

Removal of bromate ion from water using TiO₂ and alumina-loaded TiO₂ photocatalysts

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Abstract The effects of pH and the surface charge of photocatalyst on photocatalytic reduction of bromate ions in water were examined by using TiO₂ and alumina-loaded TiO₂ photocatalysts. The amount of adsorbed bromate ion on TiO₂ and the reduction rate of bromate ion by the TiO₂ photocatalyst increased with lowering pH. It was suggested that the bromate ion adsorbed predominantly on the positively charged surface sites of TiO₂ at lower pH, which thus promotes the rate of reduction. The iso-electric point of the TiO₂ photocatalyst was shifted to the higher pH region by loading alumina on the TiO₂ surface, which resulted in the increase of the adsorbed amount of bromate on the photocatalyst and the reduction rate of bromate ion by the photocatalyst at neutral pH. It was concluded from these results that the photocatalytic reduction of bromate ion can be promoted by pH control of water or by controlling the surface charge of the photocatalyst by loading alumina without pH control of water.

Keywords Bromate ion; drinking water; hydrous alumina; photocatalysis; surface charge; titanium dioxide

Introduction

The treatment of drinking water by ozone has gradually become common because it provides many benefits such as the reduction of taste and odor compounds, inactivation of microbial contaminants, and the reduction of halogenated by-products. Bromate is, however, produced during ozonation of drinking water containing bromide ion (Haag and Hoigne, 1983), and is of great concern because it is a possible carcinogen to humans. There are two major approaches to minimize the contaminant level of bromate in drinking water. One is the optimization of ozone dosage to restrict the formation of bromate during ozonation (Siddiqui *et al.*, 1994). The other is to remove the bromate ion after the ozonation process, and using photocatalysts is one of the attractive ways of doing this. The reduction of bromate ion to bromide ion by photocatalysts is a well known reaction, and bromate has been used as an additive to improve the oxidation efficiency of photocatalysts (Oosawa and Grätzel, 1988; Al-Ekabi *et al.*, 1993; Lindner *et al.*, 1997). It was also reported that bromate can be reduced in tap water by using platinumized titanium dioxide under irradiation of 254 nm UV light (Mills *et al.*, 1996). A long reaction time was, however, required to remove bromate ions in this case, which makes it difficult for practical use in water treatment.

In this paper, we proposed two ways to promote photocatalytic reduction of bromate ions. One is to control the pH of water. It is known that the iso-electric point of TiO₂ is 5 to 6 (Parks, 1965), which indicates that the surface of the TiO₂ photocatalyst is negatively charged in water at pH 7. When the pH is lowered, the surface of TiO₂ will become positively charged, which may result in the increase of adsorbed amounts of bromate ion as anion and thus may promote the photocatalytic reduction of bromate ion. The second way to promote reduction of bromate ion is to control the surface charge by loading metal hydroxides or metal oxides on the surface of the TiO₂ photocatalyst. The iso-electric point

of hydrous alumina is higher than that of titanium dioxide (Parks, 1965). When titanium dioxide is covered with hydrous alumina, the surface charge may become positive in neutral pH solution. The adsorption of bromate anion is thus expected to increase on the surface, which may result in promotion of the photocatalytic reduction of the bromate ion even without pH control. We conducted experiments with TiO_2 and alumina-loaded TiO_2 photocatalysts to examine the influence of pH and surface charge on the reduction of the bromate ion in water.

Experimental

Materials

Potassium bromate, hydrochloric acid, nitric acid, sulfuric acid, potassium hydroxide and all other chemicals were supplied by Wako Pure Chemical Industries, Ltd. in the highest purity available.

The TiO_2 photocatalyst powder used in the present work was commercial Ishihara ST-21 with an average particle size of 20 nm. The alumina-loaded TiO_2 photocatalyst was prepared by the precipitation of aluminium hydroxide on the TiO_2 photocatalyst. The TiO_2 powder was dispersed in water at pH 12 and heated to 60°C. The control of pH in water was made using sodium hydroxide solution. Sodium aluminate was dissolved in 1 mol/L sodium hydroxide at 60°C, and was added to the TiO_2 slurry. The obtained slurry was then neutralized with 1 mol/L nitric acid solution and aged for 1 hour. After cooling down to room temperature, the slurry was filtered and washed repeatedly in distilled water. The filtered cake was dried at 110°C for more than 12 hours and crushed in a mortar. The ratio of loaded alumina was varied to be 2.5, 7, 10, 20 and 40wt%, which was obtained by changing the TiO_2 and sodium aluminate content in the mixed slurry. The characteristics of the used powder are shown in Table 1. The coverage of alumina on TiO_2 surface in Table 1 was determined from the adsorbed amounts of acetaldehyde in gas phase, which is selectively adsorbed on the uncovered TiO_2 surface.

Methods

The surface charge of the photocatalysts was determined by measuring zeta potentials in a 10 mM sodium chloride solution by using the zeta potential analyzer (Otsuka Electronics Co. Ltd., ELS8000). Adjustment of pH was made using 0.1 mol/L sodium hydroxide solution or 0.1 mol/L hydrochloric acid solution.

For the measurement of adsorbed amounts of bromate ion on the photocatalysts, a known amount of standard bromate solution was added to a known amount of photocatalysts slurry at a fixed pH. The slurries were gently stirred, and allowed to equilibrate for 1 hour under dark conditions. The final pH of the slurry was measured. The amount of adsorbed bromate was calculated from the concentration difference between the solute added into the slurry and that after the removal of the solids by using a 0.45 μm disposable filter.

Table 1 Characteristics of the photocatalysts. The coverage of alumina was determined from the adsorbed amounts of acetaldehyde in gas phase

| Ratio of alumina (wt%) | Coverage of alumina (%) | BET surface area (m^2/g) |
|------------------------|-------------------------|--|
| 0 | 0 | 67.6 |
| 2.5 | 67 | – |
| 7 | 82 | 69.1 |
| 10 | 31 | – |
| 20 | 37 | 51.6 |
| 40 | 77 | 98.9 |

The experiments of bromate reduction were carried out in a glass vessel. The photocatalyst powder (20 mg) was suspended in 100 mL potassium nitrate or potassium sulfate solution. After pH adjustment, a potassium bromate solution was added and the initial concentration of bromate ion was controlled to be 0.2 mg/L. The slurry was stirred for 1 hour with magnetic stirrer to equilibrate under dark conditions. Then UV light was irradiated at 0.5 mW/cm² using black light fluorescent lamps. A small volume of the solution (2 mL) was periodically taken for bromate analysis. After the removal of the solids by 0.4 μm disposable filter, the sample was injected into the ion-chromatograph system.

The adsorption test and the measurements of the reduction rate were conducted in a potassium nitrate solution and a potassium sulfate solution to examine the effect of co-existing other anions. Adjustment of pH was made using a nitric acid or potassium hydroxide solution for the potassium nitrate solution, a sulfuric acid or potassium hydroxide solution for the potassium sulfate solution. The concentration of bromate ion was measured in the ion-chromatograph system Dionex AQ. Dionex ion-exchange column, AS9-HC/AS9-HC, and 4.5 mmol/L sodium carbonate eluent were used in the system.

Results and discussion

Effect of pH

Figure 1 shows the decrease of the bromate ion concentration during UV irradiation in 0.1 mmol/L potassium nitrate solution under various pH conditions. The reduction rate of bromate ion was highly sensitive to the pH value. The rate increased with lowering the pH of the solution. The effect of pH on the bromate reduction may be mainly explained by the change of the surface charge of TiO₂ photocatalyst. The iso-electric point of TiO₂ photocatalyst was measured to be 5.2 (see Figure 3). Around this pH, positive charge on the surface increases with lowering pH. This may enhance the electrostatic interaction between bromate ion and TiO₂ particle to make the bromate ion easily contact with the surface of TiO₂ photocatalyst. This was confirmed by the results of isotherm tests. Figure 2 shows the adsorption isotherm for bromate ion on TiO₂ photocatalyst in 0.1 mmol/L potassium nitrate solution with 4 g-TiO₂/L in dark conditions at different pH values. As shown in Figure 2, the adsorbed amounts of bromate ion increased with lowering the pH. It was suggested that the bromate ion was predominantly adsorbed on the positively charged surface at lower pH, thus promoting the photocatalytic reduction. There, it is concluded that the surface charge of photocatalyst plays an important role in promoting the reduction rate of bromate ion. Similar effect of pH on absorption and photocatalytic reaction has been reported for Ag deposition (Ohtani *et al.*, 1987) and degradation of formic acid (Kim and Anderson, 1996).

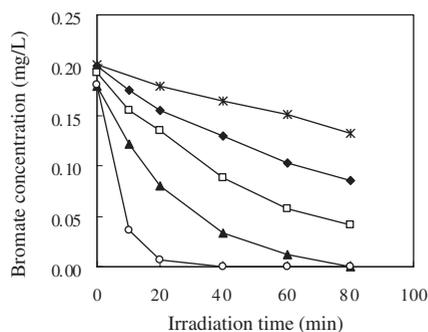


Figure 1 Effect of pH on reduction of bromate ion by TiO₂ photocatalyst. [○]: pH 5.0, [▲]: pH 5.5, [□]: pH 6.0, [◆]: pH 6.5, [*]: pH 7.0

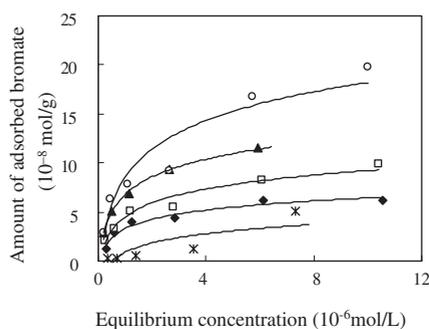


Figure 2 Effect of pH on amount of adsorbed bromate ion on TiO₂ photocatalyst under dark condition. [○]: pH 5.0, [▲]: pH 5.5, [□]: pH 6.0, [◆]: pH 6.5, [*]: pH 7.0

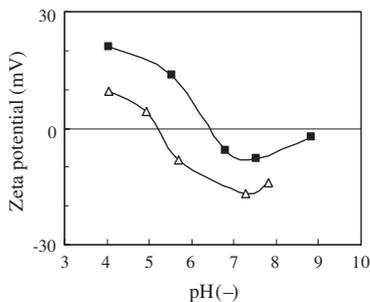


Figure 3 Zeta potentials vs. pH of photocatalysts. [Δ]: TiO_2 , [\blacksquare]: alumina loaded TiO_2

Effect of alumina loading

Zeta potential. Figure 3 shows the zeta potential curves vs. pH of TiO_2 and alumina-loaded TiO_2 (percent alumina is 7 wt%). The zeta potential curve shifted to the higher pH region by alumina loading, which indicates that the positive charge on the surface increased at a fixed pH condition. The iso-electric points obtained from the zeta potential curves were 5.2 for the TiO_2 and 6.4 for the alumina-loaded TiO_2 . The surface of the alumina-loaded TiO_2 was a mixture of the hydrous alumina and titanium dioxide, and the coverage of the hydrous alumina was 82% (see Table 1). Thus the iso-electric point of the alumina-loaded TiO_2 reflects the characters of both hydrous alumina and titanium dioxide. From the microscopic view, the hydrous alumina surface may play a role as a adsorption center for the bromate ion with positively-charged surface in water at neutral pH condition.

Promotion of photocatalytic reduction of bromate ion. Figure 4 shows the pseudo-first-order rate constants for bromate reduction as a function of the ratio of alumina at pH 7 in different aqueous solutions. From Figure 4, it is revealed that the reduction rate of bromate was increased by alumina loading. The rate constants for alumina-loaded TiO_2 photocatalysts were about 2 to 3 times larger than those for TiO_2 photocatalyst except for the case for 10 mmol/L potassium sulfate solution. Promotion of bromate reduction by alumina loading may be mainly explained by the surface charge of photocatalyst similar to the case of pH value's effect. From the results of zeta-potential measurement, the positively charged surface in neutral pH solution increased by alumina loading as mentioned above. Bromate ion may be attracted to the positively charged surface sites. As a result, the photocatalytic reduction was promoted. Figure 5 shows variation of the amount of adsorbed bromate on

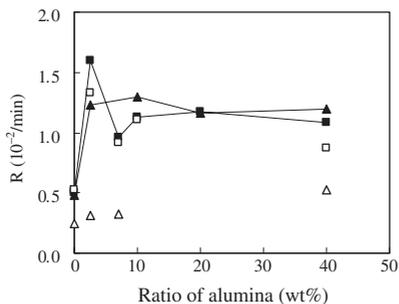


Figure 4 Variation of the pseudo-first-order rate constant for photocatalytic reduction of bromate ion, R , as a function of the ratio of alumina in different aqueous solutions. [\blacksquare]: 0.1 mmol/L KNO_3 , [\blacktriangle]: 10 mmol/L KNO_3 , [\square]: 0.1 mmol/L K_2SO_4 , [\triangle]: 10 mmol/L K_2SO_4

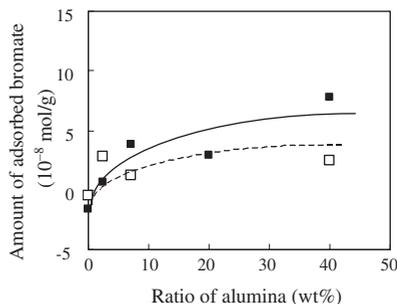


Figure 5 Variation of the amount of adsorbed bromate on photocatalysts in dark condition as a function of the ratio of alumina in different aqueous solutions. [\blacksquare]: 0.1 mmol/L KNO_3 , [\square]: 0.1 mmol/L K_2SO_4

photocatalysts as a function of the ratio of alumina at a fixed volume of standard solution added to 0.2 g-TiO₂/L of photocatalyst solution to become the initial condition of bromate ion, 0.2 mg/L. The amount of adsorbed bromate increased by alumina loading, which indicates the enhanced interaction between the bromate ion and the surface of the photocatalysts.

Competition with other anions. The rate of bromate reduction in 10 mmol/L potassium sulfate solution was much smaller than those in other solutions as shown in Figure 4. Competitive adsorption onto the photocatalyst surface might occur in this solution between bromate ion and sulfate ion. This competition was not observed with co-existence of 0.1 mmol/L sulfate ion and nitrate ion up to 10 mmol/L.

Conclusions

The reduction rate of bromate ion on TiO₂ photocatalyst was highly sensitive to pH, and it increased with lowering the pH. The adsorbed amount of bromate ion was also increased with lowering the pH, which suggests that the bromate ion was predominantly adsorbed on the positively charged surface to promote the photocatalytic reduction. The reduction rate of bromate was also increased by alumina loading on TiO₂ photocatalyst. Since the zeta potential shifted to the higher pH region after alumina loading, it was suggested that an increased number of positively charged surface sites were devoted to enhancing the adsorption and reduction at neutral pH condition. In both cases, the surface charge plays an important role in promoting the reduction of bromate ion in water. It is concluded that the photocatalytic reduction of the bromate ion can be promoted by pH control of water or by controlling the surface charge of photocatalyst by loading alumina even without pH control of water.

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