



Enhanced photocatalytic reduction of concentrated bromate in the presence of alcohols



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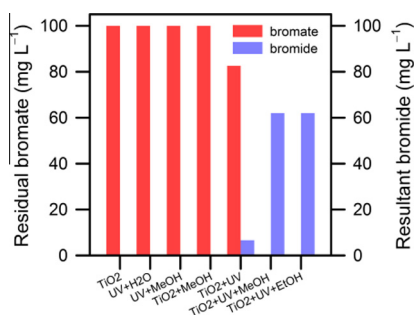
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HIGHLIGHTS

- 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.

3. Results and discussion

3.1. Enhanced conversion of bromate to bromide by TiO₂ + UV + alcohol

Fig. 1 shows bromate reduction and yield of bromide using TiO₂, UV, alcohols and their various combinations. When TiO₂, UV, UV + MeOH, and TiO₂ + MeOH were employed, no bromate was removed. This indicates that TiO₂ could not remove bromate via adsorption even with MeOH. With UV and UV + MeOH, no bromate was removed nor was bromide resulted, showing that UV and UV + MeOH could not effectively reduce bromate, either. Nevertheless, when TiO₂ was combined with UV, a small amount of bromate was removed accompanied with a detectable amount of bromide. TiO₂ irradiated by UV light can generate electrons from the conduction band of TiO₂, which then react with bromate to form bromide [17–19]. However, even though TiO₂ + UV was able to reduce bromate, the conversion was significantly low.

In contrast, once MeOH was introduced to the bromate solution and combined with TiO₂ + UV, bromate was completely removed within 150 min. Simultaneously, a significant amount of bromide (i.e., 61 mg L⁻¹) was resulted, which was equivalent to 0.78 mmol L⁻¹ of bromide, demonstrating that bromate (100 mg L⁻¹ = 0.78 mmol L⁻¹) was completely reduced to bromide by TiO₂ + UV in the presence of MeOH. When MeOH was replaced by EtOH, the similar result can be obtained (Fig. 1) and bromate was fully reduced to bromide within 150 min, revealing that the presence of alcohols in TiO₂ + UV remarkably enhanced reduction of bromate to bromide compared to TiO₂ + UV. Although EtOH is less-concerning than MeOH in terms of toxicity, MeOH is the simplest form of alcohols. Thus, MeOH was particularly selected for investigating other parameters in this study.

3.2. Kinetic comparison of bromate reduction using TiO₂ + UV, TiO₂ + UV + MeOH and TiO₂ + UV + EtOH

The reduction of bromate by TiO₂ + UV, TiO₂ + UV + MeOH and TiO₂ + UV + EtOH was further investigated by looking into reduction kinetics. Fig. 2(a) shows C_t/C₀ as a function of reaction time. TiO₂ + MeOH was again proven to be incapable of removing bromate from water via adsorption without UV irradiation. TiO₂ + UV was also found to be ineffective to reduce bromate as C_t/C₀ decreased quite slowly. Even after 150-min reaction, C_t/C₀ was not decreased below 0.8, showing that TiO₂ + UV was ineffective

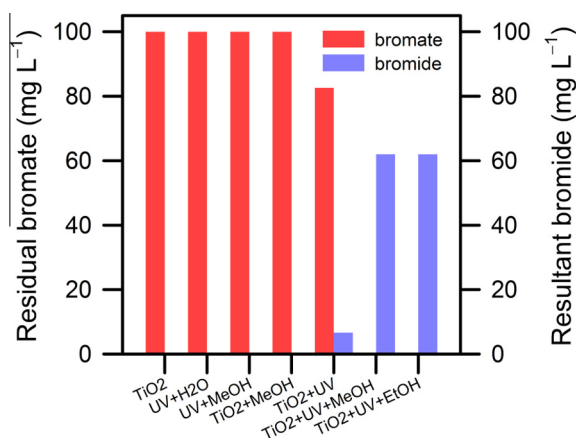


Fig. 1. Comparison of bromate reduction between the adsorption to TiO₂, UV irradiation, TiO₂ + UV and TiO₂ + UV + alcohols. (C₀ of bromate = 100 mg L⁻¹; TiO₂ = 0.3 g; T = 20 °C, reaction time = 180 min.)

for treating concentrated bromate solution. When 20% of MeOH was introduced to TiO₂ + UV, C_t/C₀ decreased rapidly and reached to zero within 60 min, demonstrating that the presence of MeOH remarkably improved the reduction of bromate in terms of conversion efficiency as well as conversion rate. The generation kinetics of bromide from bromate was shown in Fig. 2(b), which also reveals that the presence of MeOH in TiO₂ + UV improved and accelerated the reduction of bromate to bromide. It has been revealed that MeOH adsorbed on TiO₂ can form methoxy groups (CH₃O⁻) as follows (Eq. (1)) [28,29]:



As electrons from the conduction band and holes from valence band of TiO₂ are generated from TiO₂/UV as follows (Eq. (2)),



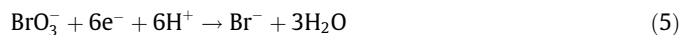
methoxy group can capture holes to form methoxy radicals [28,29] (Eq. (3))



Methoxy radicals can also capture holes and release protons to form CH₂O (Eq. (4)) which can further transform to CH₂OO on TiO₂ surface [26]. The as-generated CH₂OO species captures holes and releases protons to become formate which is then transformed to carbonates and CO₂ eventually [30].



Via the series of MeOH transformations, the photocatalytically-generated holes can be scavenged so that the electrons can be efficiently used to reduce bromate to bromide as follows (Eq. (5))



In Eq. (3), CH₃O[·] might transform to ·CH₂OH (hydroxymethyl radicals) via isomerization [31]. As ·CH₂OH radicals are reductants [24], it was also possible that bromate was reduced by ·CH₂OH. In addition, while a few studies reveal photocatalysis of water/MeOH mixture can generate H₂ [27,32,33], almost insignificant hydrogen gas was detected in this study, possibly because dosages of TiO₂ and MeOH were relatively low compared to other studies specifically for generating hydrogen from photocatalytic decomposition of MeOH/water [27]. Thus, the enhanced photocatalytic reduction in the presence of MeOH should be attributed to more efficient generation of electrons using MeOH as a hole-scavenger instead of generation of H₂ gas for hydrogenation of bromate.

Fig. 2(a) also shows that when MeOH was replaced by EtOH in TiO₂ + UV + alcohol, the similar result can be observed, showing that EtOH can also effectively scavenge holes, leading to the enhanced bromate reduction [34].

3.3. Effects of MeOH concentration and TiO₂ loading on reduction of bromate

As the addition of alcohols significantly improved the reduction of bromate using TiO₂ + UV, we further examined the effect of alcohol concentration on bromate reduction. Fig. 3(a) shows C_t/C₀ as a function of reaction time at different concentrations of MeOH. Without MeOH, as discussed previously, the reduction of bromate was extremely slow and ineffective. When MeOH concentration became 10%, the bromate reduction was noticeably improved. Despite merely 10% MeOH, bromate was still fully reduced to bromide (Fig. 3(b)). The reduction kinetics was also accelerated compared to that without MeOH. As MeOH concentration increased, the reduction kinetics became even faster. When MeOH concentration was 60%, the concentrated bromate was completely converted

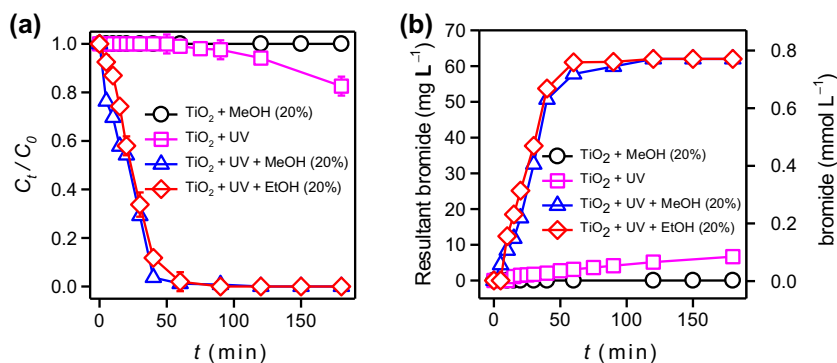


Fig. 2. Comparison of (a) bromate reduction and (b) generation of bromide between the adsorption to TiO_2 , UV irradiation, $\text{TiO}_2 + \text{UV}$ and $\text{TiO}_2 + \text{UV} + \text{alcohols}$. (C_0 of bromate = 100 mg L^{-1} ; $\text{TiO}_2 = 0.3 \text{ g}$; $T = 20 \text{ }^\circ\text{C}$.)

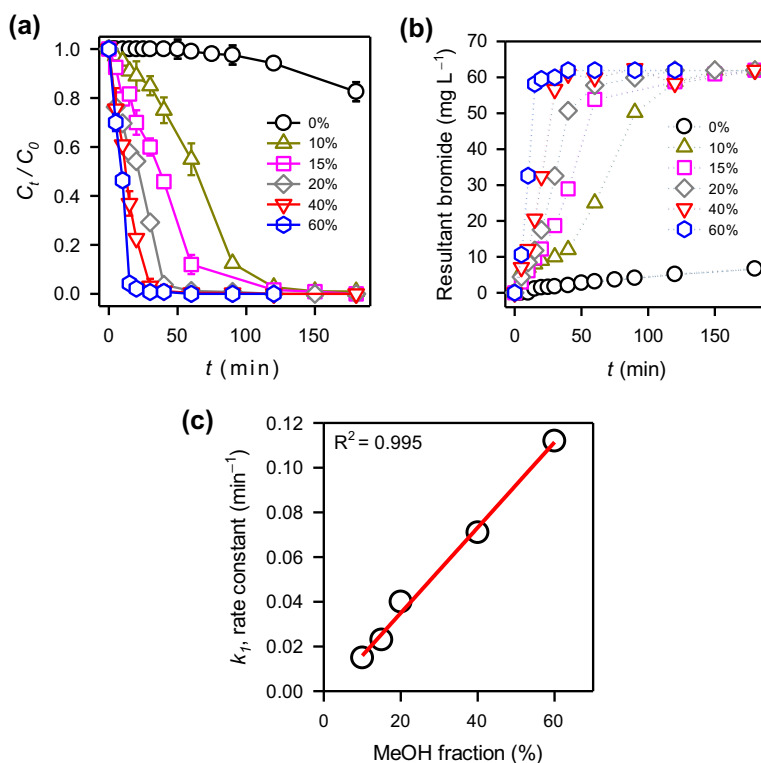


Fig. 3. Effect of MeOH concentration on (a) bromate reduction and (b) generation of bromide and (c) the pseudo first order rate constants (k_1) using $\text{TiO}_2 + \text{UV} + \text{MeOH}$ (C_0 of bromate = 100 mg L^{-1} ; $\text{TiO}_2 = 0.3 \text{ g}$; $T = 20 \text{ }^\circ\text{C}$.)

to bromide within 30 min, confirming that the presence of MeOH substantially facilitated the conversion of bromate to bromide using $\text{TiO}_2 + \text{UV}$.

To quantitatively determine the kinetic improvement at different concentrations of MeOH, the pseudo first order equation was adopted as follows (Eq. (6)):

$$C_t = C_0 \exp(-k_1 t) \quad (6)$$

where k_1 is the pseudo first order rate constant. Rate constants at different concentrations of MeOH are summarized in Table S1. The correlation coefficients (R^2) are all found to exceed 0.95, suggesting that the reduction kinetics of bromate by $\text{TiO}_2 + \text{UV} + \text{MeOH}$ can be appropriately described by the pseudo first order rate law. The k_1 value notably increased from 0.015 to 0.112 min^{-1} as MeOH concentration changed from 10 to 60%, validating that the addition of MeOH greatly facilitated the reduction of bromate. A plot of rate constant versus MeOH concentration can be seen in Fig. 3(c), in

which, interestingly, a linear relationship can be observed between rate constants and MeOH concentrations. This suggests that the hole-scavenging effect of MeOH was linearly correlated to MeOH concentrations and the amount of MeOH molecules determined the rate of bromate reduction.

Furthermore, Fig. 4(a) shows the effect of TiO_2 loading on bromate reduction. When a relatively low TiO_2 loading (0.1 g) was used, bromate was still fully reduced and converted to bromide (Fig. 4(b)). This validates the photo-catalytic role of TiO_2 as a small amount is needed to achieve full reduction of bromate in water. Once TiO_2 loading increased to 0.3 and 0.5 g, the full reduction of bromate was achieved within shorter periods, revealing that high loadings of TiO_2 indeed facilitated reduction of bromate. Fig. 4(b) also displays faster conversion rates of bromate to bromide achieved by higher loadings of TiO_2 . k_1 values obtained using different loadings of TiO_2 are summarized in Table S1. As TiO_2 loading increased from 0.1 to 0.3 and 0.5 g, k_1 increased correspondingly

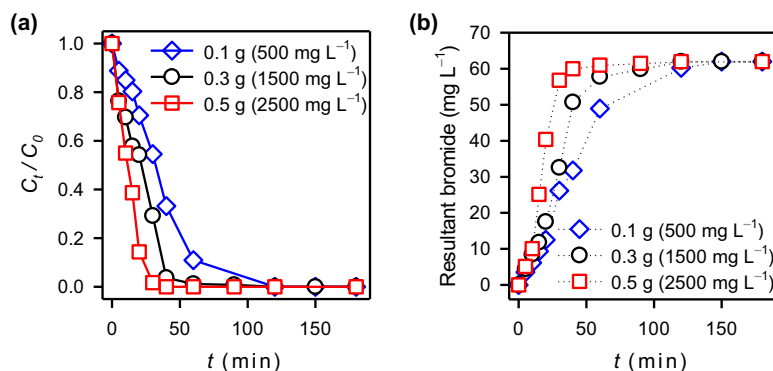


Fig. 4. Effect of TiO_2 loading on (a) bromate reduction and (b) generation of bromide using $\text{TiO}_2 + \text{UV} + \text{MeOH}$ (C_0 of bromate = 100 mg L^{-1} ; $\text{MeOH} = 20\%$; $T = 20^\circ\text{C}$).

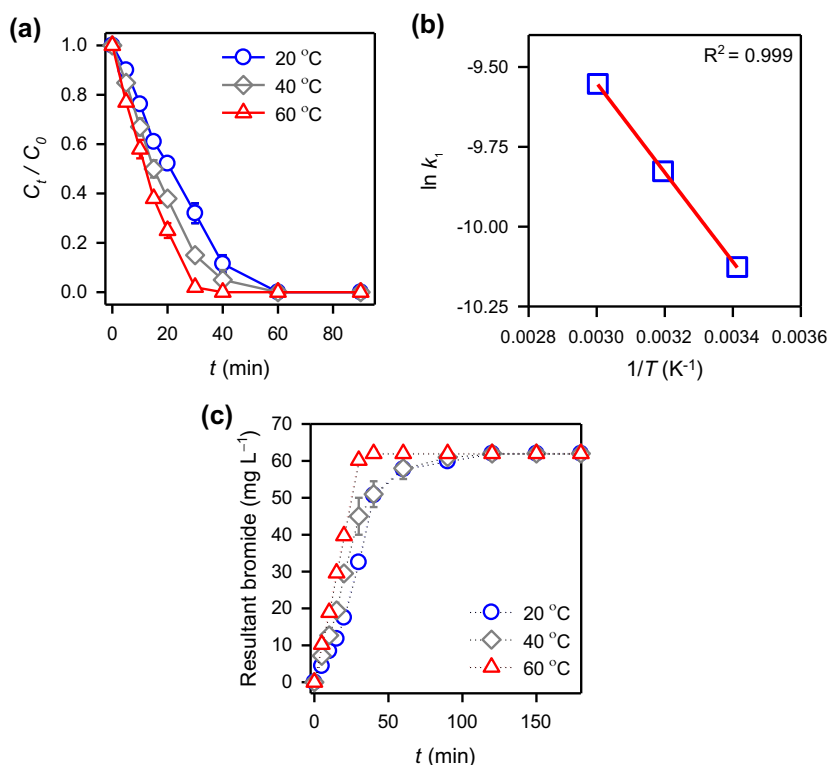


Fig. 5. (a) Bromate reduction, (b) a plot for determining the activation energy E_a for bromate reduction and (c) generation of bromide using $\text{TiO}_2 + \text{UV} + \text{MeOH}$ at different temperatures (C_0 of bromate = 100 mg L^{-1} ; $\text{TiO}_2 = 0.3 \text{ g}$; $\text{MeOH} = 20\%$).

from 0.025 to 0.04 and 0.076 min^{-1} , respectively, demonstrating the positive effect of higher loadings of TiO_2 on bromate reduction.

3.4. Effect of temperature on bromate reduction

Furthermore, temperature of bromate solution was varied from 20 to 60°C to examine the effect of temperature. Fig. 5(a) shows C_t/C_0 as a function of reaction time at different temperatures. A distinct trend can be observed that an increase in temperature noticeably accelerated the reduction kinetics. The rate constants at different temperatures are also summarized in Table S1. The k_1 value increased from 0.04 to 0.071 min^{-1} as temperature changed from 20 to 60°C , showing the positive effect of elevated temperature on the reduction kinetics. As the rate constant increased with the increasing temperature, the relationship between rate constants and temperatures was further correlated via the Arrhenius equation as follows (Eq. (7)):

$$\ln k_1 = \ln A - E_a/RT \quad (7)$$

where E_a represents the activation energy (kJ mol^{-1}); A denotes the pre-exponential factor (min^{-1}); R is the universal gas constant; and T denotes the solution temperature in Kelvin (K). According to Eq. (7), a plot of $\ln k_1$ versus $1/T$ is shown in Fig. 5(b), in which the data points are perfectly-fit by a linear regression ($R^2 = 0.999$). This indicates that the Arrhenius equation is a suitable model to predict rate constants of bromate reduction using $\text{TiO}_2 + \text{UV} + \text{MeOH}$ at different temperatures. The slope of the fitting line can be used to estimate E_a as 11.6 kJ mol^{-1} .

Fig. 5(c) shows the resulting bromide by $\text{TiO}_2 + \text{UV} + \text{MeOH}$ at different temperatures. Similarly, the elevated temperature also noticeably improved the generation of bromide in terms of reaction kinetics, validating the enhancing effect of higher temperatures. Through comparisons of kinetic results of removed bromate and resulting bromide, one can note that there was a delay between removal of bromate and formation of bromide. This

could be because intermediates might occur during the conversion of bromate to bromide. In addition, the conversion of bromate to bromide might occur on surface of TiO_2 . Thus, when bromate was converted to bromide, bromide might reside on surface of TiO_2 for a short time before bromide could be detected in water. Therefore, even though bromate was fully removed at 60 min at 20 or 40 °C, the concentration of resulting bromate was slightly less than the theoretical amount of bromide derived from bromate at 60 min. However, the concentration of bromide in water reached the theoretical amount at 90 min, showing that bromate can be almost fully reduced to bromide, however, with a delay due to the above-mentioned possibilities.

3.5. Effect of pH on bromate reduction

Furthermore, initial pH value of bromate solution was also varied to 3, 7 and 11 to examine the reduction of bromate using $\text{TiO}_2 + \text{UV} + \text{MeOH}$ under acidic, neutral and alkaline condition, respectively. The pH variations during bromate reduction were also monitored (Fig. S1). Regardless of initial pH value, pH slightly decreased during bromate reduction as H^+ was produced during the transformations of MeOH based on Eqs. (1)–(4). Fig. 6(a) shows that the bromate reduction at pH = 3 was substantially accelerated compared to that at pH = 7. The formation of bromide was correspondingly accelerated at pH = 3. In contrast, the bromate reduction was significantly hindered at pH = 11, so was the formation of bromide (Fig. 6(b)) in comparison with those at pH = 7. These results clearly indicate that pH was a crucial parameter for the bromate reduction and the acidic condition was much more preferable than the alkaline condition for the bromate reduction.

The rate constant (k_1) at pH = 3 was found to be 0.302 min^{-1} (Table S1), whereas k_1 values for pH = 7 and 11 were 0.040 and 0.007 min^{-1} , respectively. This indicates that the reaction rate could be increased significantly by lowering pH. The reason leading to the huge difference in the bromate reduction at different pH could be attributed to electrostatic effects. Under the acidic condition, a large amount of H^+ ions might deposit on the surface of TiO_2 powder, which became relatively positive [35]. Anionic bromate ions might be attracted to the positive surface of TiO_2 , increasing the contact between bromate and the surface of TiO_2 , leading to the faster reduction kinetics under the acidic condition. Nevertheless, the surface of TiO_2 became much negative under alkaline conditions because of the deposition of OH^- ions. Thus the electrostatic repulsion could be much greater between the surface of TiO_2 and bromate as well as MeOH, diminishing the bromate reduction.

3.6. Effect of co-existing anions on bromate reduction

As bromate-containing wastewater may also include other ions, especially anions such as sulfate, nitrate and phosphate, we further investigated whether these anions co-existing with bromate affected the bromate reduction using $\text{TiO}_2 + \text{UV} + \text{MeOH}$. Fig. 7(a) shows that even though the mixture contained the equal-concentration sulfate, nitrate, phosphate and bromate, $\text{TiO}_2 + \text{UV} + \text{MeOH}$ was still able to completely remove bromate. In addition, no sulfate and phosphate was removed, possibly because TiO_2 did not exhibit strong affinity toward sulfate and phosphate. Nevertheless, a small amount of nitrate was removed and nitrite could be also detected in the solution, showing that $\text{TiO}_2 + \text{UV} + \text{MeOH}$ could also reduce nitrate to nitrite. However, $\text{TiO}_2 + \text{UV} + \text{MeOH}$ clearly exhibited a high selectivity toward the bromate reduction over the nitrate reduction.

On the other hand, we also compared the bromate reduction with and without the co-existing anions in Fig. 7(b). One can see that the reduction kinetics remained almost unchanged even in the presence of other anions. The formation of bromide from bromate was also comparable when other equal-concentration anions were present. This demonstrates that $\text{TiO}_2 + \text{UV} + \text{MeOH}$ can selectively treat concentrated bromate-containing wastewater without loss of conversion efficiency.

3.7. Effect of humic acid on bromate reduction

In addition to the aforementioned anions, wastewater typically also contains natural organic matters (e.g., humic acid (HA)). Therefore, we further investigated the effect of humic acid on bromate reduction using $\text{TiO}_2 + \text{UV} + \text{MeOH}$. Fig. 8(a) shows C_t/C_0 as a function of time in the presence of different concentrations of humic acid. When HA was merely 5 mg L^{-1} , bromate reduction had been noticeably delayed in terms of kinetics even though bromate has still been completely reduced to bromide (Fig. 8(b)). Nevertheless, once HA increased to 30 and 50 mg L^{-1} , C_t/C_0 could not reach zero and the reduction kinetics became significantly slower. As k_1 is 0.040 min^{-1} in the absence of HA, k_1 becomes 0.019, 0.008 and 0.005 min^{-1} in the presence of HA = 5, 30 and 50 mg L^{-1} , respectively (Table S1). This indicates that the presence of HA substantially interfered with the bromate reduction as several studies had also reported that photocatalytic activity of photocatalysts are greatly reduced in the presence of HA [36,37].

3.8. Recyclability

As $\text{TiO}_2 + \text{UV} + \text{MeOH}$ was proposed as an alternative photocatalytic process for reducing bromate, it is important to investigate

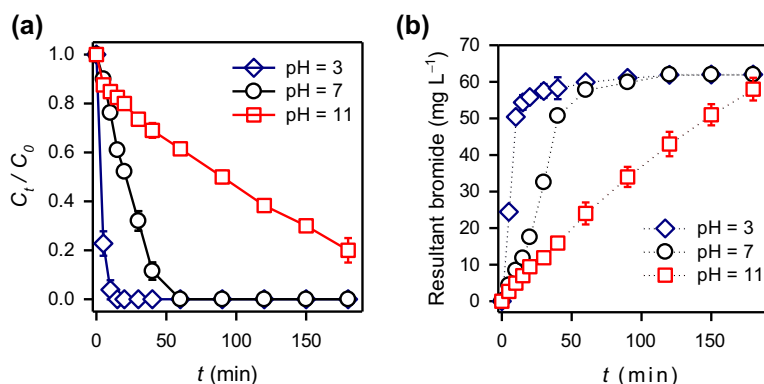


Fig. 6. (a) Bromate reduction and (b) generation of bromide using $\text{TiO}_2 + \text{UV} + \text{MeOH}$ under different pH values. (C_0 of bromate = 100 mg L^{-1} ; $\text{TiO}_2 = 0.3 \text{ g}$; MeOH = 20%; $T = 20 \text{ }^\circ\text{C}$.)

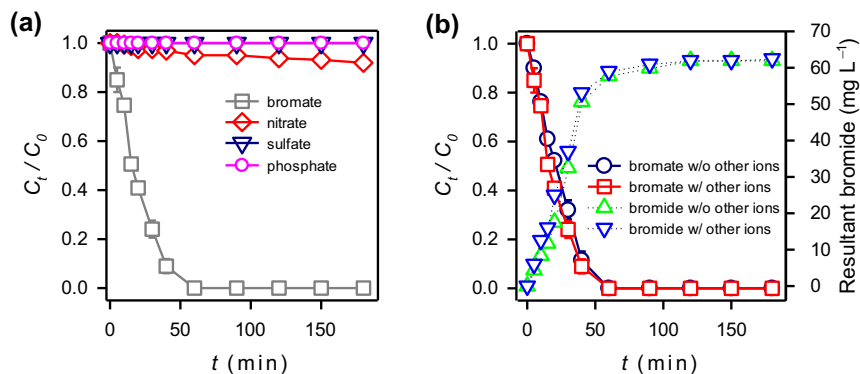


Fig. 7. Effect of co-existing anions on (a) bromate reduction and (b) generation of bromide using $\text{TiO}_2 + \text{UV} + \text{MeOH}$. (C_0 of bromate = 100 mg L^{-1} ; $\text{TiO}_2 = 0.3 \text{ g}$; $\text{MeOH} = 20\%$; $T = 20 \text{ }^\circ\text{C}$.)

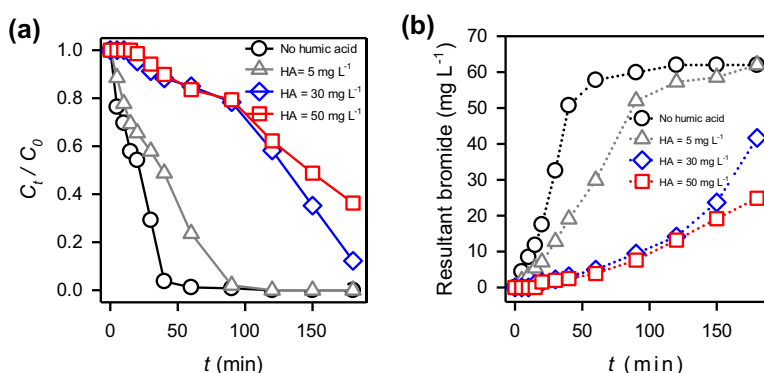


Fig. 8. Effect of humic acid (HA) on bromate reduction using $\text{TiO}_2 + \text{UV} + \text{MeOH}$ (C_0 of bromate = 100 mg L^{-1} ; $\text{TiO}_2 = 0.3 \text{ g}$; $\text{MeOH} = 20\%$; $T = 20 \text{ }^\circ\text{C}$).

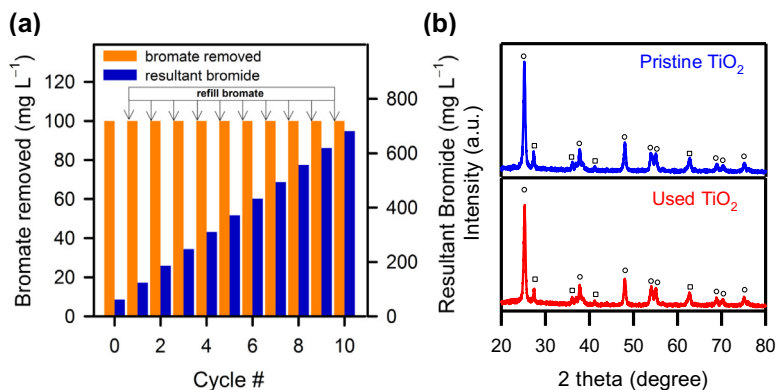


Fig. 9. (a) Recyclability of $\text{TiO}_2 + \text{UV} + \text{MeOH}$ for reduction of bromate and (b) crystalline structures of TiO_2 before and after the multiple-cycle reaction (\circ : Anatase; \square : Rutile). (C_0 of bromate = 100 mg L^{-1} ; $\text{TiO}_2 = 0.3 \text{ g}$; $\text{MeOH} = 20\%$; $T = 20 \text{ }^\circ\text{C}$.)

whether such a process can be re-used for multiple times. To evaluate its recyclability, TiO_2 powder was remained in the batch reactor after each cycle of bromate reduction and the reaction solution was not decanted. Subsequently, a concentrated bromate solution was added to the reaction solution to reach its original concentration of bromate (*i.e.*, 100 mg L^{-1}) without refilling MeOH. Fig. 9(a) reveals that even though bromate was refilled in each cycle without refilling MeOH, bromate was still completely removed over 10 cycles. Also, bromate was also totally converted to bromide which was accumulated from each cycle of bromate reduction. Although the concentration of bromide was cumulatively increased, the bromate reduction by $\text{TiO}_2 + \text{UV} + \text{MeOH}$ was not influenced. This also demonstrates that while no MeOH was refilled, $\text{TiO}_2 + \text{UV} + \text{MeOH}$

was still highly effective. Fig. 9(b) reveals that TiO_2 powder still remained intact without any crystalline changes even after the multiple cycles of bromate reduction. These results validate that $\text{TiO}_2 + \text{UV} + \text{MeOH}$ can be a promising photocatalytic approach to treat bromate in water.

4. Conclusion

The present study successfully demonstrated that $\text{TiO}_2 + \text{UV}$ in the presence of alcohols can effectively convert bromate to bromide. Compared to $\text{TiO}_2 + \text{UV}$, $\text{TiO}_2 + \text{UV} + \text{MeOH}$ (or EtOH) remarkably accelerated the reduction kinetics and improved the conversion efficiency. The enhanced bromate reduction by $\text{TiO}_2/$

UV in the presence of MeOH could be owing to significantly suppressed recombination of electron-hole using alcohols as sacrificial reagents for holes (h^+). Consequently, the photo-catalytically generated electrons could efficiently react with bromate to form bromide. A higher MeOH concentration was found to increase the reduction kinetics, and the rate constants of bromate reduction can be linearly correlated to MeOH concentrations. While the elevated temperature noticeably improved the reduction kinetics, lowering pH of bromate solution remarkably accelerated the bromate reduction. Even though the presence of humic acid hindered bromate reduction, $\text{TiO}_2 + \text{UV} + \text{MeOH}$ remained effective to reduce bromate to bromide in the presence of other anions and it exhibited a significantly high selectivity toward the bromate reduction over the nitrate reduction. $\text{TiO}_2 + \text{UV} + \text{MeOH}$ 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 enable $\text{TiO}_2 + \text{UV} + \text{MeOH}$ to be a promising and practical approach to reduce bromate in water.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2016.06.056>.

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