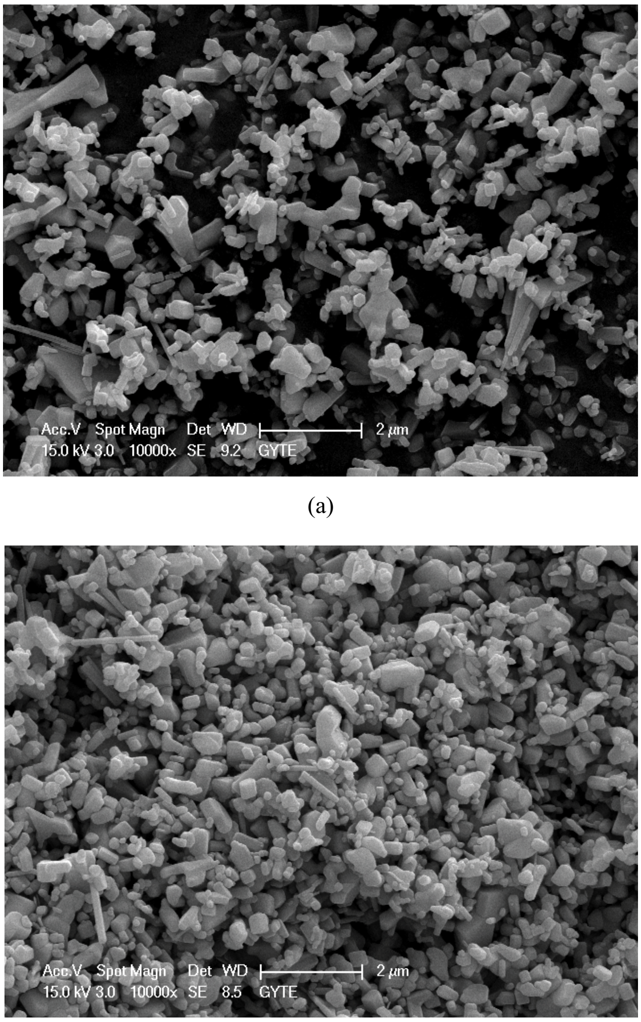


Fig. 9. Effect of catalyst reusing on BQ and TOC removal efficiencies (conditions: light intensity: 36 W, catalyst loading: 1.5 g/L, BQ concentration: 50 mg/L, initial pH: 6.05, operating time: 90 min).



(a)

(b)

Fig. 10. SEM micrograph nanosize powder ZnO catalyst particles (a) before and (b) after experiment photodegradation of BQ (conditions: light intensity: 36 W, catalyst loading: 1.5 g/L, BQ concentration: 50 mg/L, initial pH: 6.05, operating time: 90 min).

photocatalytic oxidation process. These results indicate that there is a significant reduction of the BQ with this process. On the other hand, no new absorption peaks appear during the reaction. This supports the hypothesis that intermediate products formed during the BQ degradation are also successfully degraded toward a complete mineralization. The approximately 95% decrease in the absorbance under 300 nm is also a strong indication of the degradation of the intermediates. At the end of 90 min, the absorbance spectrum in the BQ solution almost disappears. The TOC of the BQ solution is monitored during the reaction for a complete elucidation of the degradation mechanism. Meanwhile, it is clear that total mineralization needs a reaction time longer than 90 min, which may be sufficient for a successful degradation process.

Several researchers have used electrocoagulation process with aluminum electrodes for the treatment of the same compound. Researchers have shown that at neutral pH, the reduced HQ is not removed by this process, although BQ is removed approximately up to 80% [2].

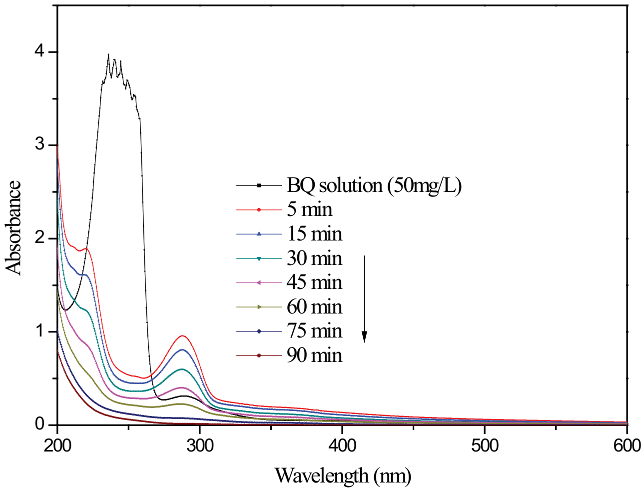


Fig. 11. Effect of time on the BQ removal efficiency (conditions: catalyst loading: 1.5 g/L, light intensity: 36 W, BQ concentration: 50 mg/L, initial pH: 6.05, operating time: 90 min).

3.7. Toxicity assessment

Toxicity experiments were conducted in samples collected before and after illuminating the photo reactor. Generally, the toxicity levels of wastewater are identified by the EC50 values. The EC50 value is the concentration of wastewater that causes 50% of bacteria reduction relative to a control sample. The decrease in bacterial luminescence (INH%) due to the toxic chemicals was calculated as follows:

$$\%\text{INH} = 100\left(\frac{\text{IT}_t}{\text{IT}_0 \times \text{KF}}\right) \times 100 \qquad (7)$$

where IT_0 and IT_t are the luminescence of the test sample at $t = 0$ and after t min of exposure time. KF is the correction factor based on the control and blank.

EC50 value of BQ solution was determined as 12.8 mg/L (Fig. 12(a)) after 15 min of exposure time. It can be said that the BQ concentrations higher than this value are toxic and lower values are nontoxic.

Fig. 12(b) shows the variation of the toxicity with the BQ degradation. The 15-min standard bioluminescence inhibition assay did not show any toxicity during 90 min of the process time. Meantime, toxicity of treated BQ solution is lower than that of untreated one. The toxicity of the BQ solution has decreased by almost half in the end of 90 min of illumination. Thus, the INH% value of the BQ solution is lower than the EC50 value, and the BQ solution itself is nontoxic. However, 98% of BQ was degraded in 90 min of process time, whereas the 49% inhibition was still observed. Moreover, as seen in Fig. 5, the resulting HQ, which was known to be highly toxic toward *V. Fisheri* bacteria (with EC50 equal to 0.08 mg/L) [44], degraded nearly completely in 90 min of process time. Therefore, other transformation and by-products might be responsible for the residual toxicity.

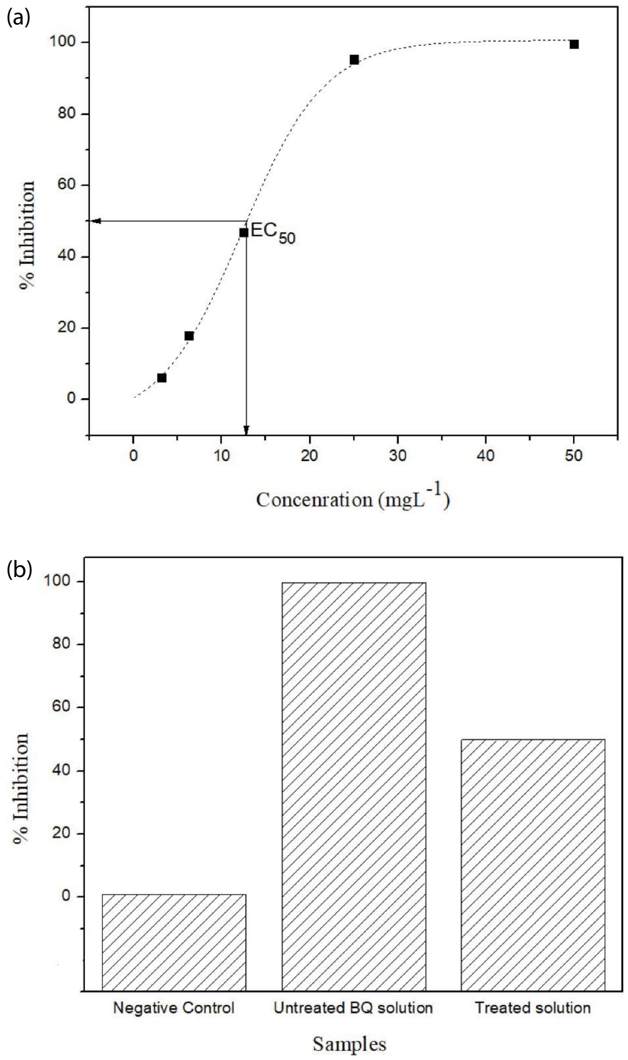


Fig. 12. Determined EC50 value of raw BQ solution (a) and toxicity behavior of treated BQ solution using the luminescent bacteria *V. fischeri* (b).

4. Conclusion

In conclusion, we have found that the photo oxidation process is successfully applied to the BQ removal from aqueous solution. The BQ and TOC removal efficiencies are found to be dependent on the BQ concentration, initial pH, catalyst loading, light intensity, and photocatalysis time. The studies show that while BQ and TOC removal efficiencies decrease with increase in the BQ concentration, they increase with the increase of the light power and catalyst loading. BQ and TOC removal efficiencies decrease from 98% to 14% and from 68% to 21%, respectively, with increase in the BQ concentration from 50 to 500 mg/L at the end of 90 min. BQ and TOC removal efficiencies also decrease from 90% to 88% and from 32% to 28%, respectively, with the increase of pH*i* from 5 to 9 during the first 30 min. TOC removal efficiency increases monotonically from 43% to 68% with the increase of light power from 12 to 36 W. The results show that ZnO photocatalyst exhibits approximately 5% higher BQ removal efficiency and 17% higher TOC removal efficiency than TiO_2 photocatalyst. ZnO photocatalyst is also resistant and stable to photo corrosion when initial pH interval is 5–10. Although BQ is nearly completely removed from aqueous solution, TOC could not be fully removed, which is probably because of more difficult oxidation of the intermediate products. Further oxidation of these intermediates gives harmless end products CO_2 and H_2O. Consequently, the photocatalytic setup described in this study is simple in design and operation and can be used effectively for further studies on this subject. Maximum BQ removal efficiency is found as 98%, which is provided in 90 min of the 36-W light power application. In addition, the sample treated by photocatalytic oxidation was lower than 50% bioluminescent bacteria inhibition threshold. The toxicity of the BQ sample decreased considerably with photocatalytic process for *V. fischeri*. Thus, treated sample was not toxic for the *V. fischeri*. This suggests that photocatalytic process with the ZnO participation may be safely applied for the removal of BQ pollution due to high rate of the degradation process and its ability of reducing toxicity level.

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