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Degradation of benzenesulfonate by heterogeneous photocatalysis combined with ozonation

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Abstract

The efficiency of the photocatalytic degradation of pollutants can be enhanced by combination with another advanced oxidation procedure such as ozonation. Application of these two methods for degradation of benzenesulfonate (BS) resulted in a synergic effect; the efficiency of the combined procedure significantly exceeded the sum of those of the individual techniques. Enhancement of the ozone dosage in this system accelerated the mineralization, i.e., the decrease of the total organic carbon content (TOC), more than the decay (transformation) of BS. The initial rates of both processes displayed a maximum at pH 5-6 in both the aerated and the ozonated systems. An increase of pH in the range of 2-7 promoted the mineralization in the ozonated system more than in the aerated one, while for the decay of BS a reversed relation was observed.

1. Introduction

The use of surface active compounds is widespread in several human activities. Among the anionic surfactants, alkanesulfonates, alkylsulfate, and alkylbenzenesulfonate are commonly applied as cleaning agents, laundry detergents, cosmetics, and personal care products [1].. The extensive use of these compounds leads also to their discharge into the environment, mainly into the water compartment. Linear alkylbenzene sulfonates were thoroughly investigated for their pollution effects and degradation possibilities, but less studies dealt with benzene- and naphthalenesulfonates [2,3]. While the alkyl derivatives were found to be readily biodegradable [4,5], other aromatic sulfonates without long side chains proved to be biorecalcitrant [6]. Biodegradability of benzene- and naphthalenesulfonates with sulfo, nitro and amino groups are especially low [7,8,9]. Due to their strong hydrophilic character (low *n*-octanol–water partition coefficients [10]), low volatility and high mobility within aquatic systems, polar aromatic sulfonates are easily transported from sewers to surface waters. Hence they are potentially hazardous with respect to contamination of ground water and drinking water supplies [11].

Various methods have been examined for the degradation of these contaminants in the past two decades. Benzenesulfonates was mineralized by contact glow discharge electrolysis [12, 13]. Ozonation was found to be efficient only in the presence of activated carbon, which ensures high local concentration of the reactants through adsorption [14].

Photocatalytic procedures proved to be appropriate for purification of waters contaminated with both inorganic and especially organic pollutants. In heterogeneous photocatalytic methods applied for the degradation of various organic contaminants the most widely used material is titanium dioxide, TiO_2 [3,15,16,17,18,19]. The determining oxidizing species generated in TiO_2-mediated photocatalysis is hydroxyl radical, which is produced in aqueous systems via oxidation of adsorbed water by the positively charged hole (h_{vb}^+) formed in the valence band of the semiconductor upon excitation (Eqs. 1, 2) [20].

$$TiO_2 + h\nu \rightarrow TiO_2\ (e_{cb}^- + h_{vb}^+) \qquad (1)$$

$$TiO_2\ (h_{vb}^+) + H_2O_{ads} \rightarrow TiO_2 + HO^\bullet + H^+ \qquad (2)$$

In air-saturated systems, electrons (e_{cb}^-) photogenerated in the conduction band can reduce dissolved oxygen, leading to the formation of superoxide and peroxide ions (Eqs. 3, 4).

$$TiO_2\ (e_{cb}^-) + O_{2ads} \rightarrow TiO_2 + O_2^{\bullet-} \qquad (3)$$

$$TiO_2\ (e_{cb}^-) + O_2^{\bullet-} \rightarrow TiO_2 + O_2^{2-} \qquad (4)$$

Procedures based on TiO_2-mediated photocatalysis were successfully applied for degradation of various amino acids [21,22] and surfactants [3,19,23,24,25]. Efficient photocatalytic mineralization of 1,5-naphthalenedisulfonate was also realized in titanium dioxide suspension [26]. In this case, according to a detailed HPLC/MS analysis, the degradation pathway leads to the formation and subsequent decay of benzenesulfonate.

Although the photocatalytic degradation of benzenesulfonate was studied in the past [27,28], the possible degradation pathways in this system were just quite recently analyzed [29].

Although TiO_2 based photocatalysis proved to be an efficient technique for degradation of benzenesulfonate (abbreviated as BS) [29], its combination with another type of advanced oxidation procedure can enhance the efficiency of its mineralization. In this study we demonstrate that ozonation is an appropriate candidate for this purpose. Even if it was successfully applied for degradation of BS only in the presence of activated carbon [14], its combination with heterogeneous photocatalysis results in a synergistic effect in the increase of the mineralization rate. Beside following the total organic carbon (TOC) content of the system treated, monitoring of the concentration of both the starting material (BS) and its hydroxylated derivatives was also carried out. The influence of the ozone dosage and the initial pH on the degradation of BS has also been investigated in order to contribute to the elucidation of this synergy. Beside their theoretical importance, the results of this work can be utilized in the design of new catalytic procedures for wastewater treatment.

2. Experimental Section

2.1. Materials

In all experiments in this study, the titanium dioxide catalyst used was Degussa P25 (70% anatase, 30% rutile; with a surface area of 50 m^2 g^{-1}). The concentration of TiO_2 was 1 g dm^{-3}

in all cases. Reagent grade benzenesulfonic acid, 4-hydroxybenzenesulfonic acid, and 2,5-dihydroxybenzenesulfonic acid (used as standards for the analyses) were purchased from Merck. Compressed air was bubbled through the reaction mixtures from gas bottles both for stirring and for serving (with its O_2 content) as electron acceptor. Beside dissolved oxygen (O_2), in most of the experiments, O_3 (produced by a LAB2B ozone generator) was also introduced in the same air stream. High purity water applied as solvent in this study was double distilled and then purified with a Milli-Q system.

2.2. Photochemical experiments

Photochemical experiments were carried out in a laboratory-scale reactor with an effective volume of 2.5 dm^3. The heterogeneous reaction mixture (TiO_2 suspension) was circulated by using a peristaltic pump through the reactor and the buffer vessel and by continuously bubbling air with a flow rate of 40 dm^3 h^{-1} within the reactor. The photon flux of the internal light source (40W, λ_{max} = 350 nm, i.e., UVA range) was measured by tris(oxalato)ferrate(III) chemical actinometry [30,31] ($I_0 = 4.3\times10^{-6}$ mol photon dm^{-3} s^{-1}).

2.3. Analytical procedures

For analysis, 4 cm^3 samples were taken from the reactors through a septum with a syringe. When the solution part of the sample had to be analyzed, the solid phase was removed by filtration using Millipore Millex-LCR PTFE 0.45 µm filters. The pH of the aqueous phase of the reaction mixture was determined by a SEN Tix 41 electrode. Mineralization was followed by measuring the total organic carbon (TOC) concentration, utilizing a Thermo Electron Corporation TOC TN 1200 apparatus.

Benzenesulfonate and its hydroxylated intermediates were followed by HPLC-MS measurements, the conditions of which were described earlier [29]. Sulfate anions were analyzed by a Dionex DX300 ion chromatographic system (Dionex, Sunnyvale, CA, USA) using suppressed conductivity detection. The injection volume was 50 µl. Separations were carried out by a Dionex IonPac AS4A-SC (250×4 mm) analytical column. The concentration, pH and flow rate of the carbonate eluent were 3.5 mM, 10.2 and 1.2 ml min^{-1}.

The ozone concetration was determined by iodometry, using sodium iodide as reagent and sodium thiosulfate for the titration of the iodine formed.

3. Results and Discussion

3.1. Mineralization of BS under various conditions

In order to demonstrate the enhancement in the mineralization rate of BS by application of the combined method ($O_3/TiO_2/UV$), the efficiencies of the simple individual methods were also determined. Fig. 1 displays the change of TOC in systems containing BS of 10^{-3} M initial concentration, during 300-min treatment by ozone alone, together with TiO_2 (in both cases in the dark), as well as UV irradiated O_3, air/TiO_2, and O_3/TiO_2.

Insert Fig. 1 about here

As the corresponding plots indicate, that the mineralization efficiencies in systems O_3, O_3/TiO_2, and O_3/UV are similar; TOC decreased about 31-32% during the 300-min irradiation period. Apparently, neither TiO_2, nor UV-vis irradiation (here 320 – 420 nm) can significantly affect the oxidation efficiency of ozone. The mineralization rate with irradiated TiO_2 in the presence of dissolved oxygen (air/TiO_2/UV) was considerably higher than in the previous cases, demonstrating the much more significant oxidation power of titanium dioxide based photocatalysis. However, combination this method with ozonation ($O_3/TiO_2/UV$) increased the mineralization efficiency much more than the simple addition of the efficiency of O_3 or O_3/TiO_2 would result in. The initial mineralization rates summarized in Table 1 clearly indicate this phenomenon: the initial rate with the combined method (52.9×10^{-2} mg dm^{-3} min^{-1}) is about 1.6 times higher than the sum of the rates observed with the two individual methods (22.9×10^{-2} + $9.8\text{-}11.2\times10^{-2}$ mg dm^{-3} min^{-1}).

Insert Table 1 about here

Accordingly, in this case total mineralization was realized within 210-min irradiation.

A similar synergistic effect was observed by Li et al [32]. It can be interpreted by the following reactions [33]:

- Direct electron transfer from TiO_2 to O_3:

$$e_{cb}^{-} + O_3 \rightarrow O_3^{\bullet -} \qquad (5)$$

$$O_2^{\bullet -} + O_3 \rightarrow O_3^{\bullet -} + O_2 \qquad (6)$$

$$O_3^{\bullet -} + H^{+} \rightarrow HO_3^{\bullet} \qquad (7)$$

$$HO_3^{\bullet} \rightarrow O_2 + {}^{\bullet}OH \qquad (8)$$

- Electron transfer between TiO_2 and O_2 molecule:
- $e_{cb}^{-} + O_2 \rightarrow O_2^{\bullet -}$ (9)

The electron scavenging by O_3 or O_2 decreases the possibility of the recombination of the photogenerated electron-hole pair. Besides, formation of very oxidative radicals (e.g., in reactions (6-8)) also enhances the degradation efficiency. Notably, UV irradiation of O_3 may increase the amount of H_2O_2 and $HO^{\bullet}$ species in the system.

3.2. Decay of BS and formation of sulfate under various conditions

Beside the rate of the mineralization, other quantitative properties of the systems such as the actual concentration of BS and sulfate ions were followed during the irradiations for investigation if the manifestation of synergistic effect can be observed also in the change of these species.

Insert Fig. 2 about here

A comparison of the initial decay rates of BS with those of the TOC regarding the whole system clearly indicates that in the previous case the rate observed at the combined technique ($O_3/TiO_2/UV$) does not exceed the sum of those of the individual methods (Figs. 1 and 2). This result suggests that the synergistic effect originates from the efficient promotion of the degradation of the intermediates formed during the decay of the starting material (BS). However, as to the rate of the sulfate formation, the increasing effect of the ozonation is much more pronounced, indicating that most of the sulfate ions in this system originated from the intermediates, not from the starting material.

3.3. Formation and decay of intermediates in aerated and ozonated systems

The actual concentrations of the starting material (BS) were directly determined from HPLC-MS measurements. Thus, the TOC values corresponding to the unreacted benzenesulfonate could also be calculated. Fig. 3A displays the TOC versus time plots belonging to the overall system, the unreacted surfactant (BS), as well as the intermediates formed during the photocatalytic degradation process in air-saturated system.

Insert Fig.3 about here

The latter curve is the difference of the previous two. The TOC values corresponding to the intermediates show a maximum at 160-180 min where the concentration of the unreacted benzenesulfonate is still considerable. At longer times (above 180 min) the TOC representing the intermediates is diminishing because the rate of the mineralization of these species exceeds that of their formation. In this period of irradiation, especially above 240 min, the total TOC exclusively belongs to the intermediates because the whole amount of the starting material (BS) has already been transformed. Hence, further decrease of TOC can be attributed to the mineralization of the intermediates. In the presence of ozone (Fig. 3B) the decay of BS, and, thus, the formation of the intermediates is much faster. Accordingly, the corresponding plot shows the maximum TOC value belonging to the intermediates already at about 80 min, and within 120 min all starting BS ions have been transformed. Also the total mineralization took place within 210 min. Since the maximum values of TOC belonging to the intermediates are about the same in both cases (air or ozone), the presence of O_3 accelerates both the formation and the decay of these species.

3.4 The effects of ozone dosage

The experiments with ozonated system, the results of which previously discussed were carried out at constant O_3 dosage (0.12 mM min^{-1}), at less than half of the performance of the ozone generator used. Thus, it was reasonable to investigate how the ozone dosage affects the degradation of BS by using the combined procedure. Fig. 4 displays both the initial rate of the BS decay (V_0(BS)) and that of the mineralization, i.e., the TOC decrease (V_0(TOC), as functions of the ozone dosage.

Insert Fig. 4 about here

It is clearly seen that the increase of V_0(TOC) is steeper than that of V_0(BS) at each value of ozone dozage, and, what is more important, the ratio of these two rates gradually increases upon increasing the O_3 dosage as shown by the data of Table 2.

Insert Table 2 about here

These data indicate that ozonation promotes the degradation of the intermediates stronger than the transformation (hydroxylation) of the starting material does. A possible explanation of this phenomenon may be that ozonation increases the steady-state concentration of superoxide in this system more than that of the hydoxyl radicals because the latter species alone cannot open the aromatic ring as it was proven in our previous work [29]. Ring-cleavage is an indispensable step for the mineralization of BS .

All the three isomers of hydroxy-benzenesulfonate formed and decay during the degradation of BS were followed by HPLC-MS measurements. In the absence of ozone the distribution of the isomers at their maximum (total) concentration is the following: 16% *ortho*, 66 % *meta*, and 18% *para*, in accordance with our earlier results (both theoretical [26] and analytical [29]). Upon ozonation, the percentage of the *o*-hydroxy isomer did not significantly change (14-17%), while that of the *meta* derivative decreased to 51%, with the increase of the *para* species to 32-35 %). Interestingly, the change of the ozone dosage in the range of 0.011 – 0.35 mM min^{-1} did not influence this distribution.

3.5. The effects of pH

The pH of this system determines the surface charge of the TiO_2 particles (pH_{zpc} = 6.25 [34], and, thus, the adsorption efficiency of the benzenesulfonic acid, which is totally dissociated (pK_{BS} = - 2.36 [14]) in the whole range of pH studied here. Besides, the formations of the reactive oxidizing agents (e.g., $HO^{\bullet}$, $O_2^{\bullet-}$) as well as their reactions are also affected by pH. Hence, V_0(BS) and V_0(TOC) were also measured as functions of the initial pH (pH_0) in the range of 2.0 – 11.0, in both aerated and ozonated systems. According to our results shown in Fig. 5, in aerated system the initial rate of both the BS decay and the mineralization display maximum values at about pH 5-6.

Insert Fig. 5 about here

In the ozonated system the highest V_0(TOC) can be observed at the same pH as in the aerated case, while the maximum of V_0(BS) is a bit lower pH value (ca. 4). These plots indicate that not the adsorption of the determining factor affected by the pH in the range of 2-6, otherwise the initial rate must increase upon acidification, due to the attraction between the positively charged catalyst surface and the anionic benzenesulfonate and their derivatives. Thus, the formation and reaction of the oxidizing agents are the key processes influenced by the pH in these systems. In order to gain more information from these results, the ratios of the initial rates (of both BS decay and TOC decrease) measured in ozonated and aerated photocatalytic systems ($V_0(O_3)/V_0(O_2)$) were plotted as functions of pH_0. As shown in Fig. 6, the transformation of BS is less favored in the ozonated than in the aerated system upon increasing pH values.

Insert Fig. 6 about here

This phenomenon can be partly attributed to the hindered formation of $HO^{\bullet}$ radicals from ozone because in these reactions ozonide ions are in protonated form (see reactions (5-8)).

On the contrary, for the ratio of the initial rates of mineralization, higher pH values (up to about 7) are more favorable for the ozonated system, which may be explained by the protonation of $O_2^{\bullet-}$, giving $HO_2^{\bullet}$ being less efficient oxidizing agent than the superoxide radical ($pK(HO_2^{\bullet}/O_2^{\bullet-}) = 4.8$ [35]). The latter species is the most probable reactant playing key role in the ring-opening, which is indispensable for the mineralization of the aromatic compounds.

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4. Conclusions

In this study it has been demonstrated that the combination of titanium dioxide based heterogeneous photocatalysis with ozonation for the oxidative degradation of benzenesulfonate results in a synergistic effect, achieving a significantly higher mineralization efficiency than the sum of those of the individual methods. Accordingly, this combination offers an advantageous technique for purification of wastewaters. Since the optimum initial pH for this joint procedure is just slightly acidic (i.e. close to neutral), this condition further promotes the practical application of this combined method.

Acknowledgments

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Figure captions

Fig. 1. Change of total organic carbon (TOC) content as functions of time in the system containing 1×10^{-3} M BS at $pH_0=3$ during the treatment by various oxidation methods: (◇) O_3, (◆) O_3 +TiO_2, (▲) O_3 + UV, (●) air+TiO_2 + UV, (O) O_3+TiO_2 + UV. (TiO_2 content is 1 g dm^{-3}).

Fig. 2. Change of the concentration of the starting material (BS) (A) and SO_4^{2-} (B) as functions of time in the system containing 1×10^{-3} M BS at $pH_0=3$ during the treatment by various oxidation methods: (▲) O_3 + UV, (●) air+TiO_2 + UV, (O) O_3+TiO_2 + UV. (TiO_2 content is 1 g dm^{-3}).

Fig. 3. Change of total organic carbon (TOC) content as functions of the irradiation time in the system containing 1×10^{-3} M BS at $pH_0=3$ during the treatment by A) air+TiO_2 + UV and B) O_3+TiO_2 + UV, indicating TOC belonging to the whole system (●), the starting material (O), and the intermediates formed (▲). (TiO_2 content is 1 g dm^{-3}).

Fig. 4. The initial rate of BS decay (●) and mineralization (O) as functions of ozone dosage in the in the system containing 1×10^{-3} M BS at $pH_0=3$, treated by the combined procedure (O_3+TiO_2 + UV). (TiO_2 content is 1 g dm^{-3}).

Fig. 5. The initial rate of BS decay (A) and mineralization (B) as functions of pH_0 in the system containing 1×10^{-3} M BS, treated by air+TiO_2 + UV (●) and O_3+ TiO_2 + UV (O). (TiO_2 content is 1 g dm^{-3}).

Fig. 6. The ratio of the initial rates measured in ozonated and aerated system containing 1×10^{-3} M BS as functions of pH_0, regarding BS decay (▲) and mineralization (△). (TiO_2 content is 1 g dm^{-3}).

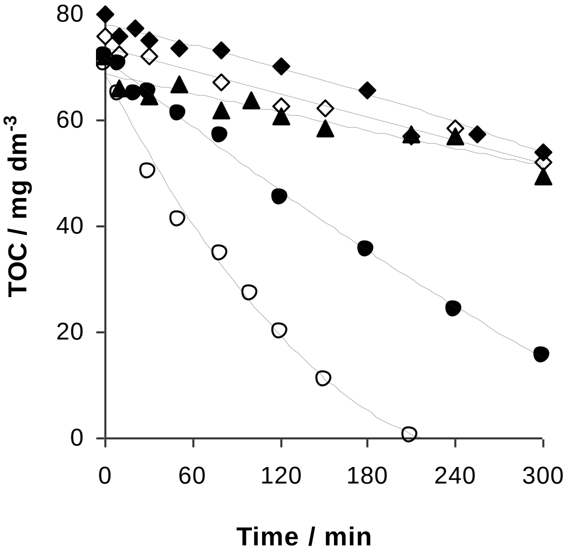
Table 1. Initial rates of mineralization (i.e., the decrease of TOC) in the system containing 1×10^{-3} M BS at $pH_0=3$ during the treatment by various oxidation methods.

Method	**Initial rate / mg dm^{-3} min^{-1}**
O_3	10.0×10^{-2}
O_3/TiO_2	9.8×10^{-2}
O_3/UV	11.2×10^{-2}
Air/TiO_2/UV	22.9×10^{-2}
O_3/TiO_2/UV	52.9×10^{-2}

Table 2. The ratios of the initial BS decay and mineralization rates at various ozone dosages in the system containing 1×10^{-3} M BS at $pH_0=3$, treated by the combined method (O_3/TiO_2/UV).

Ozone dosage (mM min^{-1})	**V_0(TOC)/V_0(BS)**
0	29.8
0.011	30.7
0.016	35.3
0.12	37.5
0.35	44.3

Fig. 1.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TOC / mg dm^{-3}
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60
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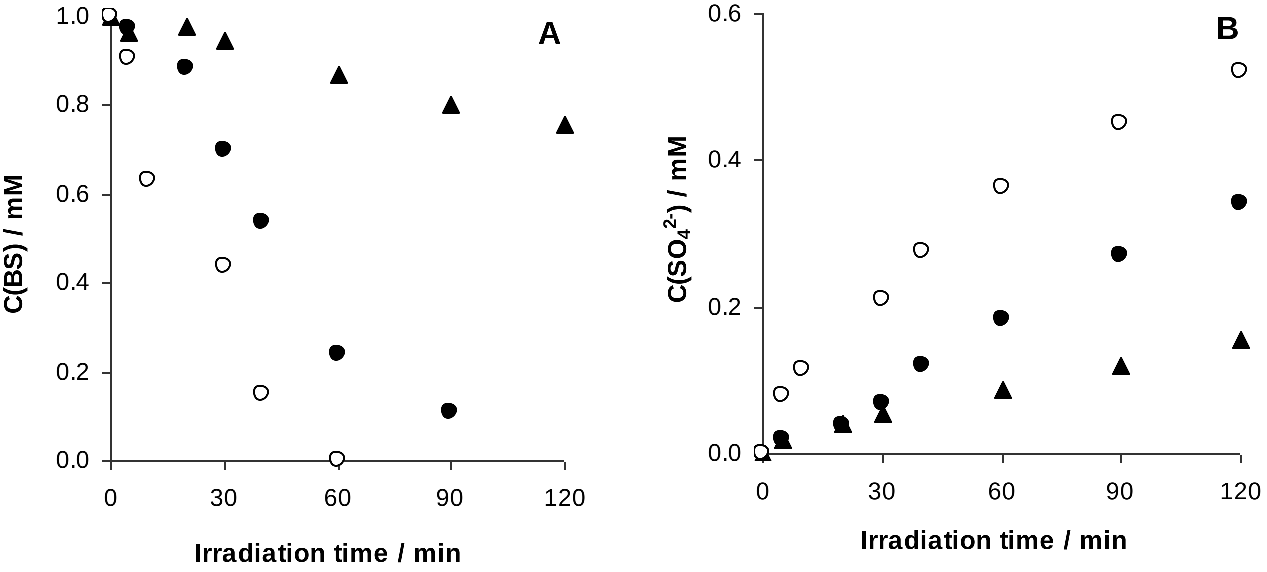
180
240
300
Time / min

Fig. 2.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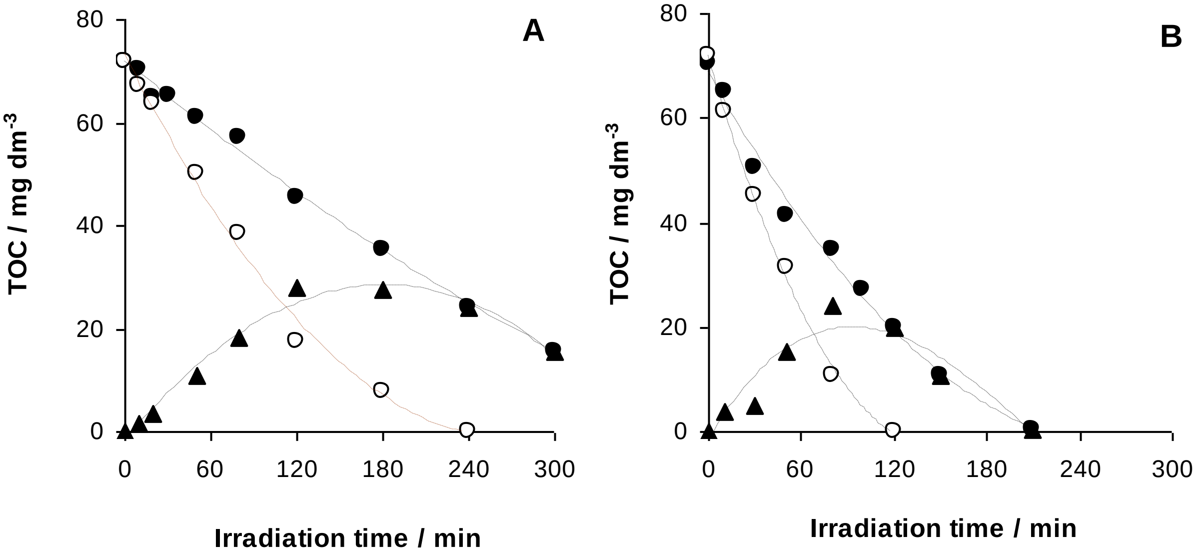
0.6
0.4
0.2
0.0
C(BS) / mM
0
30
60
90
120
Irradiation time / min
B
0.6
0.4
0.2
0.0
C(SO$_4^{2-}$) / mM
0
30
60
90
120
Irradiation time / min

Fig. 3.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B
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60
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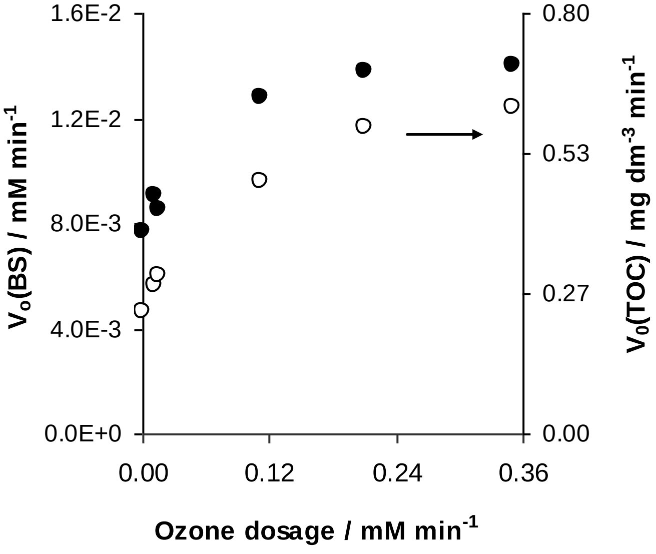
Irradiation time / min

Fig. 4.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8.0E-3
4.0E-3
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0.80
0.53
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0.00
0.12
0.24
0.36
V$_0$(BS) / mM min^{-1}
V$_0$(TOC) / mg dm^{-3} min^{-1}
Ozone dosage / mM min^{-1}

Fig. 5.

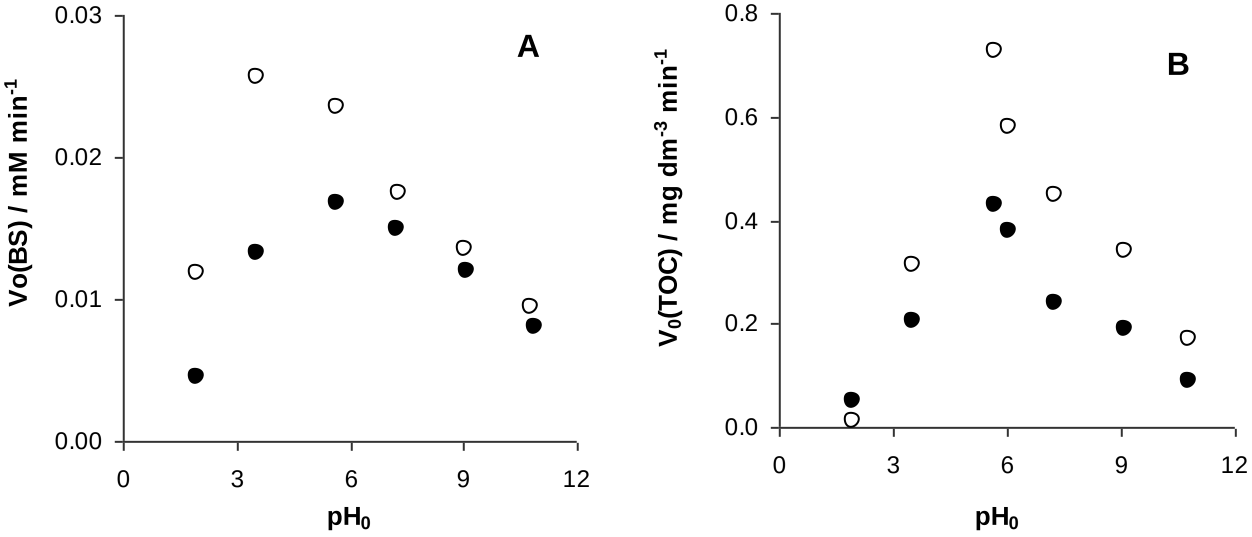
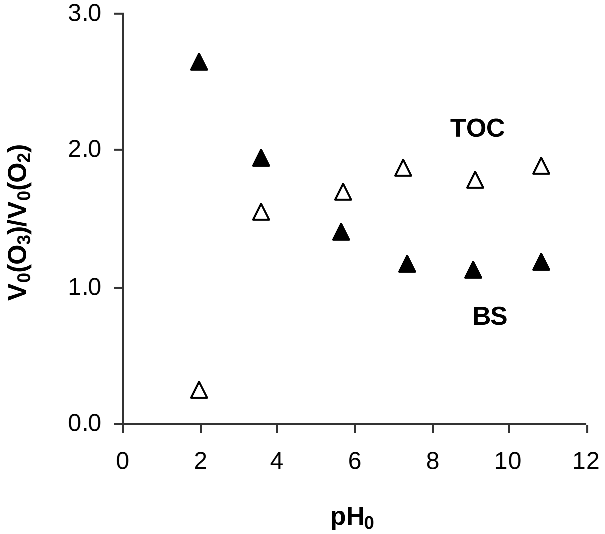
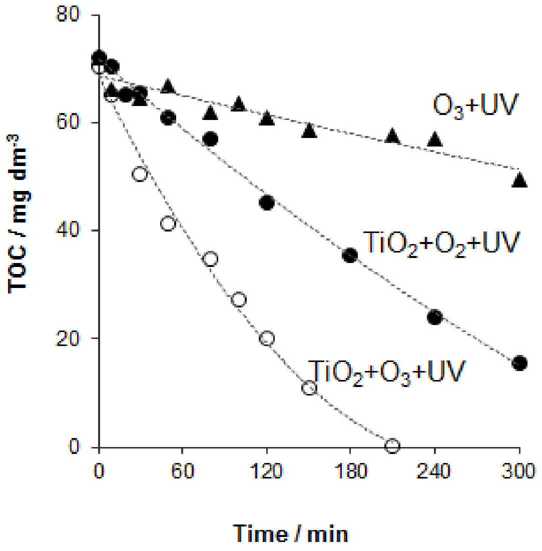

A
B
Vo(BS) / mM min^{-1}
V$_0$(TOC) / mg dm^{-3} min^{-1}
pH$_0$
0.03
0.02
0.01
0.00
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12

Fig. 6.


TOC
BS
V$_0$(O$_3$)/V$_0$(O$_2$)
pH$_0$
3.0
2.0
1.0
0.0
0
2
4
6
8
10
12

Graphical abstract



Application of TiO_2 based photocatalysis combined with ozonation for mineralization of benzenesulfonate resulted in synergistic effect, achieving much higher efficiency than the sum of those of the individual methods.