Effects of common inorganic anions on the rates of photocatalytic degradation of sodium dodecylbenzenesulfonate over illuminated titanium dioxide

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Abstract: Experiments were carried out to study the effects of several anions on the photocatalytic degradation rates of sodium dodecylbenzenesulfonate (DBS) with TiO₂ as catalyst. The anions were added as Na₂SO₄, NaNO₃, NaCl, NaHCO₃, NaH₂PO₄ and Na₂PO₄, and two levels of anion content, i.e., 12 mmol/L and 36 mmol/L in terms of Na⁺, were studied. The results revealed that: Cl⁻, SO₄²⁻, NO₃⁻ and HCO₃⁻ retarded the rates of DBS degradation to different degrees; PO₄³⁻ increased the DBS degradation rate at low concentration and decreased the rate at high concentration; H₂PO₄⁻ accelerated the rate of DBS degradation. The mechanism of the effects of anions on DBS degradation was concluded as the following three aspects: anions compete for the radicals; anions are adsorbed on the surface of catalyst and block the active site of catalyst; anions added in the solution change the pH value and influence the formation of ·OH radicals and the adsorption of DBS on catalyst.

Keywords: surfactant; anion; photocatalytic degradation; water environment

Introduction

Since early 1990s, the remediation of water organic pollution with advanced oxidation process has aroused attentions from worldwide (D’Oliveira, 1990; Ollis, 1991; Hidaka, 1995; Sunada, 1998; Tanaka, 2000). Remarkable progress has been obtained over the application of photocatalyzed oxidation process to the treatment of organic polluted water (Blake, 1991; Bedford, 1994; Hofstadler, 1994; Vinodgopal, 1995; Tsukasa, 1996; Xu, 1997; Bahnemann, 1997; Xia, 1999). Photocatalysis is a process in which the illumination of catalyst, sometimes with the combination of oxidant (such as O₂, H₂O₂), produces radicals with strong activity, e.g. ·OH, and these radicals go on to attack organic contaminants and cause mineralization through chemical reactions of addition, substitution and electron transfer. Recently, research on the rate and mechanism of single organic contaminant photodegradation has been conducted in detail (Reeves, 1992; Spadaro, 1994; Martin, 1996), while little attention has been paid to the effect of water environmental conditions on the photodegradation of contaminants in waste water (Prairie, 1992; Parent, 1996). Some associated organic contaminants and various salts often exist in waste water in addition to a certain or several organic contaminants with high concentration. For example, the sodium sulfate and sodium triphosphate which are additives of detergent often exist in waste water with high concentration of anionic surfactants. Therefore, it is important to take into account the effects of various chemical compositions on the photodegradation of the target organic contaminant so that the experimental data accord well with the waste water conditions. Some research has been conducted on the effects of inorganic anions on photocatalytic oxidation rates of several organics including salicylic acid, ethanol, 2-propanol, phenol and aniline under a fixed pH value (Abdullah, 1990). However, the addition of some anions will change the pH value in the system. So, the experiments without adjusting the pH value may comprehensively reflect the effects of anions on organic photodegradation.

In this paper, the study on the effects of anions including Cl⁻, SO₄²⁻, HCO₃⁻, NO₃⁻, PO₄³⁻ and H₂PO₄⁻ on photocatalyzed degradation rates of sodium dodecylbenzenesulfonate (DBS) over illuminated...
titanium dioxide were conducted without fixing pH value, and the mechanism of the effects of anions on DBS degradation was also discussed.

1 Material and methods

1.1 Material

The catalyst used in the experiments were TiO₂ bought from ACROS of Germany. X-ray diffraction analysis indicated an anatase to rutile ratio of 99 : 1, and the surface area is 7 m²/g. Sodium dodecylbenzenesulfonate (DBS) was of standard reagent grade obtained from National Research Center of Standard Chemicals in China. All other chemicals were of analytical reagent grade supplied by Beijing Chemical Plant.

1.2 Degradation experiments

A dispersion consisting of 400 ml solution with 20 mg/L DBS, inorganic anions of certain content and TiO₂ was contained in a 500 ml glass vessel with a surface area of 55.4 cm² and was illuminated with a high-pressure mercury lamp (250W) under continuous magnetic stirring. Cool water passed through the glass vessel continuously. The UV irradiation intensity was 53 W/m², which was close to the maximum solar UV intensity at Beijing in summer. Oxygen was replenished by opening the reaction vessel when the dispersion was sampled after a certain irradiation time. The 5 ml aliquot was sampled for analysis at each interval. Degradation rates for DBS were determined by measurement of the loss of DBS or TOC from the reaction solution. In the experiments for studying the effects of inorganic anions on DBS photodegradation, two levels of concentration, i.e. 12 mmol/L (level A) and 36 mmol/L (level B) in terms of Na⁺ for NaCl, Na₂SO₄, NaHCO₃, NaNO₃, Na₃PO₄ and NaH₂PO₄, were used. The photocatalytic degradation of DBS was fitted with first-order kinetics.

1.3 Analysis

The pH values of the dispersions in the photodegradation processes were determined with pHB-4 meter produced by Shanghai Leici Instrument Plant, China. Samples withdrawn from the reaction vessel were centrifuged to remove TiO₂ particles, and the solution was analyzed for DBS concentration and TOC. For the determination of DBS contents, methylene blue was added to the solution, leading to the formation of a blue ionpair compound with a strong absorbency at 652 nm. Then, the blue compound was extracted with chloroform and the content of DBS was determined by measuring the absorbency of chloroform solution at 652 nm with spectrophotometer of Beckman DU-8B. The total organic carbon (TOC) was determined by a Shinadzu TOC 500 (China State Environmental Protection Administration, 1989).

2 Results and discussion

2.1 The effect of amounts of catalyst on DBS degradation

DBS disappearance curves are shown in Fig. 1. Those curves followed first order kinetics. The rates of DBS photodegradation increased with the increase of the amount of TiO₂. When TiO₂ were 0.5 g/L, 1.0 g/L and 1.5 g/L, the photodegradation rate constants of DBS were 0.0107 min⁻¹, 0.0158 min⁻¹ and 0.0178 min⁻¹ respectively. The rate constant increased slightly when TiO₂ increased from 1.0 g/L to 1.5 g/L. From this relationship we chose to use 1.0 g/L TiO₂ in the following experiments.

2.2 Total organic carbon elimination and pH

![Fig. 1](image)

Fig. 1 The effect of the amount of catalyst on DBS photodegradation rate (y: DBS concentration; X: irradiation time)
change

Total organic carbon decreased gradually in the photodegradation process (Fig. 2). Its elimination rate was significantly less than DBS disappearance rate. In other words, the complete mineralization of organic compounds requires a much longer illumination time than the disappearance of DBS. In the first three hours, TOC elimination extent was only 0.75 mg/L. But TOC decreased more quickly in the second three-hour than in the first, and the disappearance rate was 2.3 mg/(L·h). The pH value decreased from 6.76 to 4.01 after 3h irradiation, then it increased gradually to 4.10 at 6h irradiation. The decrease of pH value was due to the production of organic acids. In the initial irradiation stage, DBS might be decomposed to organic acids, leading to the significant decrease of pH value and insignificant decrease of TOC. After a certain period of irradiation, the organic acids were degraded to little molecular compound and CO₂, causing the significant decrease of TOC and increase of pH value.

2.3 Effect of inorganic anions on the rate of DBS photodegradation

2.3.1 Effect of chloride

As shown in Fig. 3, sodium chloride decreased the rates of DBS degradation. When the content of sodium chloride increased from level A to level B, the degradation rate constant of DBS decreased from 0.0138 min⁻¹ to 0.0109 min⁻¹. The experiment results in our research were consistent with what reported by Pichat and Abdullah (Abdullah, 1990; Pichat, 1993). The effects of chloride on the photodegradation rate of DBS over illuminated TiO₂ may be caused by two factors; firstly, Cl⁻ will compete with DBS for the oxidizing radicals and influence the electron transfer (Sunada, 1998; Conceicao, 2000); secondly, they will be absorbed on the surface of the catalyst and block the active sites of the TiO₂ catalyst (Abdullah, 1990).

![Fig. 2 Total organic carbon elimination and pH value curves of 20 mg/L DBS photocatalyzed degradation](image1)

![Fig. 3 Effect of NaCl on the oxidation rates of DBS](image2)

2.3.2 Effect of nitrate

The addition of nitrate to the solution decreased the photocatalyzed degradation rate of DBS (Fig. 4). The rate constant decreased from 0.0158 min⁻¹ without nitrate to 0.0107 min⁻¹ with level A nitrate. However, when nitrate content increased from level A to level B, the degradation rate of DBS did not decrease significantly. The result in our experiments were consistent with that of Abdullah (Abdullah, 1990). According to his research, the effect of increasing concentration of nitrate added as NaNO₃ from 10 mmol/L to 40 mmol/L on rates of oxidation of salicylic acid to CO₂ was trivial.

2.3.3 Effect of sulphate

The addition of sulphate with low content (level A) did not exert significant impact on the photodegradation rate of DBS (Fig. 5), i. e., the rate constant just decreased from 0.0158 min⁻¹ to 0.0146 min⁻¹. However, the degradation rate constant decreased remarkably from 0.0146 min⁻¹ to 0.0015 min⁻¹ when the content of sulphate increased from level A to level B. This may be due to the
increase of absorbing quantity of sulphate on TiO₂ surface from level A to level B, giving rising to the block of active site TiO₂ surface.

**2.3.4 Effect of bicarbonate**

The existence of bicarbonate retarded the degradation rates of DBS (Fig. 6). The rate constant was reduced from 0.0158 min⁻¹ to 0.0107 min⁻¹ when adding level A bicarbonate to the solution. But the degradation rate did not decrease remarkably when the content of bicarbonate increased from level A to level B. The addition of sodium bicarbonate to the solution will lead to the increase of pH. According to the zero zeta potential experiments, the isoelectric point of ACROS TiO₂ is 4.5. The increase of pH value would make the surface of TiO₂ more negatively charged, which was favourable for the DBS’s absorption on TiO₂, leading to the inhibition of the degradation of DBS. The pH value increased from 6.76 to 8.34 when adding level A NaHCO₃ to the solution. Therefore, the existence of HCO₃⁻ lessened the degradation rate of DBS. But the pH value only increased from 8.34 to 8.38 when the content of HCO₃⁻ increased from level A to level B, so the degradation rate constant of DBS was reduced only 0.0008 min⁻¹.

**2.3.5 Effect of phosphate**

The addition of level A Na₃PO₄ to the solution increased the DBS degradation rate from 0.0158 min⁻¹ to 0.0233 min⁻¹ (Fig. 7). While the concentration of PO₄³⁻ increased to level B, the DBS degradation rate constant was reduced to 0.011 min⁻¹. The following reactions take place in TiO₂ dispersion under the UV illumination.

\[ \text{TiO}_2 + h^+ \rightarrow h^+ + e^- ; \quad (1) \quad h^+ + H_2O \rightarrow H^+ + \cdot OH ; \quad (2) \]

\[ h^+ + OH^- \rightarrow \cdot OH ; \quad (3) \quad e^- + O_2 \rightarrow O_2^- ; \quad (4) \]

\[ \text{O}_2^- + 2H^+ \rightarrow 2\cdot OH ; \quad (5) \quad \text{H}_2\text{O}_2 \rightarrow 2\cdot OH. \quad (7) \]

The increase of OH⁻ content is not helpful for the adsorption of DBS on TiO₂, but according to Reaction (3), it is favorable for the formation of \( \cdot \text{OH} \). In this experiment, the pH value of the degradation system was very high, it was enhanced from 6.76 to 11.28 with the existence of level A Na₃PO₄, and the formation of \( \cdot \text{OH} \) controlled the DBS decomposition process. Therefore, the addition of level A Na₃PO₄ to the system promoted the degradation of DBS. However, the pH value of the system only increased from 11.28 to 11.71 when the content of Na₃PO₄ increased from level A to level B (Fig. 7). The absorption of
PO$_4^{3-}$ on TiO$_2$ surface dominated the process, so the photodegradation rate was reduced.

### 2.3.6 Effect of biphosphate

As shown in Fig. 8, the existence of NaH$_2$PO$_4$ led to the increase of DBS degradation rate. But the rate did not increase with the increase of NaH$_2$PO$_4$ content. The DBS degradation rate constant increased to 0.0235 min$^{-1}$ with the addition of level A NaH$_2$PO$_4$ to the system, while it was only 0.0193 min$^{-1}$ with the addition of level B NaH$_2$PO$_4$. On one hand, the addition of NaH$_2$PO$_4$ changed pH value of the system. It was decreased from 6.76 to 4.87 and 4.68 when adding level A and level B NaH$_2$PO$_4$ to the solution respectively, which would make TiO$_2$ particles more positively charged and promoted the adsorption of DBS on the surface of TiO$_2$. In addition, according to the above mentioned Reaction (5), the formation of HO$_2^-$ radicals from O$_2^-$ and H$^+$, giving rise to H$_2$O$_2$, has been proposed as one way of producing OH radicals. This reaction will be enhanced by decreasing the pH value (D’ Oliveira, 1990). Therefore, the decrease of pH caused by the addition of NaH$_2$PO$_4$ led to the increase of DBS photodegradation rate. On the other hand, NaH$_2$PO$_4$ added to the solution would be absorbed on the surface of TiO$_2$ and blocked the active site of TiO$_2$ and retarded the DBS oxidation rate. So, the net effect of NaH$_2$PO$_4$ on DBS decomposition rate depended on the increase of rate caused by pH value change and the decrease of rate attributed to adsorption of NaH$_2$PO$_4$ on TiO$_2$. In our experiments, pH value change dominated the process, so the DBS photodegradation was accelerated.

### 2.3.7 Comparison of effects of anions on DBS photodegradation rate

As shown in Table 1, when adding level B NaCl, NaNO$_3$, Na$_2$SO$_4$, NaHCO$_3$, Na$_2$PO$_4$ and NaH$_2$PO$_4$ to the DBS degradation system, the sequence of photocatalyzed degradation constant of DBS was NaH$_2$PO$_4$ > NaCl, NaHCO$_3$, NaNO$_3$ > Na$_2$SO$_4$ > Na$_2$PO$_4$. The sequence of adsorption tendency was PO$_4^{3-}$ > SO$_4^{2-}$ > HCO$_3^-$, NO$_3^-$, Cl$^-$, H$_2$PO$_4^-$ (Chen, 1987), which was accordance with the sequence of photocatalyzed degradation constant of DBS as a whole. Among HCO$_3^-$, NO$_3^-$, Cl$^-$ and H$_2$PO$_4^-$, the photocatalyzed degradation of DBS with H$_2$PO$_4^-$ was the highest. As shown in Fig. 9, the pH values in the degradation system with NaH$_2$PO$_4$ were below 4.6 which was the lowest among the anions. As above mentioned, decreasing pH value is helpful to the degradation of DBS, therefore, the photocatalyzed oxidation rate of DBS was the highest with the presence of NaH$_2$PO$_4$. 

![Fig. 7 Effect of Na$_2$PO$_4$ on the oxidation rates of DBS](image)

![Fig. 8 Effect of NaH$_2$PO$_4$ on the oxidation rates of DBS](image)
Table 1 The effects of NaCl, NaNO₃, Na₂SO₄, NaHCO₃, Na₃PO₄ on the photodegradation rate constant (min⁻¹) of DBS fitted with first order kinetics

<table>
<thead>
<tr>
<th>Contents in terms of Na⁺, mmol/L</th>
<th>NaCl</th>
<th>NaNO₃</th>
<th>Na₂SO₄</th>
<th>NaHCO₃</th>
<th>Na₃PO₄</th>
<th>NaH₂PO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0158</td>
<td>0.0158</td>
<td>0.0158</td>
<td>0.0158</td>
<td>0.0158</td>
<td>0.0158</td>
</tr>
<tr>
<td>12 (Level A)</td>
<td>0.0138</td>
<td>0.0107</td>
<td>0.0146</td>
<td>0.0107</td>
<td>0.0233</td>
<td>0.0235</td>
</tr>
<tr>
<td>36 (Level B)</td>
<td>0.0099</td>
<td>0.0099</td>
<td>0.0011</td>
<td>0.0099</td>
<td>0.0011</td>
<td>0.0193</td>
</tr>
</tbody>
</table>

Among NaCl, NaHCO₃ and NaNO₃, the photocatalyzed decomposition rate of DBS was the highest with the addition of NaCl, which was caused by the lowest pH values in the degradation system with the presence of NaCl.

3 Conclusion

The existence of Cl⁻, SO₄²⁻, HCO₃⁻, NO₃⁻, PO₄³⁻, and H₂PO₄⁻ added as Na₂SO₄, NaNO₃, NaCl, NaHCO₃, Na₃PO₄ and NaH₂PO₄ had effects on the photocatalyzed degradation rate of DBS. Cl⁻, SO₄²⁻, NO₃⁻ and HCO₃⁻ all retarded the rates of DBS degradation at different degrees with ACROS TiO₂ as catalyst. PO₄³⁻ had a positive effect at low concentration and negative effect at high concentration; H₂PO₄⁻ accelerated the rate of DBS degradation under the experimental conditions. The influences of anions on photocatalyzed oxidation rate of DBS were attributed to the following three factors: (1) the anions compete for the radicals or assist recombination of photogenerated electrons and holes; (2) anions will be absorbed to the surface of catalyst and block the active site of catalyst; (3) anions added to the solution change the pH value and influence the formation of •OH radicals and the adsorption of DBS on catalyst. The effect of a certain anion on DBS photodegradation rate depended on the three factors synthetically.

References:


Fig. 9 The pH value curves of DBS photocatalyzed degradation with the presence of anions.


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