



Enhanced photocatalytic reduction of concentrated bromate in the presence of alcohols



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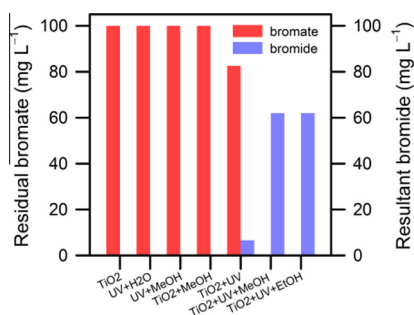
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HIGHLIGHTS

- TiO₂ + UV + alcohol is used as a more efficient photocatalytic method to reduce bromate.
- Alcohols act as sacrificial reagents to scavenge holes from the valence band.
- TiO₂ + UV + alcohol is remarkably more efficient than TiO₂ + UV for reducing bromate.
- Effects of alcohol species and fraction, temperature, pH, anions were examined.
- TiO₂ + UV + alcohol is re-used many times to reduce bromate without refilling alcohol.

GRAPHICAL ABSTRACT



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ABSTRACT

Membrane separation of bromate can continuously treat bromate-containing water; however concentrated bromate solutions would be an inevitable waste which requires proper treatments before discharge. In addition to hydrogenation of bromate using transitional metallic catalysts and hydrogen gas, chemical reduction of bromate can be also achieved by photo-catalysis. While chemically-doped photocatalysts are extensively studied to improve photocatalytic reduction of bromate, another strategy for enhancing photocatalytic efficiency of bromate reduction by adding hole-scavengers (*e.g.*, alcohols) has not been investigated. Thus, in this study, we aim to evaluate photocatalytic reduction of bromate in the presence of alcohols. As TiO₂ + UV was selected as a model photocatalytic process, TiO₂ + UV + alcohol exhibited remarkably higher reduction efficiency and faster reduction kinetics than TiO₂ + UV, possibly owing to suppressed recombination of electron-hole pair as alcohols act sacrificial reagents. A higher fraction of methanol (MeOH) also increased the reduction kinetics. The elevated temperature improved the reduction kinetics, whereas lowering pH of bromate solution substantially accelerated bromate reduction. TiO₂ + UV + MeOH remained effective to reduce bromate in the presence of other anions; it exhibited a significantly high selectivity toward the bromate reduction over the nitrate reduction. TiO₂ + UV + MeOH can be re-used for multiple cycles without loss of conversion efficiency even though no MeOH was refilled and bromide was accumulated within the reactor. These features reveal that TiO₂ + UV + MeOH is a highly effective and promising approach to treat concentrated bromate in water.

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1. Introduction

Advanced oxidation processes (AOPs) are extensively employed in wastewater and water treatment to oxidatively degrade contaminants. During the oxidative degradation, by-products can be derived and some are considered highly toxic, even carcinogenic, limiting implementation of AOPs [1,2]. Among these by-products, bromate (BrO_3^-) is one of the most-concerning compounds because it has been classified as a 2B substance according to the International Agency for Research on Cancer [3]. The United States Environmental Protection Agency and the World Health Organization also limit its maximal level to $10 \mu\text{g L}^{-1}$ in drinking water [3] due to its potential carcinogenicity. Bromate is usually derived from ozonation of bromide in water [4], while recent reports indicate that peroxymonosulfate, a common strong oxidant, can also oxidize bromide to bromate in water [5,6]. Considering threats bromate posing to human health, there is an urge need to remove bromate from water.

A number of methods have been demonstrated to remove bromate, including adsorption [7], ion exchange [8] and membrane separation [9–11]. Membrane separation, particularly, appears to be a more practical approach because it can be implemented for continuous treatment. Kliber et al. proposed using Donnan dialysis to remove bromate from water using anionic membranes [10], while Moslemi et al. also employed ceramic membrane to separate bromate from water [11]. Despite the fact that these studies successfully demonstrated usage of membrane separation to continuously remove bromate from water, concentrated bromate solutions would be an inevitable waste which still preserves toxicity of bromate, and therefore requires proper treatments before disposal.

Chemical reduction of bromate is an attractive strategy to convert toxic bromate back to its less-concerning precursor, bromide [12,13]. To do so, hydrogenation is a widely-employed technique, in which, metal catalysts are combined with hydrogen (H_2) gas to reduce bromate [12,14–16]. Thus, the hydrogenation usually involves continuous purge of H_2 gas into aqueous solutions; however the solubility of H_2 in water is significantly low, leading to waste of H_2 gas in case of no pressurization. Chemical reduction of bromate can be also achieved via photocatalytic reduction of bromate, in which photocatalytically generated electrons react with bromate to form bromide [17–19]. Nevertheless photocatalysts (e.g., Ti and Bi-based photocatalyst) typically require dopants (e.g., noble metals [13,20–22] and carbons [17,18]) in order to improve photocatalytic efficiency. While chemically-doped photocatalysts have been extensively studied, another strategy for improving photocatalysis via decreasing recombination of electron-hole by adding alcohols to bromate solutions has not been investigated. As alcohols (i.e., methanol (MeOH) and ethanol (EtOH)) have been proven as sacrificial reagents to scavenge holes from the valence band of semiconductors, aqueous photocatalysis in the presence of alcohols has been demonstrated as a promising approach for chemical reduction reactions [23–27].

However, to our knowledge, such an approach has not been adopted for reducing bromate. Adding alcohols to concentrated bromate during photocatalysis can be also advantageous owing to the following reasons: alcohols (e.g., MeOH and EtOH) are rather inexpensive; no leach-out pollutions from metallic dopants; and straightforward separation of alcohols/water after bromate reduction. Therefore, we propose to add alcohols (e.g., MeOH and EtOH) to a typical photocatalysis process, $\text{TiO}_2 + \text{UV}$, in order to enhance photocatalytic reduction of bromate. As the present study attempts to propose an alternative method to treat bromate-concentrated retentate from membrane separation of bromate-containing wastewater, the treated retentate requires further treatments because it contains high-concentration bromide reduced from bro-

mate. Methanol or other alcohols can be removed during these further treatments. Therefore, end users should not be exposed to alcohol-containing solutions which can pose threats to human in view of toxicities of alcohols (i.e., MeOH).

$\text{TiO}_2 + \text{UV}$ was specifically selected in this study because $\text{TiO}_2 + \text{UV}$ has been widely employed for wastewater and water treatment. The conventional $\text{TiO}_2 + \text{UV}$ was tested and compared with $\text{TiO}_2 + \text{UV} + \text{alcohol}$ for removing bromate in this study to validate the positive effect of alcohols on photocatalysis. Factors influencing bromate reduction by $\text{TiO}_2 + \text{UV} + \text{alcohol}$ were examined including alcohol species, alcohol concentration, temperature, pH, and co-existing compounds. Multiple-cycle operation of $\text{TiO}_2 + \text{UV} + \text{alcohol}$ without refilling alcohols was also performed to evaluate recyclability.

2. Experimental

2.1. Materials

The chemicals used in this study were commercially available and used without additional purification. TiO_2 nanoparticle (Degussa P25), sodium bromate and sodium bromide were purchased from Sigma-Aldrich (USA). MeOH and EtOH were received from Echo chemicals (Taiwan). Sodium nitrate, sodium sulfate, sodium phosphate and humic acid were purchased from Acros Organics (USA). Deionized (DI) water was prepared to less than $18 \text{ M}\Omega$.

2.2. Reduction of bromate using $\text{TiO}_2 + \text{UV} + \text{alcohol}$

The reduction of bromate using $\text{TiO}_2 + \text{UV} + \text{alcohol}$ was evaluated using batch-type experiments. In a typical experiment, a concentrated bromate solution was added to a batch reactor, to which alcohol (e.g., MeOH, 20% (v/v)) was poured to reach a final volume of 200 mL and an initial concentration of bromate, C_0 (100 mg L^{-1}). Although typical bromate concentration is relatively low ($<1 \text{ mg L}^{-1}$), bromate may accumulate in retentate of membrane separation systems and reach rather high concentrations. Thus, we particularly selected 100 mg L^{-1} , representing an extreme case of highly concentrated bromate accumulated from long-term operations. Another reason adopting this high concentration was because we wanted to magnify effects of different parameters on reduction of bromate in order to clearly reveal the bromate reduction behaviors under various conditions.

Subsequently, TiO_2 powder (0.3 g) was added to the reactor which was irradiated by UV light (Philips, 32 W (UVA)). At pre-set time, sample aliquots were withdrawn and filtrated through $0.22 \mu\text{m}$ syringe filters. The filtrate was analyzed using an ion chromatography system (Dionex ICS-1100 Basic Integrated IC System, USA) to determine residual concentration of bromate (C_r) and concentration of resultant bromide. Effect of temperature was examined by varying temperature of bromate solution from 20 to 60°C . The pH of bromate solution was also adjusted to 3, 7 and 11 by 1 M of HCl/NaOH to investigate bromate reduction under acidic, neutral and alkaline condition, respectively. Considering that bromate-containing wastewater may include other anions, effect of co-existing anions, such as sulfate, nitrate and phosphate, at the same concentration, was also studied. Effect of natural organic matters was also examined by adding different concentrations of humic acid to bromate solutions. To investigate recyclability of $\text{TiO}_2 + \text{UV} + \text{alcohol}$, no additional alcohol was re-filled to the reactor after an experimental cycle. However, concentrated bromate solution was added to the reactor to reach its original concentration (100 mg L^{-1}) for a subsequent cycle of bromate reduction.

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