

Effect of inorganic anions on the titanium dioxide-based photocatalytic oxidation of aqueous ammonia and nitrite

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Received 20 April 2006; received in revised form 23 June 2006; accepted 24 June 2006

Available online 1 August 2006

Abstract

In this study, we investigated the effects of four inorganic anions (Cl^- , SO_4^{2-} , $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$, and $\text{HCO}_3^-/\text{CO}_3^{2-}$) on titanium dioxide (TiO_2)-based photocatalytic oxidation of aqueous ammonia ($\text{NH}_4^+/\text{NH}_3$) at pH ~ 9 and ~ 10 and nitrite (NO_2^-) over the pH range of 4–11. The initial rates of $\text{NH}_4^+/\text{NH}_3$ and NO_2^- photocatalytic oxidation are dependent on both the pH and the anion species. Our results indicate that, except for CO_3^{2-} , which decreased the homogeneous oxidation rate of $\text{NH}_4^+/\text{NH}_3$ by UV-illuminated hydrogen peroxide, $\bullet\text{OH}$ scavenging by anions and/or direct oxidation of $\text{NH}_4^+/\text{NH}_3$ and NO_2^- by anion radicals did not affect rates of TiO_2 photocatalytic oxidation. While HPO_4^{2-} enhanced $\text{NH}_4^+/\text{NH}_3$ photocatalytic oxidation at pH ~ 9 and ~ 10 , $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ inhibited NO_2^- oxidation at low to neutral pH values. The presence of Cl^- , SO_4^{2-} , and HCO_3^- had no effect on $\text{NH}_4^+/\text{NH}_3$ and NO_2^- photocatalytic oxidation at pH ~ 9 and ~ 10 , whereas CO_3^{2-} slowed $\text{NH}_4^+/\text{NH}_3$ but not NO_2^- photocatalytic oxidation at pH ~ 11 . Photocatalytic oxidation of $\text{NH}_4^+/\text{NH}_3$ to NO_2^- is the rate-limiting step in the complete oxidation of $\text{NH}_4^+/\text{NH}_3$ to NO_3^- in the presence of common wastewater anions. Therefore, in photocatalytic oxidation treatment, we should choose conditions such as alkaline pH that will maximize the $\text{NH}_4^+/\text{NH}_3$ oxidation rate.

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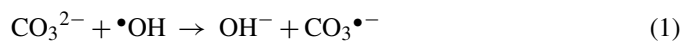
Keywords: Inorganic anions; Aqueous ammonia; Nitrite; Titanium dioxide; Hydroxyl radical

1. Introduction

Aqueous ammonia ($\text{NH}_4^+/\text{NH}_3$), a major inorganic nitrogen-containing pollutant in wastewater, is toxic to aquatic life including fish [1,2], and nitrite (NO_2^-) is a major intermediate of $\text{NH}_4^+/\text{NH}_3$ oxidation [3–7]. Inorganic anions, such as chloride (Cl^-), sulfate (SO_4^{2-}), phosphate ($\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$), and bicarbonate/carbonate ($\text{HCO}_3^-/\text{CO}_3^{2-}$), are also commonly present in wastewater with concentrations up to 1.5×10^{-3} M [8]. Many researchers have investigated the effects of inorganic anions on titanium dioxide (TiO_2)-based photocatalytic degradation of organic compounds [9–18], in which UV-illuminated TiO_2 generates hydroxyl radical ($\bullet\text{OH}$), a non-selective oxidant, to degrade organic compounds. To the best of our knowledge, only Chen and Cao [19] have studied the effect of Cl^- , SO_4^{2-} , and NO_3^- on NO_2^- photocatalytic oxidation using TiO_2 supported on hollow glass microbeads at pH 5. However, no sys-

tematic study has been done on the effect of inorganic anions on the TiO_2 -based photocatalytic oxidation of both $\text{NH}_4^+/\text{NH}_3$ and NO_2^- as a function of pH. Accordingly, to effectively remove $\text{NH}_4^+/\text{NH}_3$ and NO_2^- from water and wastewater, it is critical to study whether inorganic anions could influence their photocatalytic oxidation. In this research, we investigated the effects of Cl^- , SO_4^{2-} , $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$, and $\text{HCO}_3^-/\text{CO}_3^{2-}$ on $\text{NH}_4^+/\text{NH}_3$ and NO_2^- photocatalytic oxidation in TiO_2 suspensions for the pH range of 4–11.

Previous studies have shown that inorganic anions can scavenge $\bullet\text{OH}$ to form the corresponding anion radicals [20–25]. An example of $\bullet\text{OH}$ scavenging by CO_3^{2-} to form the carbonate radical ($\text{CO}_3^{\bullet-}$) [20] is shown below:



Hydroxyl radical scavenging by the anions Cl^- , SO_4^{2-} , and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ as well as formation of the corresponding anion radicals ($\text{HOCl}^{\bullet-}$, $\text{SO}_4^{\bullet-}$, $\text{H}_2\text{PO}_4^{\bullet}/\text{HPO}_4^{\bullet-}$) have also been shown in aqueous solutions [20]. Hydroxyl radical scavenging of the anions Cl^- , $\text{HCO}_3^-/\text{CO}_3^{2-}$, SO_4^{2-} , and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ may influence the photocatalytic oxidation

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of organic compounds [11,15,16,18,23] by destroying the reactive species $\bullet\text{OH}$. The corresponding anion radicals can themselves oxidize organic and inorganic compounds at different rates [20,26,27], which can also influence overall rates of photocatalytic oxidation.

Previous researchers [9–13,18] have proposed that competitive adsorption of the inorganic anions for active sites on the TiO_2 surface may also influence the photocatalytic degradation of organic compounds. For example, 0.01 M Cl^- was found to decrease the degradation rate of 2-chlorophenol and 2-nitrophenol at pH values lower than the TiO_2 point of zero charge (pH_{pzc}) (6.2–7.5 for Degussa TiO_2 P 25 [28,29]), while Cl^- had no inhibitory effect at pH values greater than the pH_{pzc} due to negligible adsorption to the negatively charged TiO_2 surface [11]. Similarly, SO_4^{2-} and H_2PO_4^- decreased the rate of photocatalytic degradation of ethanol, salicylic acid, and aniline at pH 4.1, which was attributed to electrostatic adsorption of these anions to the TiO_2 surface [9]. Decreased photocatalytic oxidation rates of an azo dye at neutral pH in the presence of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ were also observed [16]. This was possibly because of specific (i.e., non-electrostatic) adsorption of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ to the TiO_2 surface [30,31].

In this research, we hypothesized that inorganic anions would influence rates of $\text{NH}_4^+/\text{NH}_3$ and NO_2^- photocatalytic oxidation in one of the following ways: (i) $\bullet\text{OH}$ scavenging by inorganic anions, (ii) direct oxidation of $\text{NH}_4^+/\text{NH}_3$ and NO_2^- by anion radicals, or (iii) adsorption of inorganic anions to the TiO_2 surface. We studied the photocatalytic oxidation of $\text{NH}_4^+/\text{NH}_3$ and NO_2^- as a function of pH with the four inorganic anions (Cl^- , SO_4^{2-} , $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$, and $\text{HCO}_3^-/\text{CO}_3^{2-}$) that are commonly present in water and wastewater. Since $\bullet\text{OH}$ can be generated by UV illumination of H_2O_2 [32], we used UV-illuminated H_2O_2 to study $\bullet\text{OH}$ scavenging by inorganic anions and direct oxidation of $\text{NH}_4^+/\text{NH}_3$ and NO_2^- by anion radicals. Adsorption experiments were also conducted to measure the extent of adsorption of the different anions to the TiO_2 surface.

2. Materials and methods

2.1. Chemicals

Degussa TiO_2 P 25 (Akron, OH) was used without purification unless specifically mentioned. This catalyst had a BET surface area of $50 \pm 15 \text{ m}^2/\text{g}$ and an average primary particle size of 21 nm [33]. According to personal communication with the Degussa Corporation, the estimated BET surface area for a specific batch of TiO_2 should be much narrower than this reported range. Nanopure water (18.1 M Ω cm) from an InfinityTM ultra-pure water system (model D8961, Barnstead; Dubuque, IA) was used to prepare solutions in this study. The chemicals NaNO_2 , NaNO_3 (Sigma–Aldrich; Milwaukee, WI), NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$ (Alfa Aesar, Ward Hill, MA), $(\text{NH}_4)_2\text{CO}_3$, and $(\text{NH}_4)_2\text{HPO}_4$ (Fisher Scientific, Fairlawn, NJ) were used as NO_2^- , NO_3^- , and $\text{NH}_4^+/\text{NH}_3$ sources. Sodium salts [Na_2SO_4 , NaCl (Alfa Aesar), $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ (Aldrich), and $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ (Fisher Scientific)] were used as inorganic anion sources. Thirty per-

cent H_2O_2 (Fisher Scientific) was used for the homogeneous photochemical oxidation of $\text{NH}_4^+/\text{NH}_3$ and NO_2^- .

2.2. Photocatalytic oxidation experiments

The photochemical reactor (model 7840-185, Ace Glass, Vineland, NJ) consisted of three major components: a cylindrical Pyrex glass reactor, a double-walled quartz cooling water jacket, and a 450 W medium pressure Hg lamp. The cooling water jacket was inserted into the reactor, and the UV lamp was then placed inside the quartz cooling jacket. More details about the experimental apparatus have been reported in Ref. [6]. Our previous study showed that when 3 g/L TiO_2 was used there was no significant homogeneous photochemical reaction of $\text{NH}_4^+/\text{NH}_3$, because the high concentration of TiO_2 blocked UV transmittance to the interior portions of the reactor [6]. Therefore, to accurately evaluate photocatalytic oxidation of $\text{NH}_4^+/\text{NH}_3$ and NO_2^- in the presence of inorganic anions, 3 g/L TiO_2 was used in this study, except for homogeneous photochemical reactions where H_2O_2 and not TiO_2 was used as the $\bullet\text{OH}$ source. The reaction solution was stirred with a magnetic stirrer to maintain a homogeneous TiO_2 suspension. Samples were taken during kinetic studies and filtered through 0.1 μm filter membranes, and the filtrates were used for measurement of pH, $\text{NH}_4^+/\text{NH}_3$, NO_2^- , and NO_3^- .

2.3. Adsorption experiments

Since the commercial Degussa TiO_2 P 25 contains $\leq 0.3\%$ Cl^- by weight [33] and we measured 0.95 mg dissolved Cl^-/g TiO_2 as an impurity, the TiO_2 was washed with nanopure water until the aqueous concentration of Cl^- was lower than the detection limit of the ion chromatograph (1×10^{-6} M). No significant difference in the initial rate of NO_2^- photocatalytic oxidation at pH ~ 10 in the presence of 1×10^{-3} M Na_2SO_4 between the washed and unwashed TiO_2 was observed. In addition, the extent of adsorption to the washed and unwashed TiO_2 was the same when $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and SO_4^{2-} were used as the adsorbates. These experiments show that neither the Cl^- impurity nor the washing treatment affected the TiO_2 reactivity or adsorption behavior.

Sodium perchlorate (NaClO_4 , 0.01 M) was used as an inert electrolyte for adsorption experiments to maintain a constant ionic strength. To obtain a range of anion adsorption densities on the TiO_2 (3 g/L) surface over the pH range of 3–11, 2×10^{-4} M was chosen as the initial concentration of Na_2SO_4 , NaH_2PO_4 , or NaCl . Adsorption of $\text{HCO}_3^-/\text{CO}_3^{2-}$ to the TiO_2 surface in acidic solutions was not measured because HCO_3^- would be protonated to form dissolved CO_2 and carbonic acid under these conditions. Adsorption of $\text{HCO}_3^-/\text{CO}_3^{2-}$ to the TiO_2 surface also was not measured in alkaline solutions due to interference by desorption of CO_2 from the Degussa TiO_2 P 25, as determined by a Shimadzu Total Organic Carbon Analyzer (TOC 5050A/ASI 5000A). At neutral pH, however, no significant adsorption of HCO_3^- was observed by measuring the inorganic carbon in the equilibrated aqueous solution using the TOC 5050A/ASI 5000A, and adsorption would likely be

even lower in alkaline solutions, due to the increased negative charge of the TiO₂ surface at higher pH values.

The suspensions were adjusted to the target pH values using 1 M HClO₄ or NaOH and shaken for 24 h in a constant temperature chamber (Sheldon Manufacturing, Model 2020, Cornelius, OR) at 25 °C. The equilibrated suspensions were then filtered through the 0.1 μm membranes, and the filtrates were used for measurement of Cl⁻, SO₄²⁻, H₂PO₄⁻/HPO₄²⁻, and HCO₃⁻. The percent adsorbed for each anion was calculated by dividing the adsorbed concentration of the anion by its total concentration.

2.4. Analytical methods

The concentrations of NO₂⁻, NO₃⁻, Cl⁻, SO₄²⁻, and H₂PO₄⁻/HPO₄²⁻ were determined using a Dionex ion chromatograph with an Ion Pac[®] AG 11 guard column (4 mm × 50 mm), an Ion Pac[®] AS 11 anion analytical column (4 mm × 250 mm), and an ED 50 conductivity detector, as described in Ref. [6]. An ammonia gas-sensing electrode (model 95-12, Thermo Orion; Beverly, MA) was used to determine the concentration of NH₄⁺/NH₃, and the measurement procedure is also reported in Ref. [6]. A pH electrode (91-56, Thermo Orion) was used for pH measurement.

Five-point external standard calibration curves were used to calculate the concentrations of NH₄⁺/NH₃, NO₂⁻, NO₃⁻, Cl⁻, HCO₃⁻, SO₄²⁻, and H₂PO₄⁻/HPO₄²⁻. The standard solutions were prepared daily, and analysis of the standards was repeated every 20 samples. To minimize the potentially confounding effect of variable pH during the reaction, the initial rate was calculated from the best linear fit of NH₄⁺/NH₃ or NO₂⁻ concentration versus time for the time period where both the pH and slope were nearly constant, and the error bars in Figs. 1 and 4 are 95% confidence intervals of the initial rates.

3. Results and discussion

3.1. NH₄⁺/NH₃ photocatalytic oxidation

To examine the effects of inorganic anions on NH₄⁺/NH₃ photocatalytic oxidation, we chose pH values of ~9 (8.7–9.1) and ~10 (10.1–10.3), because the photocatalytic oxidation of NH₄⁺/NH₃ is very slow or negligible at pH values lower than 9 [3–6]. In addition, pH ~11 (11.0–11.1) was chosen to separate the effects of HCO₃⁻ and CO₃²⁻ on NH₄⁺/NH₃ photocatalytic oxidation, because the speciation of HCO₃⁻/CO₃²⁻ is pH dependent with a pK_a value of 10.3 for HCO₃⁻ [34]. For comparison, three control experiments (where no anions were added) were also conducted at pH ~9, ~10, and ~11. Fig. 1 illustrates the initial rates of NH₄⁺/NH₃ photocatalytic oxidation in the presence of inorganic anions, as well as the control experiments, at these pH values.

When no anions were added, the initial rate of NH₄⁺/NH₃ photocatalytic oxidation was approximately 50% higher at pH ~10 compared to pH ~9, and the same trend was observed in the presence of Cl⁻ and SO₄²⁻ (Fig. 1). This increase in rates with pH is consistent with the fact that at pH ~10 versus ~9

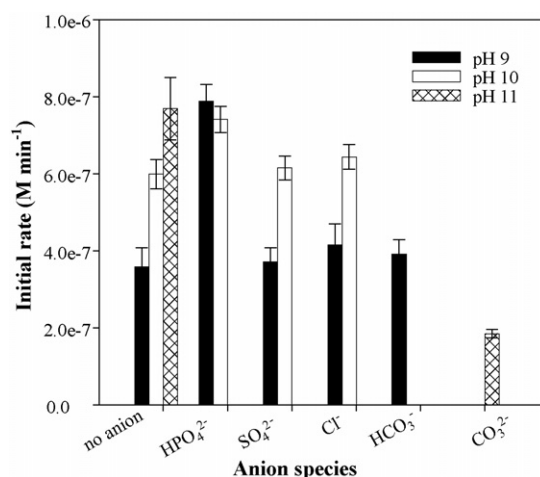


Fig. 1. Effect of inorganic anions on NH₄⁺/NH₃ photocatalytic oxidation at pH ~9 and ~10 (pH ~11 for CO₃²⁻). [NH₄⁺/NH₃]: (9.6 ± 0.6) × 10⁻⁵ M; [anion]: 1 × 10⁻³ M; [TiO₂]: 3 g/L; error bars are 95% confidence intervals.

a greater fraction of NH₄⁺/NH₃ is in the form of neutral NH₃, which is more reactive with electrophilic •OH than is NH₄⁺ [35]. Compared to the control experiments, SO₄²⁻, Cl⁻, and HCO₃⁻ yielded similar rates of NH₄⁺/NH₃ photocatalytic oxidation at a given pH, while HPO₄²⁻ yielded a higher rate, and CO₃²⁻ yielded a lower rate (Fig. 1). We first postulated that these differences were due to either (i) different rates of •OH scavenging by Cl⁻, SO₄²⁻, HPO₄²⁻, HCO₃⁻/CO₃²⁻ [36] and/or (ii) different rates of direct oxidation of NH₄⁺/NH₃ by the corresponding anion radicals, with the fastest rate of direct oxidation by HPO₄^{•-}.

3.1.1. Role of •OH scavenging by anions and/or direct oxidation by anion radicals

To determine whether •OH scavenging and/or direct oxidation by anion radicals were responsible for rate differences between the different anions, we performed NH₄⁺/NH₃ oxidation experiments with UV-illuminated H₂O₂ (UV/H₂O₂) in the presence of Cl⁻, SO₄²⁻, HPO₄²⁻, and HCO₃⁻/CO₃²⁻ at pH ~10, and CO₃²⁻ at pH ~11. In this system, H₂O₂ generates •OH under UV irradiation [32], which can be scavenged by anions in the solution to form the corresponding anion radicals (e.g., reaction (1)). A Vycor filter (ACE glass) was used to block wavelengths lower than 220 nm to prevent possible reactions of aqueous NH₃ with oxidants other than •OH, including ozone generated from photodissociation of O₂ [37]. The results of these experiments are shown in Fig. 2.

There was no significant NH₄⁺/NH₃ oxidation in the presence of either HCO₃⁻/CO₃²⁻ (pH ~10) or CO₃²⁻ (pH ~11), but significant oxidation in the presence of Cl⁻, SO₄²⁻, and HPO₄²⁻ (Fig. 2), which is evidence that CO₃²⁻ is a better •OH scavenger than Cl⁻, SO₄²⁻, or HPO₄²⁻. In the presence of CO₃²⁻ at pH ~11, the initial rate of the TiO₂-based NH₄⁺/NH₃ photocatalytic oxidation was about one third the rate when Cl⁻, SO₄²⁻, or HPO₄²⁻ was present at pH ~10 (Fig. 1), which is additional evidence of efficient •OH scavenging by CO₃²⁻ under these conditions. Since approximately 50% of HCO₃⁻/CO₃²⁻

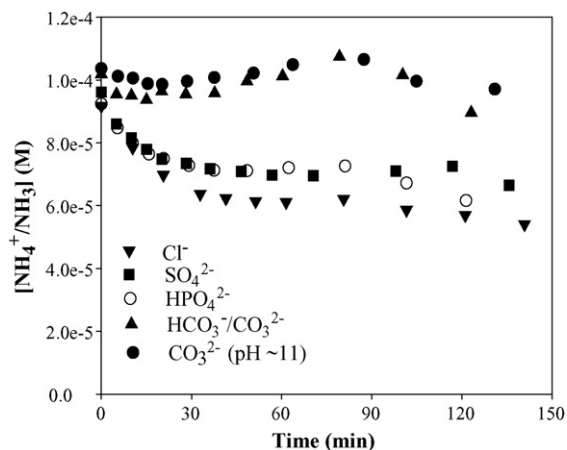


Fig. 2. Effect of inorganic anions on the homogeneous photochemical oxidation of $\text{NH}_4^+/\text{NH}_3$ by $\text{UV}/\text{H}_2\text{O}_2$ with a Vycor filter at $\text{pH} \sim 10$, except for the data series labeled CO_3^{2-} , which was done at $\text{pH} \sim 11$. $[\text{NH}_4^+/\text{NH}_3]$: $(9.6 \pm 0.6) \times 10^{-5}$ M; $[\text{H}_2\text{O}_2] = 0.001$ M; [anion]: 0.005 M.

is in the form of CO_3^{2-} at $\text{pH} \sim 10$, our experiments do not provide information on the relative $\bullet\text{OH}$ scavenging efficiency of CO_3^{2-} versus HCO_3^- . However, Buxton et al. [36] reported that CO_3^{2-} scavenges $\bullet\text{OH}$ more rapidly than HCO_3^- with second order rate constants of $3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for CO_3^{2-} and $8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for HCO_3^- . This can explain why we observed a smaller initial rate of $\text{NH}_4^+/\text{NH}_3$ photocatalytic oxidation at $\text{pH} \sim 11$ (when CO_3^{2-} was the predominant species) than at $\text{pH} \sim 9$ (when HCO_3^- was the predominant species) (Fig. 1). As a practical matter, these results suggest that carbonate alkalinity can strongly affect the rates of $\text{NH}_4^+/\text{NH}_3$ photocatalytic oxidation at pH values where significant CO_3^{2-} is present.

Fig. 2 also shows that there was no significant difference in initial rates of $\text{NH}_4^+/\text{NH}_3$ oxidation by $\text{UV}/\text{H}_2\text{O}_2$ in the presence of Cl^- , SO_4^{2-} , or HPO_4^{2-} , unlike the results from TiO_2 -based $\text{NH}_4^+/\text{NH}_3$ photocatalytic oxidation (Fig. 1), where HPO_4^{2-} led to faster rates than the other anions. This suggests that, unlike CO_3^{2-} and possibly HCO_3^- , $\bullet\text{OH}$ scavenging by Cl^- , SO_4^{2-} , or HPO_4^{2-} or direct oxidation of $\text{NH}_4^+/\text{NH}_3$ by the corresponding anion radicals do not influence reaction rates in the TiO_2 photocatalytic system. If these processes did control reaction rates in the UV/TiO_2 system, we would expect the same trends in reactivity in both the UV/TiO_2 and the $\text{UV}/\text{H}_2\text{O}_2$ systems, which we did not observe. Based on this, we next examined whether adsorption of anions to the TiO_2 surface was responsible for the differences in TiO_2 photocatalytic oxidation rates when HPO_4^- versus SO_4^{2-} , Cl^- , or HCO_3^- was present (Fig. 1).

3.1.2. Role of anion adsorption

The adsorption of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$, SO_4^{2-} , and Cl^- to the TiO_2 surface over the pH range of 3–11 is shown in Fig. 3. There was significant adsorption of HPO_4^{2-} , but no significant adsorption of Cl^- and SO_4^{2-} , at $\text{pH} \sim 9$ and ~ 10 . Based on this, as well as the greater rate of $\text{NH}_4^+/\text{NH}_3$ photocatalytic oxidation in the presence of HPO_4^{2-} versus Cl^- , SO_4^{2-} , and HCO_3^- (Fig. 1), we concluded that adsorption of HPO_4^{2-} actually enhanced the

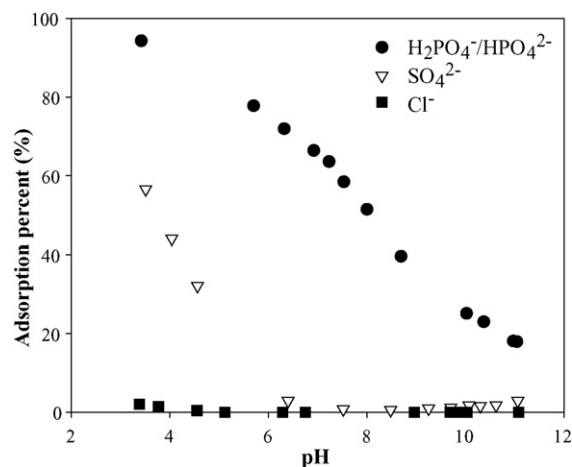


Fig. 3. Adsorption of chloride (Cl^-), sulfate (SO_4^{2-}) and phosphate ($\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$). [Anion]: 2×10^{-4} M; $[\text{NaClO}_4]$: 0.01 M; $[\text{TiO}_2]$: 3 g/L; adsorption equilibrium time: 24 h.

initial rate of $\text{NH}_4^+/\text{NH}_3$ photocatalytic oxidation. This may be because adsorption of HPO_4^{2-} increased the negative charge of the TiO_2 surface [38], leading to neutralization of NH_4^+ to NH_3 near the TiO_2 surface. This would result in a greater initial rate of $\text{NH}_4^+/\text{NH}_3$ photocatalytic oxidation, because NH_3 reacts more rapidly with $\bullet\text{OH}$ than does NH_4^+ [35].

3.2. NO_2^- photocatalytic oxidation

Since NO_2^- is an important intermediate in the photocatalytic oxidation of $\text{NH}_4^+/\text{NH}_3$ [3–7], we also studied how inorganic anions affected NO_2^- photocatalytic oxidation. For these experiments, we chose a broad pH range of 4–11 since the different phenomena that could affect reaction rates, such as adsorption, would likely vary significantly over this pH range. Note that we did not study NO_2^- photocatalytic oxidation in the presence of HCO_3^- at acidic pH (< 7.5), because HCO_3^- would be protonated to form dissolved CO_2 and carbonic acid under these conditions. The initial rate of NO_2^- photocatalytic oxidation was also measured when no anions were added (control experiment). Fig. 4 shows the initial rates of NO_2^- photocatalytic oxidation in the presence of the anions, as well as the control experiment.

A comparison of Figs. 1 and 4 shows that NO_2^- photocatalytic oxidation occurs much faster than $\text{NH}_4^+/\text{NH}_3$ photocatalytic oxidation in the presence of common wastewater anions at $\text{pH} \sim 9$ and ~ 10 (the pH values below which no significant photocatalytic oxidation of $\text{NH}_4^+/\text{NH}_3$ is observed). Thus, photocatalytic oxidation of $\text{NH}_4^+/\text{NH}_3$ to NO_2^- is the rate-limiting step in the complete oxidation of $\text{NH}_4^+/\text{NH}_3$ to NO_3^- in the presence of these anions.

In alkaline solutions ($\text{pH} > 7.5$), the initial rates of NO_2^- photocatalytic oxidation decreased with increasing pH in the presence of all anions (Fig. 4). This decrease in rate may be explained by decreasing adsorption of NO_2^- to the TiO_2 surface with increasing pH due to electrostatic repulsion [6] and/or the involvement of one or more acid-conjugate base pairs of possible intermediates, such as HOONO/OONO or

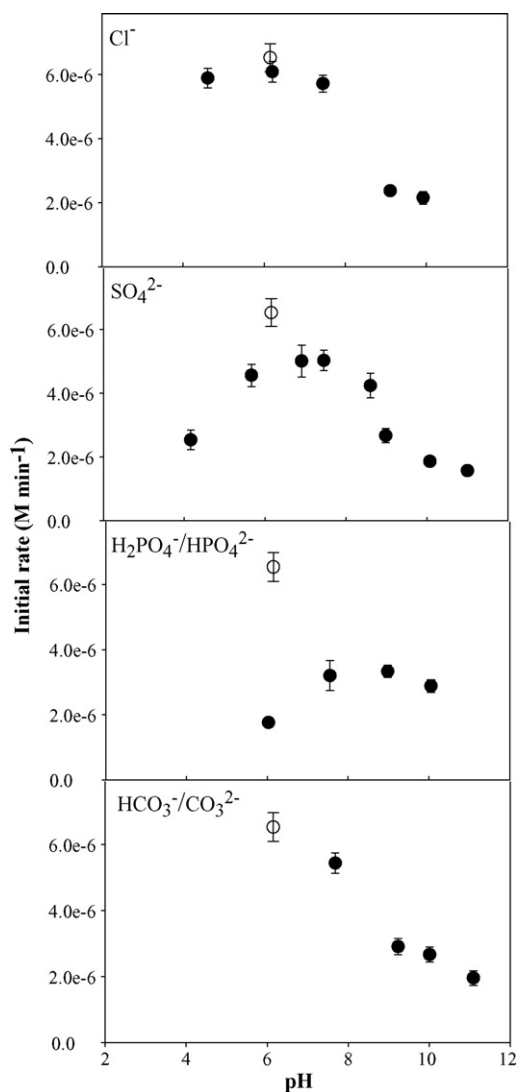


Fig. 4. Effect of inorganic anions on NO_2^- photocatalytic oxidation over the pH range of 4–11. $[\text{NO}_2^-]$: $(1.9 \pm 0.1) \times 10^{-4}$ M; [anion]: 1×10^{-3} M; $[\text{TiO}_2]$: 3 g/L; error bars are 95% confidence intervals. Some data for the SO_4^{2-} panel were previously reported in Ref. [6]. Open circles represent the initial rate of NO_2^- photocatalytic oxidation at pH ~ 6 when no anions were added.

$\text{HOONO}_2^-/\text{OONO}_2^-$, in which the conjugate base acts as a $\bullet\text{OH}$ radical scavenger or otherwise slows the oxidation of NO_2^- to NO_3^- [6]. Both phenomena could explain the uniform trend of decreasing reaction rates with increasing pH in this pH region.

Compared to the control experiment, SO_4^{2-} and H_2PO_4^- , but not Cl^- , inhibited NO_2^- photocatalytic oxidation at pH ~ 6 . In addition, at low to neutral pH in the presence of SO_4^{2-} and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$, the initial rate of NO_2^- photocatalytic oxidation increased with increasing pH to a maximum at pH ~ 7.5 (Fig. 4). However, nearly constant initial rates were observed for Cl^- in this pH range. All these phenomena are possibly due to different adsorption densities of the anions to the TiO_2 surface. Next we correlated the initial rates of NO_2^- photocatalytic oxidation with adsorption densities of anions at low to neutral pH values.

3.2.1. Role of anion adsorption

The negligible adsorption of Cl^- to the TiO_2 surface at low to neutral pH (Fig. 3) is likely responsible for the nearly constant initial rates for Cl^- in this pH region (i.e., no rate increase with increasing pH). The decrease in adsorption densities of SO_4^{2-} and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ on the TiO_2 surface with increasing pH up to pH ~ 7.5 , as shown in Fig. 3, can explain the increasing initial rates in the presence of these anions. At low to neutral pH values, greater adsorption of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ to the TiO_2 surface (Fig. 3) decreased the rate of NO_2^- photocatalytic oxidation more than the other anions, for which adsorption was less significant. This is because greater adsorption of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ would result in competition with NO_2^- for adsorption sites, slowing the NO_2^- oxidation rate. The different kinetic behavior for NO_2^- and $\text{NH}_4^+/\text{NH}_3$ photocatalytic oxidation in the presence of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ (i.e., increased reaction rates for $\text{NH}_4^+/\text{NH}_3$ photocatalytic oxidation and decreased reaction rates for NO_2^- photocatalytic oxidation) may be due in part to the fact that rates of NO_2^- photocatalytic oxidation are more surface-area-dependent than rates of $\text{NH}_4^+/\text{NH}_3$ photocatalytic oxidation [6], perhaps due to a closer association of NO_2^- with the TiO_2 surface.

Consistent with these observations, Fig. 4 also illustrates that for any given pH value lower than 7.5, initial rates of NO_2^- photocatalytic oxidation increased in the order $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-} < \text{SO}_4^{2-} < \text{Cl}^-$, which correlates with decreasing extent of adsorption to the TiO_2 surface ($\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-} > \text{SO}_4^{2-} > \text{Cl}^-$) (Fig. 3). Additional evidence that anion adsorption inhibits NO_2^- photocatalytic oxidation below neutral pH comes from experiments at pH ~ 6 in which the concentration of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ was varied. When the concentration of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ was decreased from 1×10^{-3} to 1×10^{-4} M, the initial rate increased from $(1.76 \pm 0.1) \times 10^{-6}$ to $(4.98 \pm 0.27) \times 10^{-6}$ M min^{-1} . Interestingly, despite significant adsorption of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ to the TiO_2 surface over a range of pH values, NO_2^- photocatalytic oxidation was never completely inhibited, which has practical application for treatment of high $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ wastewaters.

4. Conclusions

In this study, we systematically investigated $\text{NH}_4^+/\text{NH}_3$ and NO_2^- photocatalytic oxidation in the presence of common inorganic anions in a bench scale reactor. Neither hydroxyl radical scavenging by Cl^- , SO_4^{2-} , or HPO_4^{2-} , nor direct oxidation by the corresponding anion radicals, was significant in TiO_2 photocatalytic oxidation of $\text{NH}_4^+/\text{NH}_3$, but CO_3^{2-} significantly inhibited $\text{NH}_4^+/\text{NH}_3$ oxidation due to its efficient $\bullet\text{OH}$ scavenging. The presence of Cl^- , SO_4^{2-} , or HCO_3^- did not inhibit photocatalytic oxidation since there was negligible adsorption of these species at the pH values at which $\text{NH}_4^+/\text{NH}_3$ oxidation occurs (>9). Adsorption of HPO_4^{2-} resulted in enhanced $\text{NH}_4^+/\text{NH}_3$ photocatalytic oxidation.

At pH values lower than ~ 7.5 , Cl^- had no effect on the initial rates of NO_2^- photocatalytic oxidation, while SO_4^{2-} and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ slowed NO_2^- oxidation due to adsorption to the TiO_2 surface. At pH greater than ~ 7.5 , the initial rates of

NO_2^- photocatalytic oxidation were similar and independent of the anion present. $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ did not dramatically hinder NO_2^- photocatalytic oxidation, despite the fact that there was significant adsorption of HPO_4^{2-} in this pH region.

Our results indicate that photocatalytic oxidation of $\text{NH}_4^+/\text{NH}_3$ to NO_2^- is the rate-limiting step in the complete oxidation of $\text{NH}_4^+/\text{NH}_3$ to NO_3^- in the presence of common wastewater anions. Therefore, conditions such as alkaline pH should be chosen to maximize the $\text{NH}_4^+/\text{NH}_3$ oxidation rate, and not the NO_2^- oxidation rate, in treatment processes designed to remove $\text{NH}_4^+/\text{NH}_3$ from water and wastewater. In addition, pretreatment to lower carbonate alkalinity is likely needed for wastewater with high carbonate alkalinity prior to $\text{NH}_4^+/\text{NH}_3$ removal by TiO_2 photocatalytic oxidation at pH values above ~ 9 . Typical wastewater concentrations of Cl^- , SO_4^{2-} , and HPO_4^{2-} should not adversely affect $\text{NH}_4^+/\text{NH}_3$ removal by TiO_2 photocatalytic oxidation.

Acknowledgements

The authors thank the National Aeronautics and Space Administration (NCC 5-586) and the Oklahoma State Regents for Higher Education for financial support. We thank the anonymous reviewers for helpful comments on this manuscript.

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