



Rapid Ti(III) reduction of perchlorate in the presence of β -alanine: Kinetics, pH effect, complex formation, and β -alanine effect

Chao Wang^{a,1}, Zhengdao Huang^b, Lee Lippincott^c, Xiaoguang Meng^{a,*}

^a Center for Environmental Systems, Stevens Institute of Technology, Hoboken, NJ 07030, USA

^b Xiamen Water Group Co., Ltd., 24th Floor, Water Building, No. 157, Lianqian West Road, Xiamen, Fujian 361000, China

^c New Jersey Department of Environmental Protection, P.O. Box 409, Trenton, NJ 08625, USA

ARTICLE INFO

Article history:

Received 16 June 2009

Received in revised form

23 September 2009

Accepted 25 September 2009

Available online 2 October 2009

Keywords:

Perchlorate

Ti(III)

β -Alanine

Complexation

ABSTRACT

Ti(III) reduction of perchlorate might be a useful method for the treatment of highly perchlorate-contaminated water. Though the reaction rate was usually low, we observed that β -alanine ($\text{HOOCCH}_2\text{CH}_2\text{NH}_2$) could significantly promote the reaction. A complete (>99.9%) perchlorate removal was obtained in a solution containing $[\text{ClO}_4^-] = 1.0 \text{ mM}$, $[\text{Ti(III)}] = 40 \text{ mM}$, and $[\beta\text{-alanine}] = 120 \text{ mM}$ after 2.5 h of reaction under 50°C . The effects of both pH and complex formation on the reaction were then studied. The results showed that without β -alanine the optimal pH was 2.3. When pH increased from 1.6 to 2.3, the reduction rate increased remarkably. In the pH range >2.3, however, the reduction was significantly inhibited, attributed to the formation of Ti(III) precipitate. The presence of β -alanine at a molar ratio of $[\beta\text{-alanine}]:[\text{Ti(III)}] = 3:1$ significantly increased the reduction rate of perchlorate even at near neutral pH. This is because β -alanine formed complexes with Ti(III), which greatly improved the total soluble $[\text{Ti(III)}]$ in the pH range between 3.5 and 6. The findings may lead to the development of rapid treatment methods for intermittent and small stream of highly perchlorate-contaminated water, which are resulted from the manufacturing, storage, handling, use and/or disposal of large quantities of perchlorate salts.

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1. Introduction

Perchlorate has been widely and increasingly found in ground and surface water. It was estimated that the perchlorate-contaminated water is present in at least 37 US states [1]. The perchlorate-contaminated water falls into two categories (Table S1 in the Supplemental Material): (i) the water with low perchlorate levels ($\mu\text{g/L}$ range), and (ii) the water with high levels of perchlorate (mg/L range). The former is partially associated with migratory plume of highly perchlorate-contaminated water through geochemical processes [2]. The latter is the direct result of manufacturing, storage, handling, use and/or disposal of large quantities of perchlorate salts in at least 43 states in the US [3].

Proper disposal of perchlorate-contaminated water is important and necessary since perchlorate affects thyroid hormone function by inhibiting the uptake of iodide anion into the thyroid gland [4]. A variety of physicochemical technologies, such as anion exchange, activated carbon adsorption, reverse osmosis,

ultrafiltration, nanofiltration, and electrodialysis [5–13], have been developed for treating perchlorate-contaminated water. These techniques, however, are not economical for highly perchlorate-contaminated water treatment. Moreover, they cannot convert perchlorate into non-hazardous chloride. A subsequent procedure involving high-temperature (around 100°C or even higher) is usually required to chemically destruct the concentrated perchlorate [7,14–16]. Meanwhile, biological approaches for reducing perchlorate to chloride have been proven effective and economically attractive [17]. Nevertheless, because biological treatment systems can be especially sensitive to the incoming water chemistry (e.g., redox potential and carbon-limitation), require closer supervision, and cannot be operated intermittently [15,18], biological methods may not be the optimal options.

Development of chemical perchlorate reduction techniques is thus necessary. Previously, quite a few chemical reduction methods [14,15,18–26] have been reported. For example, Hurley and Shapley [15] developed a heterogeneous $\text{ReO}/\text{Pd}/\text{C}$ catalyst to promote the perchlorate reduction by H_2 under mildly acidic conditions and under room temperature. In this study, we investigated the approach of perchlorate reduction by Ti(III) since titanium is cheap and environmentally benign [27]. Alternatively, the method might be useful in some cases. Moreover, reports showed that perchlorate could be reduced to chloride [27–30]

* Corresponding author. Tel.: +1 201 216 8014; fax: +1 201 216 8303.

E-mail address: xmeng@stevens.edu (X. Meng).

¹ Present address: Department of Plant and Soil Sciences, University of Delaware, Newark, DE 19716, USA.

during the oxidation of Ti(III) to the Ti(IV) species or the TiO₂ precipitates [22]. Though the rate of Ti(III) reduction of perchlorate was usually low, two synthesized macrocyclic ligands, 6-amino-6-(4-aminobenzyl)-1,4,8,11-tetraazacyclotetradecane and 1,4,8,11-tetraazacyclotetradecane, could catalytically promote the Ti(III) reduction of perchlorate [31]. We therefore investigated some relatively simple and common ligands, which were expected to enhance the Ti(III) reduction of perchlorate. Our trial experimental results showed that β-alanine (HOOCCH₂CH₂NH₂) greatly improved the Ti(III) reduction of perchlorate among six tested ligands (Fig. S1 and Table S2 in the Supplemental Material). The purpose of this paper was thus to: (1) evaluate the kinetics of Ti(III) reduction of perchlorate in the presence and absence of β-alanine; (2) investigate the mechanism of enhanced perchlorate reduction that was caused by β-alanine, through the evaluation of pH effect, complex formation, and β-alanine effect.

2. Materials and methods

2.1. Chemicals

High purity DI (De-ionized) water with a resistivity of 18.2 MΩ cm was prepared using a Millipore filtering system. TiCl₃ (99.99% pure) powder and β-alanine (COOHCH₂CH₂NH₂) (>99% pure) were purchased from the Sigma–Aldrich. Trace metal grade 12 M concentrated HCl, and ACS grade solid NaClO₄·H₂O and NaOH were purchased from the Fisher Scientific. Argon gas (99.985% pure) and oxygen-free nitrogen were supplied by the AGL Welding Supply Company.

2.2. Solution preparation

DI water used was de-aerated by vigorously purging with oxygen-free nitrogen for >30 min. The 400 mM Ti(III) stock solution was prepared before use by dissolving the TiCl₃ powder with DI water in a Protector glove box (Labconco Corporation). The glove box was filled with about 101.3 kPa argon gas. The stock solutions of 10 mM ClO₄⁻, 0.5 M NaOH, and 4.0 M β-alanine were made by dissolving NaClO₄·H₂O, NaOH, and COOHCH₂CH₂NH₂ solids with DI water in the glove box, respectively. The 0.5 M HCl stock solution was prepared by diluting the 12 M HCl outside the glove box. It was then vigorously purged with oxygen-free nitrogen for >30 min, sealed, transferred, and stored in the glove box.

The test solution was prepared in the glove box at room temperature. It was made by quickly adding the calculated volumes of DI water and stock solution(s) into a 1.5–1.7 mL polypropylene microcentrifuge tube (Fisher Scientific) (please refer to Supplemental Table S3 for some examples). The tube was then capped with the locking lid and wrapped with Parafilm (Fisher Scientific). The test solution with a volume of 1.5 mL commonly contained 0–40 mM Ti(III) and 0–400 mM β-alanine with various initial pH values. It was prepared in the absence of perchlorate unless noted otherwise, and was used for the following experiments.

2.3. Batch kinetic experiments

The microcentrifuge tubes containing the desired test solutions (1.0 mM perchlorate present) were transferred to a preheated (50 ± 0.5 °C) oven without stirring. After every specific reaction time one tube was removed from the oven and was placed in an ice-water bath for about 1 min. The tube was then centrifuged for 3 min at a speed of 10,000 rpm (rotations per min) in an IEC/Micromax centrifuge (International Equipment Company). The 500 μL clear supernatant was sampled for the immediate measurement of residual ClO₄⁻ using a Dionex ion chromatography (IC) in a Model IC25.

The final pH of the reacted solutions was measured with a 920Aplus advanced ISE/pH/mV/ORP meter (Thermo Orion).

The above used Dionex IC25 was equipped with an EG40 eluent generator, a 1.0 mL sample loop, a set of 4 mm × 250 mm AS16 and AG16 columns, and a 4-mm ASRS Ultra II suppressor. The suppressor current used was 100 mA. The eluent concentration was set to 50 mM (KOH). The sample injection volume was in the range from 25 to 200 μL. To minimize matrix effects, standard solutions used for perchlorate analysis were prepared in solutions with similar chemical composition as in the samples. The detection limit for perchlorate analysis was 1 μM.

2.4. Ti(III) solubility measurement

Once the test solutions were prepared, the microcentrifuge tubes containing the solutions were rigorously shaken 10 times by hand. Before centrifugation they were placed at room temperature for 7 min. The tubes were then centrifuged for 3 min at a speed of 10,000 rpm. The 500 μL supernatant in each tube was withdrawn and properly diluted with acidified (0.1% HNO₃) DI water. The soluble Ti(III) concentration was measured with an Inductively Coupled Plasma-Optical Emission Spectrometer (Varian VISTA-MPX ICP-OES). The final pH of the solution was measured.

2.5. UV-visible spectrophotometric measurements

UV-visible spectrophotometric measurements were used to determine the formation of Ti(III) and β-alanine complexes. Briefly, the microcentrifuge tubes containing the desired test solutions were rigorously shaken by hand. The tubes were placed at room temperature for 10 min. The 1.5 mL solution in each tube was transferred to a 1.0 cm cuvette, for the spectrophotometric measurement using a Hewlett-Packard HP 8952A Diode-Array Spectrophotometer.

3. Results and discussion

3.1. Rapid perchlorate reduction kinetics in the presence of β-alanine

The kinetics of Ti(III) reduction of perchlorate in the presence and absence of β-alanine were tested. The kinetics of direct perchlorate reduction by β-alanine was also evaluated as a control experiment. The measured kinetic data were processed using linear regression according to Eq. (2), which is obtained from the pseudo-first-order equation (Eq. (1)) by integration. The obtained rate constant, *k*, was used to calculate the perchlorate reduction half-life, *t*_{1/2}, defined by Eq. (3). The final linear plots of ln([ClO₄⁻]/[ClO₄⁻]₀) vs *t* with the parameters of *k* and *t*_{1/2} are shown in Fig. 1. It should be noted that the zero subscripts throughout this paper denote initial concentrations.

$$\frac{d[\text{ClO}_4^-]}{dt} = -k[\text{ClO}_4^-] \quad (1)$$

$$\ln \frac{[\text{ClO}_4^-]}{[\text{ClO}_4^-]_0} = -kt \quad (2)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (3)$$

Fig. 1 shows that for the solution containing [ClO₄⁻] = 1.0 mM and [Ti(III)] = 40 mM, *k* was 0.16 h⁻¹ (*R*² = 0.98) and *t*_{1/2} = 4.33 h. When β-alanine coexisted with Ti(III) and perchlorate, the *k* value increased to 1.08 h⁻¹ (*R*² = 0.97) and the half-life for perchlorate reduction decreased to 0.64 h. This was a significant decrease of perchlorate half-life, approximately a factor of 7 decrease. It made the reaction sufficiently rapid to accomplish a complete

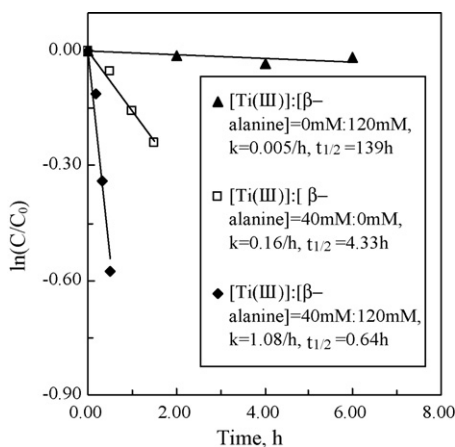


Fig. 1. Kinetics of perchlorate reduction in β -alanine, Ti(III), and the mixed systems under 50 °C, $[\text{ClO}_4^-]_0 = 1.0 \text{ mM}$.

perchlorate removal (>99.9%) after 2.5 h of reaction under 50 °C (data not shown). The temperature 50 °C was used here and throughout this study since under 32 °C and with $[\text{ClO}_4^-] = 1.0 \text{ mM}$, $[\text{Ti(III)}] = 40 \text{ mM}$, and $[\beta\text{-alanine}] = 120 \text{ mM}$, the reaction was not rapid sufficiently and a complete (99.9%) removal of perchlorate was not achieved after 24 h (data not shown).

Fig. 1 also shows that for the solution containing $[\text{ClO}_4^-] = 1.0 \text{ mM}$ and $[\beta\text{-alanine}] = 120 \text{ mM}$, k was 0.005 h^{-1} ($R^2 = 0.25$) and $t_{1/2} = 139 \text{ h}$. The high $t_{1/2}$ value suggests that the direct perchlorate reduction by β -alanine was a very slow process. Accordingly, the amount of perchlorate reduced by β -alanine was negligible during the experimental time period. The enhanced Ti(III) reduction of perchlorate caused by β -alanine could thus be attributed to two possible reasons. The first one was that the increase of pH from 1.7 to 2.8 caused by the addition of β -alanine possibly promoted the Ti(III) reduction of perchlorate. The second was that the complex formation between Ti(III) and β -alanine probably promoted the perchlorate reduction. These two hypotheses were investigated and are discussed in the subsequent sections.

3.2. pH effect on the Ti(III) reduction of perchlorate

The effect of pH on the kinetics of Ti(III) reduction of perchlorate was studied in a pH range from 1.6 to 6.2. The plots of $\ln([\text{ClO}_4^-]/[\text{ClO}_4^-]_0)$ vs t and $t_{1/2}$ against pH are shown in Fig. 2a and b, respectively. It should be noted that the pH in Fig. 2a and b were the final values. The change of pH in each process can be seen in Fig. S2 in the Supplemental Material.

Fig. 2a shows that the plots of $\ln([\text{ClO}_4^-]/[\text{ClO}_4^-]_0)$ vs t at various pH values were linear ($R^2 > 0.88$), indicating that the kinetics of perchlorate reduction was pseudo-first-order. Fig. 2b demonstrates that the $t_{1/2}$ values were significantly different at various pH values with a minimum at pH 2.3. In the pH range from 1.6 to 2.3, the $t_{1/2}$ value decreased from 4.44 to 0.37 h, decreasing by a factor of about 12. In the pH range from 2.3 to 6.2, the $t_{1/2}$ value increased from 0.37 to 4.00 h, an increase of about a factor of 11.

The climbing $t_{1/2}$ value with increasing pH from 2.3 to 6.2 indicates that the reaction was inhibited at higher pH. This was attributed to the dramatic formation of Ti(III) precipitation. When pH increased from 2.3 to 6.2, lots of black precipitate, which was probably Ti(OH)_3 (Pecsok and Fletcher [32]), was quickly formed. The quick formation of Ti(III) precipitation with the ascending pH resulted in a significant decrease in soluble $[\text{Ti(III)}]$, and the consequent inhibition of Ti(III) reduction of perchlorate.

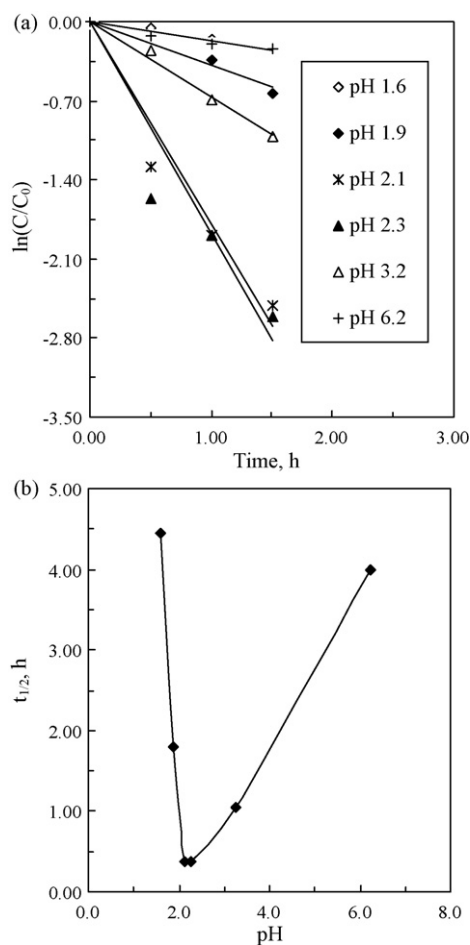
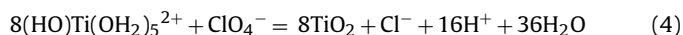


Fig. 2. pH effect on the kinetics of Ti(III) reduction of perchlorate, 50 °C, $[\text{ClO}_4^-]_0 = 1.0 \text{ mM}$, $[\text{Ti(III)}] = 40 \text{ mM}$, and $[\beta\text{-alanine}] = 0 \text{ mM}$. (a) Linear plot of $\ln([\text{ClO}_4^-]/[\text{ClO}_4^-]_0)$ vs t at various pHs. (b) Plot of $t_{1/2}$ against final pH.

The significantly decreasing $t_{1/2}$ value with increasing pH from 1.6 to 2.3 indicated that the rate of Ti(III) reduction of perchlorate increased with the rising pH (or $[\text{OH}^-]$). Such a positive dependence on $[\text{OH}^-]$ might be partially explained by the reaction pathway proposed as follows:



$(\text{HO})\text{Ti}(\text{OH}_2)_5^{2+}$ in Eq. (4) is the predominant Ti(III) species in a freshly prepared TiCl_3 solution [32]. The detection of an absorption peak at about 480 nm for the TiCl_3 solution proved the presence of $(\text{HO})\text{Ti}(\text{OH}_2)_5^{2+}$ species (Fig. S3a, Table 1). TiO_2 precipitate is

Table 1

Summary of the pronounced UV–visible absorption of the various Ti(III) complexation species.

Prominent Ti(III) complexes	Pronounced absorption wavelength (nm)	References
$[\text{Ti}(\text{OH}_2)_6]^{3+}$	500–504	[33–35]
$[(\text{HO})\text{Ti}(\text{OH}_2)_5]^{2+}$	480–485	[32,36]
$\text{TiO}(\text{TiOH})^{3+a}$	700	[32]
$\text{Ti}(\text{C}_2\text{O}_4)^+$	380	[37]
$\text{Ti}(\text{C}_2\text{O}_4)_2^-$	390	[33]
TiAc^{2+}	270	[38]
$\text{Ti}(\text{ClAc})^{2+}$	270	[38]
$\text{Ti}(\text{Cl}_2\text{Ac})^{2+}$	290	[38]
$\text{Ti(III)}(\text{Hedta})$	550	[39]
$\text{Ti(III)}(\text{-ethanol})$	400	[27]
$\text{Ti(III)}(\text{-}\beta\text{-alanine})$	370	This paper

^a Polynuclear Ti(III) species.

Table 2
Summary of $[H^+]$ effect on the kinetics of Ti(III) reduction of perchlorate.^a

Reactants	$[H^+]$ (M)	$[Ti(III)]$ (M)	$[ClO_4^-]$ (M)	μ^b (M)	T (°C)	$[H^+]$ dependence ^c	References
Ti(III), ClO_4^-	0.065–0.42	0.9×10^{-2}	Excess ^d	4.40	25	Positive	[31]
Ti(III), ClO_4^-	0.23–1.00	1.5×10^{-2}	0.5	2.00	40	Positive	[28]
Ti(III), ClO_4^-	0.10–0.60	$(0.5–1.0) \times 10^{-2}$	1.0	1.00	25	Positive	[29]
Ti(III), ClO_4^-	<0.006	4.0×10^{-2}	1.0×10^{-3}	<0.15	50	Positive	This study
Ti(III), ClO_4^-	0.006–0.025	4.0×10^{-2}	1.0×10^{-3}	<0.15	50	Negative	This study

^a Only the Ti(III) reduction of perchlorate in the absence of organic ligands is summarized in this table.

^b “ μ ” denotes the ionic strength.

^c “positive” means the reaction rate rose with the increasing $[H^+]$, “negative” represents that the rate decreased with the increasing $[H^+]$.

^d The exact concentration range is unknown.

the main oxidation product of Ti(III) [22] because lots of white precipitation was nearly always observed in the reacted solutions. The white precipitate might also be $Ti(OH)_4$, but in either case the reaction contributes to proton production. Cl^- is the main ultimate reduction product of perchlorate [27–30] since Ti(III) was in large excess (about 5-fold of perchlorate) in the solutions. However, Cl^- was not monitored in the present study. This is because the high initial $[Cl^-]$ (~ 120 mM), which was caused by the dissolution of 40 mM $TiCl_3$, masked the small change of $[Cl^-]$ (<1.0 mM). In addition, chlorate (ClO_3^-), chlorite (ClO_2^-), and hypochlorite (ClO^-) are three possible degradation intermediates. Their concentrations were not measured, either, because the high $[Cl^-]$ (~ 120 mM) in the reacted solutions significantly interfered with the IC analysis of these compounds. Nevertheless, they might be negligible since they have great reactivity and are readily reduced to Cl^- [14,16,18,26]. Overall, the reaction pathway in Eq. (4) predicts that protons are produced during the reactions. This prediction was consistent with the observed pH decrease in the experiments (Fig. S2 in the Supplemental Material). From a thermodynamic perspective and Eq. (4), high pH or $[OH^-]$ favors the reduction of perchlorate by soluble Ti(III).

The effect of pH on the kinetics of Ti(III) reduction of perchlorate has been studied in several papers. The literature results are summarized in Table 2. These results indicated that the reduction rate of perchlorate increased with increasing acidity in a $[H^+]$ range from 0.065 to 1.00 M, or correspondingly with decreasing pH from about 1.2 to 0. Therefore, it was generally considered that an acidic condition enhanced the Ti(III) reduction of perchlorate. The results in Fig. 2, however, show that in a higher pH range from 1.6 to 2.3 the effect of pH on Ti(III) reduction of perchlorate was different (Table 2).

3.3. Complex formation between Ti(III) and β -alanine

The effect of β -alanine on the solubility of Ti(III) is illustrated in Fig. 3a. At $pH < 2.3$ and without β -alanine, all Ti(III) was in a soluble form in a solution containing total $[Ti(III)] = 40$ mM. The amount of soluble Ti(III) decreased dramatically to less than 10% when the pH increased to 4.0. The addition of β -alanine obviously increased the Ti(III) solubility at the same pH. When the β -alanine concentration was 120 and 400 mM and the pH 4.0, the amount of soluble Ti(III) increased to about 73% and 98%, respectively. This behavior typically indicated the formation of soluble Ti(III) and β -alanine complexes.

The formation of Ti(III) and β -alanine complexes was further determined with spectrophotometric analysis. Various Ti(III) complexation species demonstrate different UV–visible absorption peaks as summarized in Table 1. In this study we observed that a new absorption peak at 370 nm appeared after β -alanine was added to the Ti(III) solutions (Fig. 3b). This absorption peak indicated the formation of Ti(III) and β -alanine complexes because β -alanine did not have a peak at such a position (data not shown). To be noted is that a broad absorption peak at about 700 nm was also

observed (Fig. 3b). It was attributed to the formation of a polynuclear titanium species, $TiOTiOH^{3+}$, with the increasing pH caused by the continuous addition of β -alanine (Fig. 3b, Table 1). Such a phenomenon of $TiOTiOH^{3+}$ formation with the increasing pH has been spectrophotometrically demonstrated at 700 nm by Pecsok and Fletcher [32]. The total $[Ti(III)]$ used in the spectrophotometric measurements was 5 mM. This is because, if high $[Ti(III)]$ was employed, the absorption spectrum at about 370 nm region was too strong and not smooth (Fig. S3b in the Supplemental Material). There was no peak at about 370 nm for the solution with $[Ti(III)]:[\beta\text{-alanine}] = 1:3$ (Fig. 3b). The reason is that the concentration of formed complexes was too low at $[Ti(III)] = 5$ mM. When $[Ti(III)]$

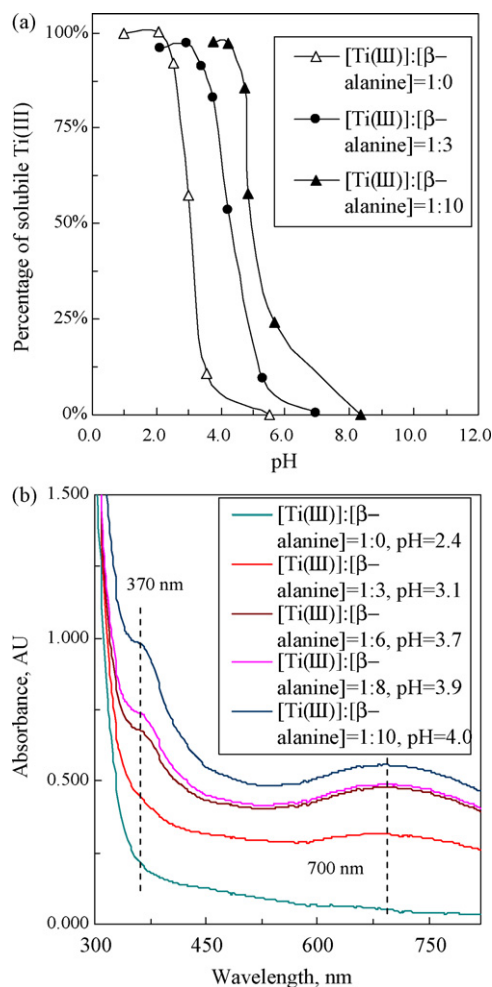


Fig. 3. Evidences of complex formation between Ti(III) and β -alanine, no perchlorate present. (a) Plot of soluble Ti(III) percent against pH under various $[Ti(III)]:[\beta\text{-alanine}]$ molar ratio, $[Ti(III)] = 40$ mM. (b) UV–visible spectra with various $[Ti(III)]:[\beta\text{-alanine}]$, the ratio decreased from 1:0 (bottom line) to 1:10 (top), $[Ti(III)] = 5$ mM.

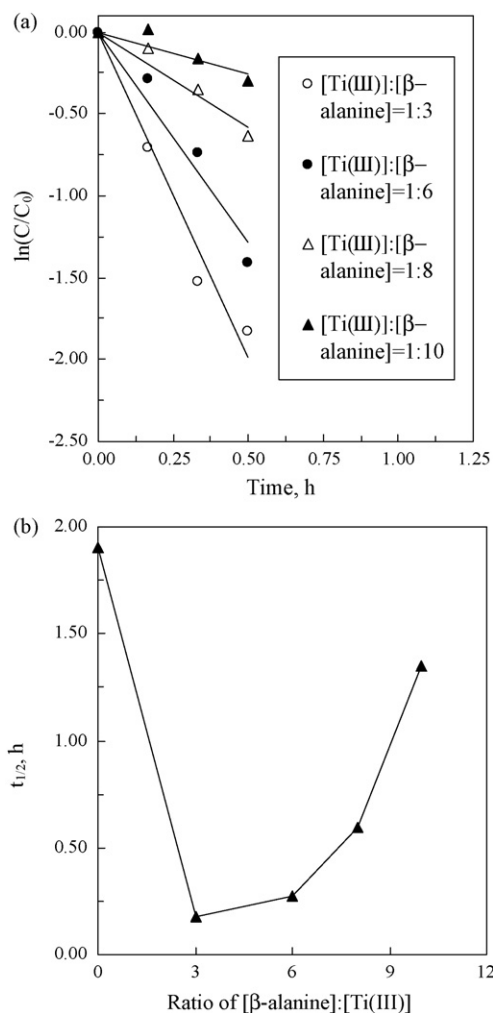


Fig. 4. β-Alanine effect on the Ti(III) reduction of perchlorate, pH 4.0, 50 °C, $[ClO_4^-]_0 = 1.0$ mM, and $[Ti(III)] = 40$ mM. (a) Linear plot of $\ln([ClO_4^-]/[ClO_4^-]_0)$ vs t under various $[Ti(III)]:[\beta\text{-alanine}]$. (b) Plot of $t_{1/2}$ against $[\beta\text{-alanine}]:[Ti(III)]$.

increased to 10 mM and at the same $[Ti(III)]:[\beta\text{-alanine}]$ ratio, the peak at 370 nm showed (Fig. S3b in the Supplemental Material).

The formation of Ti(III) and β-alanine complexes is quite rapid. The addition of 60 mM β-alanine to a solution containing 20 mM Ti(III) led to a sudden change in color from pink to green. When the reaction time increased from 5 to 60 min, the intensity of absorbance at 370 nm increased less than 8% for the solution with $[Ti(III)] = 5$ mM and $[\beta\text{-alanine}] = 30$ mM (data not shown). The results indicated that the majority of complexation was completed within 5 min. Chaudhuri and Diebler [40] studied the complexation kinetics between Ti(III) and other ligands, such as $CH_3CO_2^-$, $HC_2O_4^-$, and CH_3CO_2H . Their results also indicated rapid formation of the complexes.

3.4. β-Alanine effect on the Ti(III) reduction of perchlorate

The kinetics of Ti(III) reduction of perchlorate at different $[\beta\text{-alanine}]:[Ti(III)]$ ratios was studied at pH 4.0. Fig. 4a shows a linear correlation between $\ln([ClO_4^-]/[ClO_4^-]_0)$ and t ($R^2 > 0.94$ except $R^2 = 0.83$ at the ratio 10), indicating that the perchlorate reduction kinetics was still pseudo-first-order. Fig. 4b shows that the $t_{1/2}$ values were significantly different at various $[\beta\text{-alanine}]:[Ti(III)]$ ratios, with a minimum at the ratio around 3. The $t_{1/2}$ value decreased from 1.90 to 0.17 h with the rising $[\beta\text{-alanine}]:[Ti(III)]$ ratio from 0 to 3, by a factor of about 11. This was mainly because

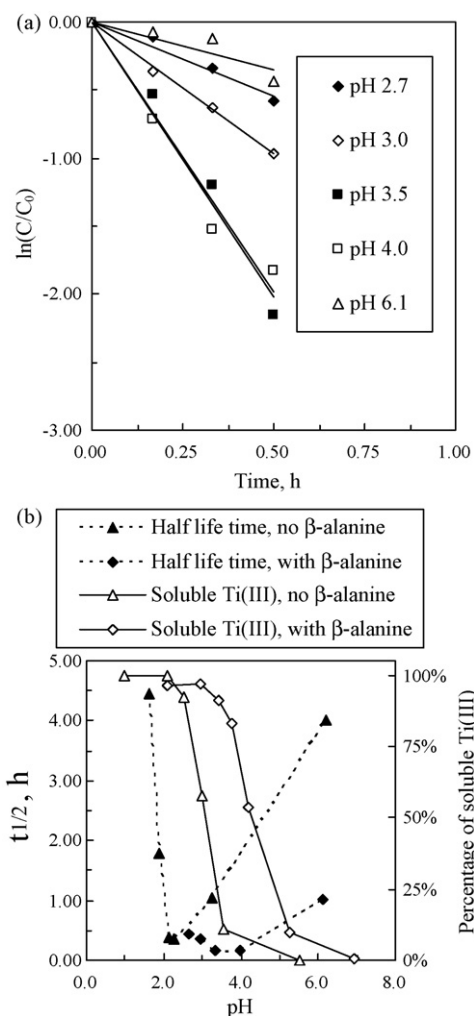


Fig. 5. Demonstration of β-alanine enhanced perchlorate reduction in the pH range from 2.7 to 6.1, 50 °C, $[ClO_4^-]_0 = 1.0$ mM, and $[Ti(III)] = 40$ mM. (a) Linear plot of $\ln([ClO_4^-]/[ClO_4^-]_0)$ vs t , $[Ti(III)]:[\beta\text{-alanine}] = 1:3$. (b) Plot of $t_{1/2}$ and Ti(III) solubility against the final pH in the presence ($[Ti(III)]:[\beta\text{-alanine}] = 1:3$) and absence ($[Ti(III)]:[\beta\text{-alanine}] = 1:0$) of β-alanine.

the presence of β-alanine increased the soluble $[Ti(III)]$ at pH 4.0 (Fig. 3a). By contrast, the $t_{1/2}$ value increased from 0.17 to 1.35 h with a further increase in $[\beta\text{-alanine}]:[Ti(III)]$ ratio from 3 to 10, suggesting that the perchlorate reduction kinetics was hindered at high ligand to Ti(III) ratios. Excessive addition of β-alanine is, therefore, not necessary and unfavorable. In this case, the optimal $[\beta\text{-alanine}]:[Ti(III)]$ ratio was about 3.

The kinetics of Ti(III) reduction of perchlorate in a broad pH range was thus studied at $[Ti(III)]:[\beta\text{-alanine}] = 1:3$. Fig. 5a shows the pseudo-first-order reduction kinetics in the pH range from 2.7 to 6.1 ($R^2 > 0.97$ except $R^2 = 0.80$ at pH 6.1). The corresponding $t_{1/2}$ values with $[\beta\text{-alanine}]:[Ti(III)] = 3$ and without β-alanine as well are presented in Fig. 5b. Fig. 5b demonstrates that the presence of β-alanine significantly improved the perchlorate reduction in a broad pH range from 2.7 to 6.1. This improvement was ascribed to the increased soluble $[Ti(III)]$ due to the presence of β-alanine (Fig. 5b). Note that the change of pH during the reactions can be seen in Fig. S2 and S4 in the Supplemental Material.

4. Conclusions

The kinetics of Ti(III) reduction of perchlorate in the presence and absence of β-alanine were studied. The pH effect, complex

formation, and β -alanine effect were thereafter investigated. A summary of conclusions is as follows:

- (1) β -Alanine ($\text{HOOCCH}_2\text{CH}_2\text{NH}_2$) could significantly enhance the Ti(III) reduction of perchlorate. A complete (99.9%) perchlorate removal could be achieved in a solution containing $[\text{ClO}_4^-] = 1.0 \text{ mM}$, $[\text{Ti(III)}] = 40 \text{ mM}$, and $[\beta\text{-alanine}] = 120 \text{ mM}$ after 2.5 h of reaction under 50°C .
- (2) The optimal pH for the Ti(III) reduction of perchlorate in the absence of β -alanine was 2.3. When pH increased from 1.6 to 2.3, the reduction rate increased remarkably. In the pH range >2.3 , however, the reduction was significantly inhibited, attributed to the formation of Ti(III) precipitate.
- (3) When β -alanine was added to the Ti(III) solutions, a sudden change in color from pink to green was observed. An increased Ti(III) solubility was generally demonstrated. A new UV absorptivity peak at 370 nm appeared. These observations typically indicated the formation of Ti(III) and β -alanine complexes.
- (4) At a molar ratio of $[\beta\text{-alanine}]:[\text{Ti(III)}] = 3:1$ the reduction rate of perchlorate by Ti(III) was significantly increased even at near neutral pH. This is because β -alanine formed complexes with Ti(III), which greatly improved the total soluble $[\text{Ti(III)}]$ in the pH range between 3.5 and 6.

The above findings may lead to the development of rapid treatment methods for intermittent and small stream of highly perchlorate-contaminated water (Table S1 in the Supplemental Material), which are resulted from the manufacturing, storage, handling, use and/or disposal of large quantities of perchlorate salts. Nevertheless, further laboratory and field tests are necessary to be performed for the evaluation of some important affecting factors such as the natural organic matter, nitrate, and sulfate.

Acknowledgments

This research was supported by the New Jersey Department of Environmental Protection. Thanks are expressed to Dr. Chuanyong Jing, Mengqiang Zhu, Julius Pavlov, Nan Xu, and Backbang Sun for their kind assistance.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.09.143.

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