

## Perchlorate removal in Fe<sup>0</sup>/H<sub>2</sub>O systems: Impact of oxygen availability and UV radiation

Jong-Kwon Im<sup>a</sup>, Hyun-Seok Son<sup>b</sup>, Kyung-Duk Zoh<sup>a,\*</sup>

<sup>a</sup> Department of Environmental Health, School of Public Health, Seoul National University, Seoul, Republic of Korea

<sup>b</sup> Department of Applied Chemistry, Konkuk University, Chungju, Republic of Korea

### ARTICLE INFO

#### Article history:

Received 26 August 2010

Received in revised form 9 May 2011

Accepted 10 May 2011

Available online 7 June 2011

#### Keywords:

Anoxic/oxic conditions

Co-precipitation

OH radical

Perchlorate

Zerovalent iron

### ABSTRACT

In this study, the removal of perchlorate (0.016 mM) using Fe<sup>0</sup>-only (325 mesh, 10 g L<sup>-1</sup>) and Fe<sup>0</sup> (10 g L<sup>-1</sup>) with UV (254 nm) reactions were investigated under oxic and anoxic conditions (nitrogen purging). Under anoxic conditions, only 2% and 5.6% of perchlorate was removed in Fe<sup>0</sup>-only and Fe<sup>0</sup>/UV reactions, respectively, in a 12 h period. However, under oxic conditions, perchlorate was removed completely in the Fe<sup>0</sup>-only reaction, and reduced by 40% in the Fe<sup>0</sup>/UV reaction, within 9 h. The pseudo-first-order rate constant ( $k_1$ ) was  $1.63 \times 10^{-3} \text{ h}^{-1}$  in Fe<sup>0</sup>-only and  $4.94 \times 10^{-3} \text{ h}^{-1}$  in Fe<sup>0</sup>/UV reaction under anoxic conditions. Under oxic conditions,  $k_1$  was  $776.9 \times 10^{-3} \text{ h}^{-1}$  in Fe<sup>0</sup>-only reaction and  $35.1 \times 10^{-3} \text{ h}^{-1}$  in the Fe<sup>0</sup>/UV reaction, respectively. The chlorine in perchlorate was recovered as chloride ion in Fe<sup>0</sup>-only and Fe<sup>0</sup>/UV reactions, but lower recovery of chloride under oxic conditions might due to the adsorption/co-precipitation of chloride ion with the iron oxides. The removal of perchlorate in Fe<sup>0</sup>/UV reaction under oxic conditions increased in the presence of methanol (73%, 9 h), a radical scavenger, indicating that OH radical can inhibit the removal of perchlorate. The removal of perchlorate by Fe<sup>0</sup>-only reaction under oxic condition was highest at neutral pH. Application of the Langmuir–Hinshelwood model indicated that removal of perchlorate was accelerated by adsorption/co-precipitation reactions onto iron oxides and subsequent removal of perchlorate during further oxidation of Fe<sup>0</sup>. The results imply that oxic conditions are essential for more efficient removal of perchlorate in Fe<sup>0</sup>/H<sub>2</sub>O system.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

Perchlorate (ClO<sub>4</sub><sup>-</sup>), which is derived primarily from military equipment such as weapons, explosives, and rocket fuel, is a toxic chemical and is considered recalcitrant due to its high stability and tendency to participate in thermodynamically favorable reactions in both natural groundwater and surface water [1]. It has also been detected in firework powder, roadside flares, airbag inflators, and fertilizers [2]. Recently, perchlorate has been found in lakes, surface water, groundwater, milk, urine, and blood [3–6] and is included on the US EPA contaminant candidate list (CCL) [7].

Ingestion of perchlorate leads to a decrease in thyroid hormone [8]. The U.S. Centers for Disease Control (CDC) reported that newborns, children, and pregnant women showed increased sensitivity to and adverse effects of perchlorate [9]. Recently, the U.S. EPA set the drinking water equivalent level (DWEL) of perchlorate at 4.5 μg L<sup>-1</sup> [10].

Because perchlorate is highly water-soluble, non-complexing, non-volatile, and chemically stable in the environment, removal of perchlorate using traditional water treatment methods is difficult

[2,11]. Sorption on activated carbon and ion exchange techniques has been applied to remove perchlorate from water [12,13]. However, application of these technologies is limited due to the slow sorption rate and generation of unwanted brine by-products [14,15].

Recently, a reduction process using zero-valent iron (ZVI, Fe<sup>0</sup>) was introduced to treat perchlorate under anoxic condition (purging N<sub>2</sub> or argon gas) [16]. However, removal of perchlorate in the presence of Fe<sup>0</sup> was very slow (only 66% degradation within 2 weeks, respectively) at pH 7 [16]. In order to enhance the removal rate of perchlorate, external energy source was needed; for example, complete degradation of perchlorate was reported within 60 min using Fe<sup>2+</sup> at 195 °C [17]. The degradation rate of perchlorate using Fe<sup>0</sup> has also been enhanced with increased reaction temperatures using microwaves [14,18,19]. These results imply that external energy can potentially facilitate the reaction of Fe<sup>0</sup> and perchlorate under anoxic condition, lowering the kinetic barrier for perchlorate reduction. However, providing such a high external energy source is too costly for treating perchlorate.

Adsorption onto and co-precipitation with iron corrosion products, possibly followed by reduction with dissolved or sorbed Fe<sup>2+</sup> was proposed as a fundamental contaminant removal mechanism in Fe<sup>0</sup>/H<sub>2</sub>O systems by Noubactep and co-workers [20–24]. This mechanism could explain the efficiency of Fe<sup>0</sup>/H<sub>2</sub>O systems

\* Corresponding author. Tel.: +82 2 880 2737; fax: +82 2 762 2888.

E-mail address: [zohkd@snu.ac.kr](mailto:zohkd@snu.ac.kr) (K.-D. Zoh).

for the removal of any aqueous species (ionic, neutral, organic and inorganic). The mechanism adsorption/co-precipitation in  $\text{Fe}^0/\text{H}_2\text{O}$  system can be described as follows;  $\text{Fe}(\text{II})$  species from  $\text{Fe}^0$  oxidation are released in the aqueous solution and are further oxidized to  $\text{Fe}(\text{III})$  species by dissolved  $\text{O}_2$ . The solubility of  $\text{Fe}(\text{III})$  hydroxides/oxides at  $\text{pH} > 4.5$  is very low; therefore, precipitates are formed. The most common  $\text{Fe}(\text{III})$  species in natural waters is hydrated  $\text{Fe}(\text{III})$  hydroxide oxide, which commonly positively charged [25]. The precipitates of  $\text{Fe}(\text{III})$  can electrostatically co-precipitate negatively charged anions such as perchlorate. The different perchlorate removal rate under anoxic and oxic conditions can be from the difference of corrosion rate of  $\text{Fe}^0$ , and the continuous generation rate of co-precipitation products of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  [21,22]. This mechanism implies that enhancing removal of perchlorate can be achieved by the formation of iron oxides in  $\text{Fe}^0/\text{H}_2\text{O}$  systems, and fast corrosion can be predicted under the presence of dissolved oxygen [26].

Therefore, in the present study, the effect of oxygen on the removal of perchlorate was investigated in both  $\text{Fe}^0$ -only and  $\text{Fe}^0/\text{UV}$  reactions. The effects of  $\text{pH}$  and initial concentration of perchlorate on the removal of perchlorate, and the effect of radical scavenger on in the  $\text{Fe}^0/\text{UV}$  reaction were also examined. Furthermore, adsorption phenomenon using Langmuir–Hinshelwood model was discussed. Finally, based on the results, the main removal mechanism of perchlorate in the aqueous solution was suggested.

## 2. Materials and methods

### 2.1. Materials

Sodium perchlorate ( $\text{NaClO}_4$ , ACS reagent, >98%) was purchased from Sigma–Aldrich. As reference materials for determining ionic by-products from perchlorate removal, sodium chlorate ( $\text{NaClO}_3$ , ACS reagent, 99%), sodium chlorite ( $\text{NaClO}_2$ , ACS reagent, 80%), sodium hypochlorite ( $\text{NaOCl}$ , available chlorine 10–13%), and sodium chloride ( $\text{NaCl}$ , >99%) were purchased from Sigma–Aldrich. Sodium hydroxide solution ( $\text{NaOH}$ , ACS reagent, 50%) was purchased from Mallinckrodt. Iron powder (ZVI) (325 mesh, 99%) was purchased from ACROS Organics. Hydrofluoric acid (ACS reagent, 64%) was purchased from Merck. A  $1000 \text{ mg L}^{-1}$  stock solution of perchlorate was prepared in deionized water ( $R = 18.2 \text{ M}\Omega \text{ cm}^{-1}$ , Milli-Q). All chemicals were used as received without further purification.

### 2.2. Pretreatment of ZVI with acid

To increase the removal efficiency of perchlorate in the presence of  $\text{Fe}^0$ , acid washing of  $\text{Fe}^0$  was performed [16,27,28]. To avoid interference in the quantification of chloride residue from perchlorate removal [16], iron ( $\text{Fe}^0$ ) particles were washed using 1 N hydrofluoric acid for 10 min ( $50 \text{ g Fe}^0:50 \text{ mL HF}$  solution) instead of washing with hydrochloric acid. The particles were rinsed 10 times with deaerated Milli-Q water ( $50 \text{ g Fe}^0:1000 \text{ mL water}$ ) for 1 h until the  $\text{pH}$  of the solution was neutral.

From ion chromatography analysis, no chloride or fluoride levels were detected from iron-rinsed water. The wet iron was then freeze-dried using a vacuum suction device for 24 h prior to use. The color (gray) of the treated  $\text{Fe}^0$  was the same before and after acid washing. After acid washing, the specific surface area of  $\text{Fe}^0$  increased from  $19.3$  to  $32.4 \text{ m}^2 \text{ g}^{-1}$ , as determined by BET analysis.

### 2.3. Reactor system

Fig. 1 illustrates the photoreactor system consisting of a UV (254 nm) lamp cover, agitator, and a reservoir. The intensity

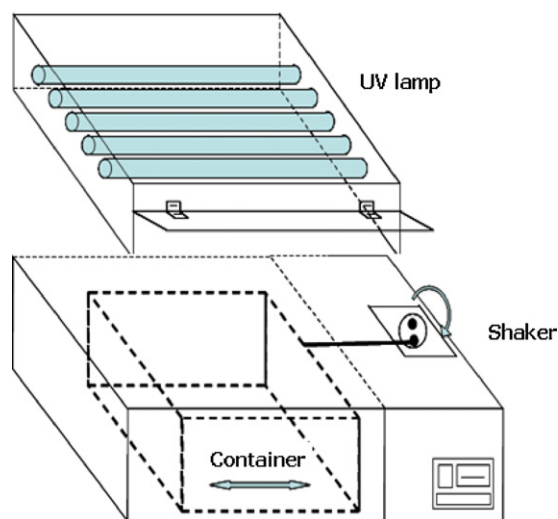


Fig. 1. Schematic of the photoreactor system consisting of a UV-C lamp cover, an agitator, and reservoir bath.

of one UV lamp measured using a VLX-3W radiometer (Cole-Parmer, USA) was  $3.4 \text{ mW cm}^{-2}$ . The UV intensity was controlled by adjusting the number of UVC lamps and the cover of the reactor system, which was designed to open and shut manually for sampling convenience. The reservoir (reactor) within the photoreactor system was shaken at 70 rpm to maximize the mixing between the solution and acid-washed  $\text{Fe}^0$ . To provide anoxic conditions, nitrogen purging during the overall reaction was conducted to make anoxic condition in both  $\text{Fe}^0$ -only and  $\text{Fe}^0/\text{UV}$  reactions.

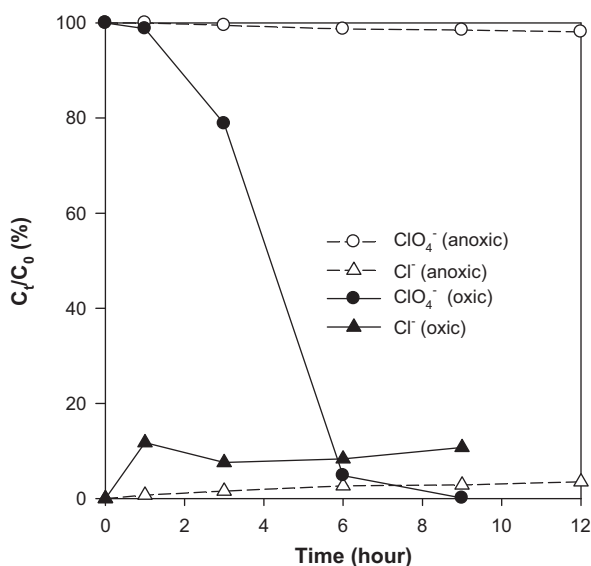
### 2.4. Analysis

After filtration of iron particles using a  $0.2 \mu\text{m}$  mixed cellulose ester (MCE) membrane filter and subsequent treatment with an OnGuard II H cartridge (Dionex) to remove dissolved iron species, perchlorate and ionic by-products such as chlorate ( $\text{ClO}_3^-$ ), chlorite ( $\text{ClO}_2^-$ ), and hypochlorite ( $\text{OCl}^-$ ), and chloride ( $\text{Cl}^-$ ) in the solution were analyzed using a Dionex DX-120 ion chromatography system with an AS-40 autosampler.

To measure perchlorate, a Dionex IonPac AG-16 column ( $4 \times 250 \text{ mm}$ ) and IonPac AS-16 guard column ( $4 \times 50 \text{ mm}$ ) were used. The injection volume was  $1000 \mu\text{L}$ , and the eluent was  $60 \text{ mM NaOH}$ .  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$ , and  $\text{OCl}^-$  were analyzed using an AS-9 column ( $4 \times 250 \text{ mm}$ ) and an AS-9 guard column ( $4 \times 50 \text{ mm}$ ) with  $3.5 \text{ mM Na}_2\text{CO}_3$  and  $1 \text{ mM NaHCO}_3$  as the eluent. The injection volume was  $250 \mu\text{L}$ .

Chloride and fluoride ions were also measured using a Dionex DX-120 ion chromatography system with an AS14 column ( $4 \times 250 \text{ mm}$ ) and an AS14 guard column ( $4 \times 50 \text{ mm}$ ) with  $9 \text{ mM NaHCO}_3$  as the eluent. The flow rate for the elution of all these ions was set at  $1.0 \text{ mL min}^{-1}$ , and the detection limits of  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$ , and  $\text{OCl}^-$  were 5, 11, 10, 9.5, and  $10 \mu\text{g L}^{-1}$ , respectively.

Measurement of  $\text{pH}$  was performed using a model 52A instrument (Orion). The specific surface area of the  $\text{Fe}^0$  was determined using a Brunauer–Emmett–Teller (BET) krypton gas adsorption isotherm and a Micromeritics ASAP 2010 system. The surface morphology of the ZVI was observed with a field-emission scanning electron microscope (FE-SEM; SUPRA 55VP, Carl Zeiss, Germany) at  $1000\times$  magnification.



**Fig. 2.** Removal of perchlorate ( $\text{ClO}_4^-$ ) and production of chloride ions ( $\text{Cl}^-$ ) in the  $\text{Fe}^0$ -only reaction under anoxic and anoxic conditions ( $[\text{perchlorate}]_{\text{initial}} = 0.016 \text{ mM}$ ,  $[\text{Fe}^0] = 10 \text{ g L}^{-1}$ ; pH 6).

### 3. Results and discussion

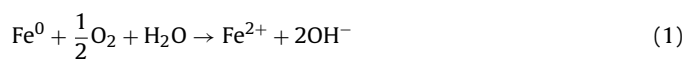
#### 3.1. Removal of perchlorate in the $\text{Fe}^0$ -only reaction under anoxic and oxic conditions

Under anoxic conditions, perchlorate was barely removed by  $\text{Fe}^0$ -only reaction, even after 12 h, while under oxic conditions, its removal was significantly improved (Fig. 2). Perchlorate by the  $\text{Fe}^0$ -only reaction was completely removed within 9 h under oxic conditions. Thus, perchlorate can be more effectively removed under oxic conditions than anoxic conditions.

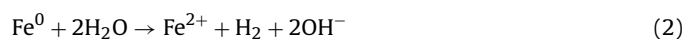
Fig. 2 also shows the mass balance of chlorine under anoxic and oxic conditions. Although the removal of perchlorate was poor, the recovery of chlorine under anoxic conditions approached 100%. In contrast, the recovery of chloride under oxic conditions was significantly lower compared to the removal of perchlorate (Fig. 2). This result indicates that chloride ion produced during the removal of perchlorate existed in the bulk solution under anoxic conditions. In contrast, the chloride ion produced under oxic condition might be adsorbed onto iron oxides surface.

The mechanism of perchlorate removal has been reported to consist of adsorption onto the iron surface followed by removal with dissolved or sorbed  $\text{Fe}^{2+}$  [16,29]. The different perchlorate removal rate under anoxic and oxic conditions can be from the difference of corrosion rate of  $\text{Fe}^0$  [21,22].

Iron corrosion is initiated by



in oxic environment, or by



in anoxic environments [30].

Under anoxic condition, the slower perchlorate removal is due to slower Fe corrosion rate, and lack of iron corrosion products. Magnetite, which is formed under anoxic condition, passivates the  $\text{Fe}^0$  surface. This iron product can suppress the reactivity of  $\text{Fe}^0$ , resulting in slower removal of perchlorate [30]. On the other hand, ferrihydrite is known to form in the presence of oxygen, and to be stabilized by the adsorption of perchlorate in the presence of oxygen in  $\text{Fe}^0/\text{H}_2\text{O}$  system [30]. These iron oxides with large surface

areas may be beneficial for the immobilization of contaminants through sorption or co-precipitation with perchlorate and/or its intermediates. This mechanism implies that enhancing removal of perchlorate can be achieved by the formation of iron oxides in  $\text{Fe}^0/\text{H}_2\text{O}$  system, and fast corrosion can be predicted under the presence of dissolved oxygen [26].

The unbalance in the chloride recovery under oxic condition can be due to the co-precipitation for iron oxides with chloride. In fact, Moore and co-workers [16,29] showed perchlorate removal by increasing chloride concentration, indicating the removal mechanism might be the perchlorate sorption and subsequent removal on the iron surfaces under anoxic condition when purging with nitrogen and argon gas. The slow perchlorate removal under anoxic condition can be due to slow  $\text{Fe}^0$  corrosion rate. In contrast, the fast corrosion rate of  $\text{Fe}^0$  surface under oxic condition signifies fast generation of electron for perchlorate removal and fast generation of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  for co-precipitation with perchlorate and/or its intermediates.

Since the mechanism of adsorption and co-precipitation of products or intermediates with iron oxides was regarded as a non-specific removal mechanism [22], along with perchlorate, chloride ion can adsorb onto iron oxide surface. Fig. 3 shows the SEM images (1000 $\times$ ) of  $\text{Fe}^0$  after perchlorate removal under anoxic and oxic conditions. The difference in the iron surface also may have been due to the adsorption of materials such as chloride produced during the removal of perchlorate, which were subjected to adsorbed and co-precipitated with iron oxides under oxic conditions. This result can explain the unbalance recovery of chloride concentration under oxic conditions.

#### 3.2. By-product identification and removal during perchlorate removal

Perchlorate is biologically removed by the reductive reaction from perchlorate to chlorate ( $\text{ClO}_3^-$ ), to chlorite ( $\text{ClO}_2^-$ ), and finally to chloride under anoxic conditions [31]. This reductive mechanism can also be applied to abiotic processes. However, in this study, only chloride was detected in the bulk solution during perchlorate removal; other by-products such as chlorate ( $\text{ClO}_3^-$ ), chlorite ( $\text{ClO}_2^-$ ), and hypochlorite ( $\text{ClO}^-$ ) were not detected in the solution. This result indicates that perchlorate and other chlorinated by-products may have combined with iron oxide. In fact, Moore et al. [16,30] reported that the chloride adsorbed on  $\text{Fe}^0$  was released into the bulk solution when the concentration of  $\text{Fe}^{2+}$  from oxidation of  $\text{Fe}^0$  was exhausted. Previous research has also reported that the reduction of perchlorate to chlorate ( $\text{ClO}_3^-$ ) is a rate-determining step due to the unstable formation of chlorate [16–18].

To examine the removal mechanism of perchlorate in the  $\text{Fe}^0$ -only reaction under oxic conditions, the removal trend of chlorate as chlorinated by-products and chloride from  $\text{Fe}^0$ -only reaction was investigated.

Fig. 4(a) shows the trends of chlorate ( $\text{ClO}_3^-$ ) removal and chloride production in the  $\text{Fe}^0$ -only reaction under oxic conditions. Chlorate was almost completely removed within 3 h in the  $\text{Fe}^0$ -only reaction. The imbalance of chlorate removal and chloride production in the  $\text{Fe}^0$ -only reaction supports the adsorption of chloride onto the surface of iron oxide under oxic condition.

The removal of chloride in the  $\text{Fe}^0$ -only reaction under oxic conditions is also shown in Fig. 4(b). Because chloride could not be further reduced, the result in Fig. 4(b) indicates that chloride is removed from the solution by the co-precipitation with iron oxides. This result explains the lower recovery of chloride from perchlorate removal in the  $\text{Fe}^0$ -only reaction under oxic conditions (Fig. 2).

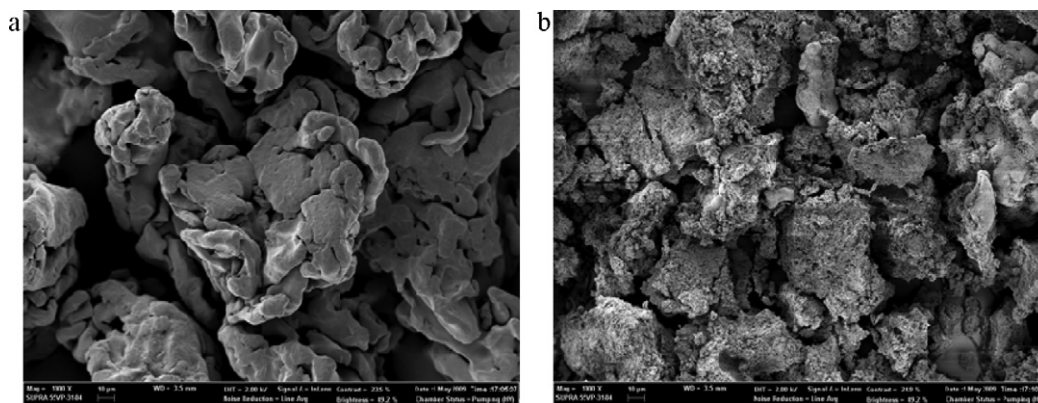


Fig. 3. SEM images of Fe<sup>0</sup> after perchlorate removal under (a) anoxic and (b) oxic conditions (1000 $\times$ ).

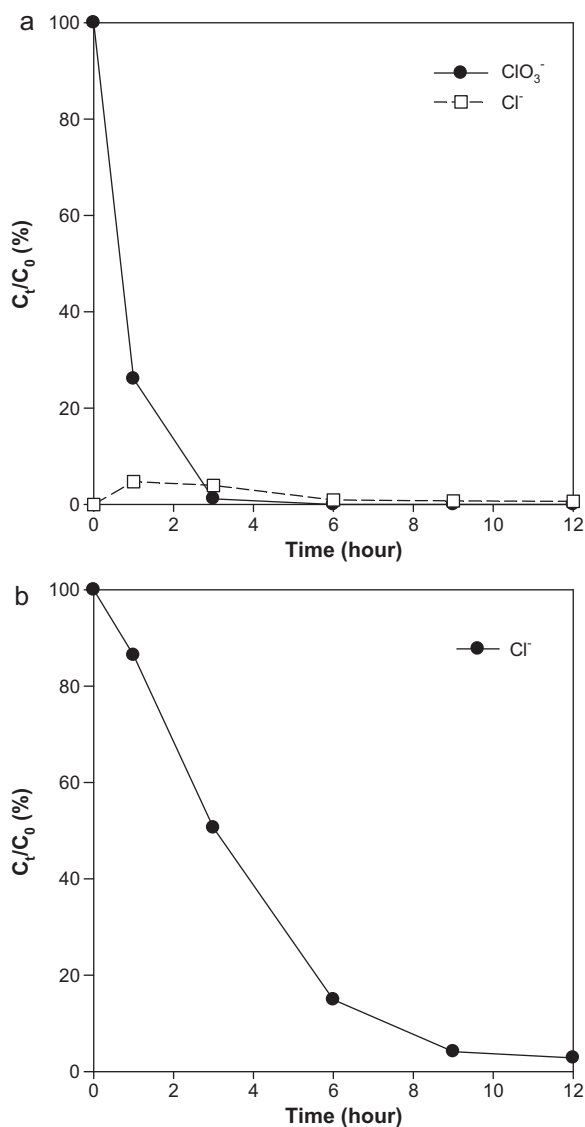


Fig. 4. Removal of (a) chlorate ( $\text{ClO}_3^-$ ) and (b) chloride ( $\text{Cl}^-$ ) in the Fe<sup>0</sup>-only reaction under oxic conditions (experimental conditions: (a)  $[\text{chlorate}]_{\text{initial}} = 0.02 \text{ mM}$ , (b)  $[\text{chloride}]_{\text{initial}} = 0.02 \text{ mM}$ ,  $[\text{Fe}^0] = 10 \text{ g L}^{-1}$ ).

### 3.3. Effect of pH on perchlorate removal under oxic conditions

To examine the effect of pH, the removal of perchlorate in the Fe<sup>0</sup>-only reaction under oxic conditions was performed at initial pH of 3, 6, and 11. Fig. 5 shows that, while only 33% of the perchlorate was removed within 12 h at pH 3 ( $k_{\text{obs}} = 0.019 \text{ h}^{-1}$ ), in the same reaction time, approximately 75% of the perchlorate was removed at pH 11 ( $k_{\text{obs}} = 0.115 \text{ h}^{-1}$ ). In contrast, near complete removal of perchlorate was achieved at pH 6 ( $k_{\text{obs}} = 0.772 \text{ h}^{-1}$ ).

Fe<sup>0</sup> has been reported to oxidize to dissolved Fe<sup>2+</sup> and Fe<sup>3+</sup>, which precipitate as iron oxides with increasing pH in the Fe<sup>0</sup>/H<sub>2</sub>O reaction [32]. It is also known that the adsorption of oxygen onto iron oxides is active at neutral pH [23,33]. Also, the production of iron oxides can be inhibited in acidic solution due to the reduction of oxygen to H<sub>2</sub>O, according to Eq. (1) [29,34]. This result implies that the oxidation reaction of Fe<sup>0</sup> is favorable at higher pH, and the direct removal of perchlorate from the oxidation of Fe<sup>0</sup> in bulk solution occurs at pH < 4. Based on the results presented in Fig. 5, the direct removal of perchlorate by electrons produced by Fe<sup>0</sup> can be major perchlorate removal mechanism at acidic pH, and the adsorption on the iron oxide followed by the co-precipitation or

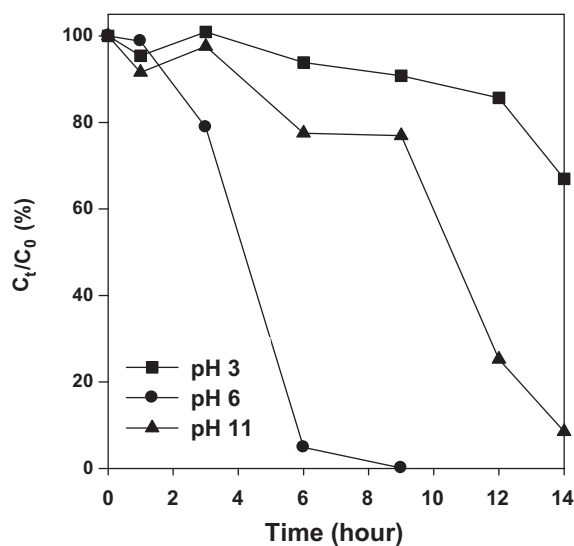


Fig. 5. Effect of pH in solution on the removal of perchlorate in the Fe<sup>0</sup>-only reaction under oxic conditions ( $[\text{perchlorate}]_{\text{initial}} = 0.016 \text{ mM}$ ,  $[\text{Fe}^0] = 10 \text{ g L}^{-1}$ ).



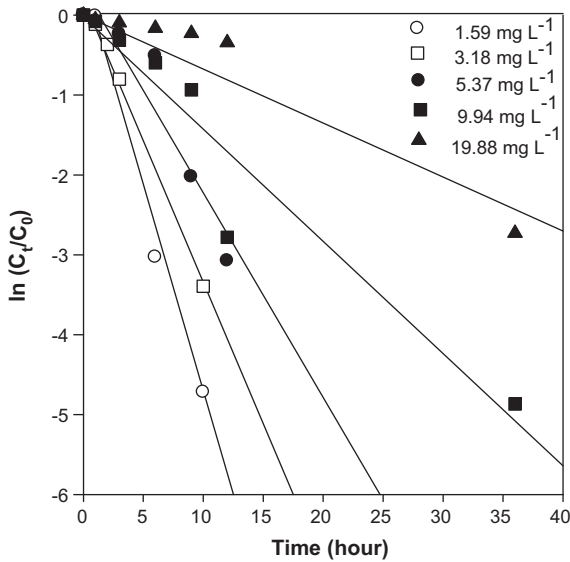


Fig. 6. Effect of the initial concentration of perchlorate in the Fe<sup>0</sup>-only reaction ([Fe<sup>0</sup>]<sub>initial</sub> = 10 g L<sup>-1</sup>; pH 6).

reduction is an important removal mechanism at higher pH in the Fe<sup>0</sup>-only reaction under oxic condition.



Interestingly, the removal rate of perchlorate at pH 11 was less than at pH 7 (Fig. 5). This may have been due to the solubility of iron oxides at pH 11 than pH 7. The solubility of Fe(III)-oxides such as Fe(OH)<sub>3</sub> is known as much higher at pH 11 than at pH 7 [35]. Therefore, lesser Fe(OH)<sub>3</sub> precipitates are formed at pH 11 than pH 7. Since adsorption and co-precipitation of perchlorate with iron oxides is the main mechanism, the perchlorate removal rate at pH 11 can be less than at pH 7.

### 3.4. Applying adsorption model during the reaction of perchlorate with Fe<sup>0</sup>

In order to investigate the adsorption mechanism of perchlorate with Fe<sup>0</sup>, Langmuir isotherm and Langmuir–Hinshelwood model were applied.

Fig. 6 showed that the perchlorate removal rates decreased with increasing perchlorate concentration in the Fe<sup>0</sup>-only reaction. Based on R<sup>2</sup> values, the removal of perchlorate was fitted to a pseudo-first-order kinetic model. This result implies that the concentration of Fe<sup>0</sup> was important in the removal rate of perchlorate, and the removal of perchlorate was a surface reaction on Fe<sup>0</sup>.

To further investigate the removal mechanism of perchlorate in the Fe<sup>0</sup>-only reaction, the data in Fig. 6 were applied to the Langmuir isotherm (Eq. (4)) and Langmuir–Hinshelwood model (Eq. (5)),

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{K_c q_m C} \quad (4)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{K_{\text{ads}} k_{\text{rxn}}} + \frac{[C_0]}{k_{\text{rxn}}} \quad (5)$$

where *q* and *q<sub>m</sub>* are the amount and the maximum amount adsorbed on the adsorbent (mg<sub>adsorbate</sub>/g<sub>adsorbent</sub>), respectively; *K<sub>c</sub>* and *K<sub>ads</sub>* are equilibrium adsorption constants (Lmg<sup>-1</sup>) for the Langmuir isotherm and Langmuir–Hinshelwood model, respectively; *k<sub>obs</sub>* and *k<sub>rxn</sub>* represent the pseudo-first-order rate constant (h<sup>-1</sup>) and the second-order rate constant (mgL<sup>-1</sup> h<sup>-1</sup>), respectively; and *C* and *C<sub>0</sub>* represent the equilibrium and initial concentrations of perchlorate (mg L<sup>-1</sup>), respectively.

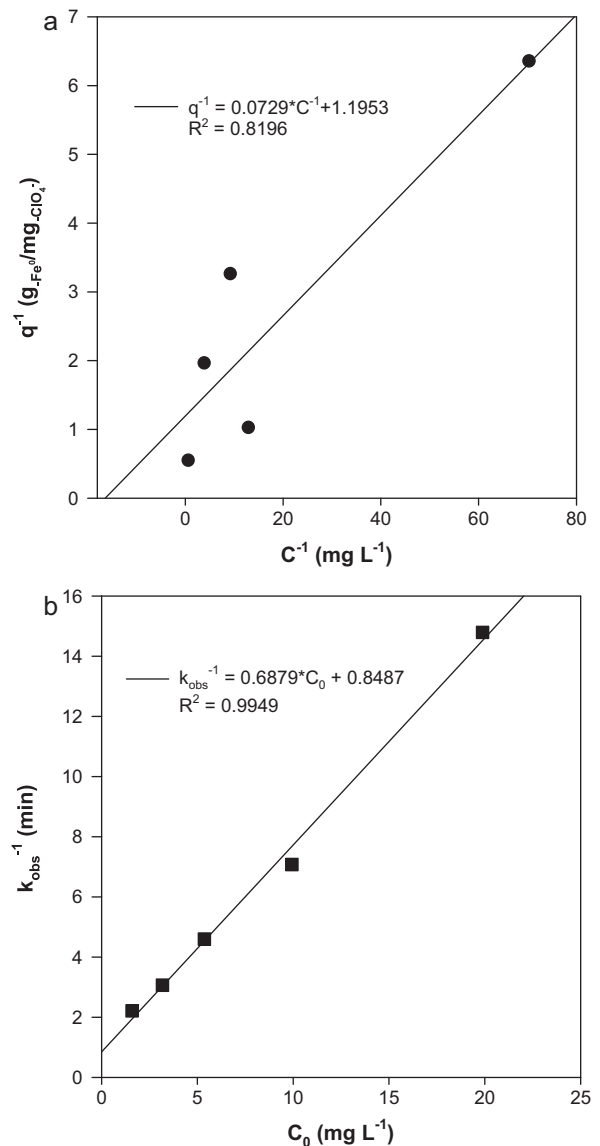
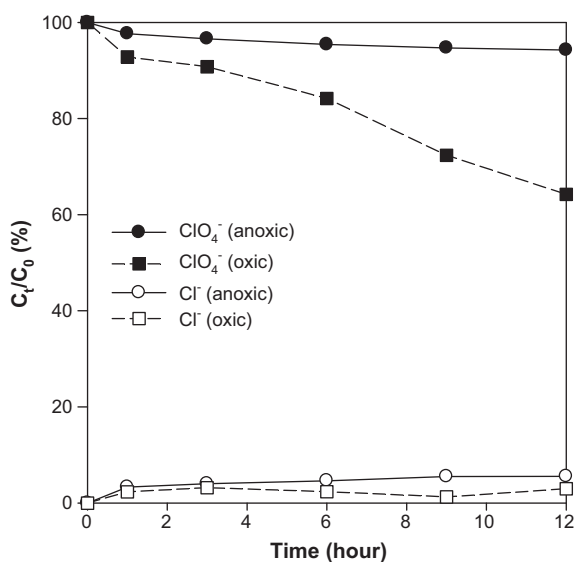


Fig. 7. Lines fit to the removal data of perchlorate in the Fe<sup>0</sup>-only reaction using (a) the Langmuir isotherm and (b) the Langmuir–Hinshelwood model (experimental conditions: [Fe<sup>0</sup>] = 10 g L<sup>-1</sup>, pH 6).

Fig. 7 shows the result of fitting data to these two models. The removal in the Fe<sup>0</sup>-only reaction conformed to the Langmuir–Hinshelwood model rather than to the Langmuir adsorption isotherm, according to the R<sup>2</sup> values of each model. The *K<sub>c</sub>* value (16.3964 Lmg<sup>-1</sup>) was much greater than *K<sub>ads</sub>* (0.8107 Lmg<sup>-1</sup>), and *k<sub>rxn</sub>* was 1.4535 mgL<sup>-1</sup> h<sup>-1</sup>. Considering the significant decrease in the adsorption constant, this result implies that the removal of perchlorate in the Fe<sup>0</sup>-only reaction was initiated by the adsorption of perchlorate on Fe<sup>0</sup>, followed by the reduction reaction at the surface of Fe<sup>0</sup>. However, based on the result of the intermediates analysis, the removal of perchlorate occurs only slightly. That is, perchlorate was primarily removed by the adsorption and co-precipitation on Fe<sup>0</sup>.

### 3.5. Removal of perchlorate in the combined reaction of Fe<sup>0</sup> with UV

Fig. 8 shows the removal of perchlorate in the combined reaction of Fe<sup>0</sup> with UV under anoxic and oxic conditions. The removal of perchlorate was improved under oxic conditions compared with



**Fig. 8.** Removal of perchlorate ( $\text{ClO}_4^-$ ) and production of chloride ( $\text{Cl}^-$ ) ion in the  $\text{Fe}^0/\text{UV}$  reaction under oxic and anoxic conditions ( $[\text{perchlorate}]_{\text{initial}} = 0.016 \text{ mM}$ ,  $[\text{Fe}^0] = 10 \text{ g L}^{-1}$ , UV-C intensity =  $3.4 \text{ mW cm}^{-2}$ , pH 6).

anoxic conditions, however, the production of chloride was smaller under oxic conditions compared with anoxic conditions. Interestingly, the degree of chloride production under anoxic conditions almost completely matched perchlorate removal in both the  $\text{Fe}^0$ -only (Fig. 2) and the  $\text{Fe}^0/\text{UV}$  reactions (Fig. 8).

It is reported that the chlorine in  $\text{Fe}^0$ -related reactions of chlorinated compounds is usually changed to chloride ions in bulk solution, or precipitate on iron oxides [36]. Also, perchlorate can react with hydrogen ions ( $\text{H}^+$ ) in the presence of  $\text{Fe}^0$ , resulting in the reduction of perchlorate to chloride in the absence of oxygen (Eq. (6)) [29]. This result implies that perchlorate may be directly reduced to chloride by  $\text{Fe}^0$  under anoxic conditions, and the chloride ion produced is not adsorbed on the  $\text{Fe}^0$  surface, but can exist in bulk solution under anoxic condition.

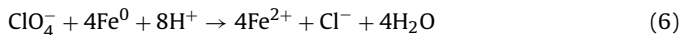
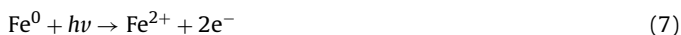


Table 1 shows that the removal of perchlorate under anoxic conditions increased in the  $\text{Fe}^0/\text{UV}$  reaction compared with the  $\text{Fe}^0$ -only reaction. It was recently reported that the oxidation rate of  $\text{Fe}^0$  to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  could be enhanced by UV irradiation [37] (Eq. (7)). Therefore, the resulting electron can be efficiently used for the perchlorate removal.



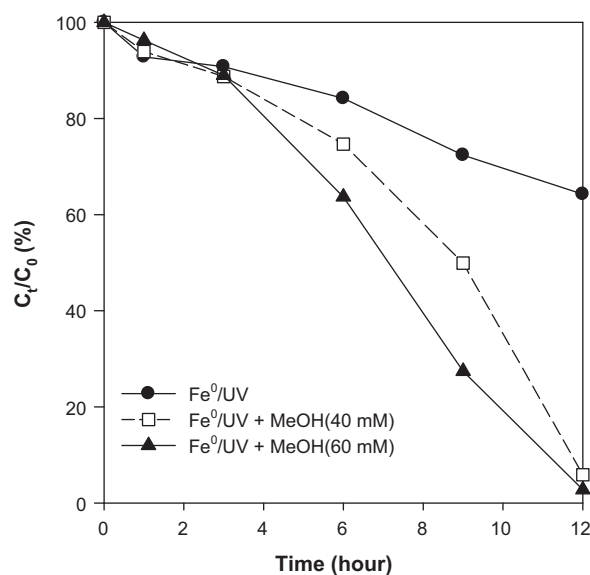
However, the removal rate of perchlorate in the  $\text{Fe}^0/\text{UV}$  reaction under oxic condition was significantly decreased than  $\text{Fe}^0$ -only reaction than (Table 1).

Son et al. [38] and Morgada et al. [39] found that the combined reaction of  $\text{Fe}^0$  and UV induced a Fenton-like reaction, which produced more OH radicals. This result implies that OH radicals produced in the  $\text{Fe}^0/\text{UV}$  reaction might inhibit the removal of per-

**Table 1**

Pseudo-first-order rate constants ( $k_1$ ) for perchlorate removal and  $R^2$  values in the  $\text{Fe}^0$ -only and  $\text{Fe}^0/\text{UV}$  reactions ( $[\text{perchlorate}]_{\text{initial}} = 0.016 \text{ mM}$ ,  $[\text{Fe}^0] = 10 \text{ g L}^{-1}$ ; UV-C intensity =  $3.4 \text{ mW cm}^{-2}$ , pH 6).

Reaction	Anoxic conditions		Oxic conditions	
	$k_1 \times 10^{-3} \text{ (h}^{-1}\text{)}$	$R^2$	$k_1 \times 10^{-3} \text{ (h}^{-1}\text{)}$	$R^2$
$\text{Fe}^0$ -only	1.63	0.963	776.9	0.904
$\text{Fe}^0/\text{UV}$	4.94	0.931	35.1	0.975



**Fig. 9.** Effect of methanol on the removal of perchlorate ( $\text{ClO}_4^-$ ) in the  $\text{Fe}^0/\text{UV}$  reaction ( $[\text{perchlorate}]_{\text{initial}} = 0.016 \text{ mM}$ ,  $[\text{Fe}^0] = 10 \text{ g L}^{-1}$ ; UV-C intensity:  $3.4 \text{ mW cm}^{-2}$ , pH 6).

chlorate due to the competing reaction of perchlorate and OH radicals with electrons.

Thus, finally, the experiment in the presence of methanol as a radical scavenger was conducted to investigate the role of OH radical generated during the  $\text{Fe}^0/\text{UV}$  reaction. Fig. 9 shows that the removal of perchlorate in  $\text{Fe}^0/\text{UV}$  reaction under oxic conditions increased in the presence of 60 mM methanol (73%, 9 h), indicating methanol, a radical scavenger, inhibited OH radical.

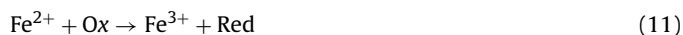
In fact, the effect of methanol on the degradation of azo dye in  $\text{Fe}^0/\text{H}_2\text{O}$  system was studied by Devi et al. [40]. In this study, methanol was used to quench hydroxyl radical.



They found that Fenton reaction occurred in  $\text{Fe}^0/\text{H}_2\text{O}$  under irradiating UV, and methanol reacts with hydroxyl radical, with second-rate constant  $9.7 \times 10^8 \text{ min}^{-1} \text{ s}^{-1}$  as shown in Eq. (8), and the rate decrease in azo dye removal was observed. This result can support methanol effect in our study. Since perchlorate is reduced by electron produced from  $\text{Fe}^0$  oxidation, and OH radicals are known to be effectively produced by Fenton-type reaction in  $\text{Fe}^0/\text{UV}$  system [40], the presence of UV in  $\text{Fe}^0/\text{H}_2\text{O}$  system can inhibit perchlorate removal by the reaction of OH radical with electron. Therefore, adding methanol can increase perchlorate removal by scavenging OH radical produced by Fenton-type reaction in  $\text{Fe}^0/\text{UV}$  system under oxic condition.

### 3.6. The mechanism of perchlorate removal in $\text{Fe}^0$ -only reaction under anoxic and oxic conditions

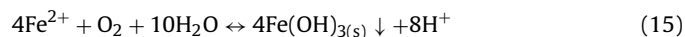
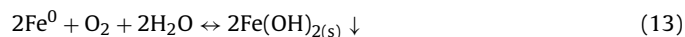
The mechanism of perchlorate removal using  $\text{Fe}^0$  under anoxic conditions can be summarized as following two reactions (Eqs. (9)–(11)) [22]:



where Ox is oxidized form such as perchlorate, red is reduced form of perchlorate such as chloride ion.

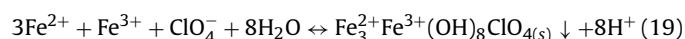
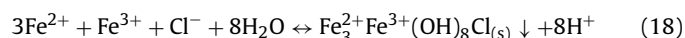
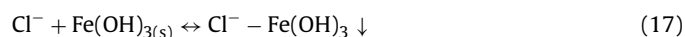
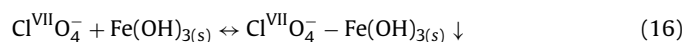
In contrast,  $\text{Fe}^0$  under oxic conditions was oxidized to  $\text{Fe}^{2+}$  (Eq. (12)) or settled as  $\text{Fe}(\text{OH})_{2(\text{s})}$  (Eq. (13)). The oxidized  $\text{Fe}^{2+}$  iron from

Fe<sup>0</sup> under oxic conditions can be further oxidized to Fe<sup>3+</sup> (Eq. (14)) or Fe(OH)<sub>3(s)</sub> (Eq. (15)) [39].



According to the reaction shown in Eq. (15), the net reaction resulted in decreased solution pH. Different Fe(II)/(III) oxides or hydroxides (Eqs. (13) and (15)) are formed as corrosion products, which is called here generically ferric (or ferrous) oxides [39]. Su and Puls [41] also reported that the green rust, composed of solid precipitates, usually existed at neutral pH (pH 6.5–8.0).

The perchlorate and the generated chloride from perchlorate reduction can combine with existing iron oxides or Fe<sup>2+</sup> and Fe<sup>3+</sup> iron, resulting in the co-precipitation [36], as shown in Eq. (16) through Eq. (19);



These reactions can explain the lower recovery of chloride in the Fe<sup>0</sup>-only reaction under oxic conditions.

#### 4. Conclusions

Fe<sup>0</sup>-induced perchlorate removal was significantly enhanced at neutral pH under oxic conditions. The removal of perchlorate in the Fe<sup>0</sup>/UV reaction under oxic conditions increased in the presence of methanol, a radical scavenger, indicating that removal of perchlorate in the combined reaction of Fe<sup>0</sup> with UV under oxic conditions was inhibited by OH radical production. Applying the Langmuir–Hinshelwood model indicated that the removal of perchlorate was accelerated by adsorption onto iron oxides and subsequent reaction by the oxidation of Fe<sup>0</sup>. The results from this study imply that oxic conditions are essential for more efficient removal of perchlorate in Fe<sup>0</sup>-only reaction to provide adsorption and co-precipitation between perchlorate and iron oxide. Thus, this process can be more practical in real-world applications without providing external energy such as higher temperature.

#### Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (MEST) (no. 2010-0014222).

#### References

- [1] E.T. Urbansky, Issues in managing the risks associated with perchlorate in drinking water, *J. Environ. Manage.* 56 (2) (1999) 79–95.
- [2] E.T. Urbansky, Perchlorate chemistry: implications for analysis and remediation, *Biorem. J.* 2 (2) (1998) 81–95.
- [3] Q. Cheng, L. Perlmutter, P.N. Smith, S.T. McMurry, W.A. Jackson, T.A. Anderson, A study on perchlorate exposure and absorption in beef cattle, *J. Agric. Food Chem.* 52 (11) (2004) 3456–3461.
- [4] K.B. Kirk, P.K. Martinelango, K. Tian, A. Dutta, E.E. Smith, P.K. Dasgupta, Perchlorate and iodide in dairy and breast milk, *Environ. Sci. Technol.* 39 (7) (2005) 2011–2017.
- [5] S.A. Snyder, B.J. Vanderford, D.J. Rexing, Trace analysis of bromated chlorate iodate and perchlorate in natural and bottled waters, *Environ. Sci. Technol.* 39 (12) (2005) 4586–4593.
- [6] L. Valentin-Blasini, J.P. Mauldin, D. Maple, B.C. Blount, Analysis of perchlorate in human urine using ion chromatography and electrospray tandem mass spectrometry, *Anal. Chem.* 77 (8) (2005) 2475–2481.
- [7] R. Perciasepe, Part III, U.S. Environmental Protection Agency, Announcement of the Drinking Water Contaminant Candidate List, *Fed. Reg.* 63 (49) (1998) 10273–10287.
- [8] J. Wolff, Perchlorate and the thyroid gland, *Pharmacol. Rev.* 50 (1) (1998) 89–105.
- [9] B.C. Blount, J.L. Pirkle, J.D. Osterloh, L. Valentin-Blasini, K.L. Caldwell, Urinary perchlorate and thyroid hormone levels in adolescent and adult men and women living in the United States, *Environ. Health Perspect.* 114 (12) (2006) 1865–1871.
- [10] U.S. EPA Federal Facilities Restoration and Reuse Office (FFRRO), <http://www.epa.gov/safewater/contaminants/unregulated/perchlorate.html>.
- [11] P.E. Hatzinger, Perchlorate biodegradation for water, *Environ. Sci. Technol.* 39 (11) (2005) 239A–247A.
- [12] W. Chen, F.S. Cannon, J.R. Rangel-Mendez, Ammonia-tailoring of GAC to enhance perchlorate removal. II: perchlorate adsorption, *Carbon* 43 (3) (2005) 581–590.
- [13] Z. Xiong, P. Dimick, D. Zhao, A. Kney, J. Tavakoli, Removal of perchlorate from contaminated water using a regenerable polymeric ligand exchanger, *Sep. Sci. Technol.* 41 (11) (2006) 2555–2574.
- [14] S.Y. Oh, P.C. Chiu, B.J. Kim, D.K. Cha, Enhanced reduction of perchlorate by elemental iron at elevated temperatures, *J. Hazard. Mater.* 129 (1–3) (2006) 304–307.
- [15] Z. Xiong, D. Zhao, G. Pan, Rapid and complete destruction of perchlorate in water and ion-exchange brine using stabilized zero-valent iron nanoparticles, *Water Res.* 41 (15) (2007) 3497–3505.
- [16] A.M. Moore, C.H. De Leon, T.M. Young, Rate and extent of aqueous perchlorate removal by iron surfaces, *Environ. Sci. Technol.* 37 (14) (2003) 3189–3198.
- [17] B. Gu, W. Dong, G.M. Brown, D.R. Cole, Complete degradation of perchlorate in ferric chloride and hydrochloric acid under controlled temperature and pressure, *Environ. Sci. Technol.* 37 (10) (2003) 2291–2295.
- [18] G.C. Lang, G. Horanyi, Some interesting aspects of the catalytic and electrochemical reduction of perchlorate ions, *J. Electroanal. Chem.* 552 (30) (2003) 197–211.
- [19] G. Horanyi, Investigation of the specific adsorption of HSO<sub>4</sub><sup>-</sup> (SO<sub>4</sub><sup>2-</sup>) and Cl<sup>-</sup> ions on Co and Fe by radiotracer technique in the course of corrosion of the metals in perchlorate media, *Corros. Sci.* 46 (7) (2004) 1741–1749.
- [20] C. Noubactep, A. Schöner, G. Meinrath, Mechanism of uranium (VI) fixation by elemental iron, *J. Hazard. Mater.* 132 (2006) 202–212.
- [21] C. Noubactep, Processes of contaminant removal in Fe<sup>0</sup>/H<sub>2</sub>O systems revisited: the importance of co-precipitation, *Open Environ. J.* 1 (2007) 9–13.
- [22] C. Noubactep, A critical review on the process of contaminant removal in Fe<sup>0</sup>-H<sub>2</sub>O systems, *Environ. Technol.* 29 (2008) 909–920.
- [23] C. Noubactep, Characterizing the discoloration of methylene blue in Fe<sup>0</sup>/H<sub>2</sub>O systems, *J. Hazard. Mater.* 166 (2009) 79–87.
- [24] C. Noubactep, An analysis of the evolution of reactive species in Fe<sup>0</sup>/H<sub>2</sub>O systems, *J. Hazard. Mater.* 168 (2009) 1626–1631.
- [25] Y. Satoh, K. Kikuchi, S. Kinoshita, H. Sasaki, Potential capacity of co-precipitation of dissolved organic carbon (DOC) with iron(III) precipitates, *Limnol.* 7 (2006) 231–235.
- [26] A. Ghauch, H. Abou Assi, A. Tuqan, Investigating the mechanism of clofibrac acid removal in Fe<sup>0</sup>/H<sub>2</sub>O systems, *J. Hazard. Mater.* 176 (2010) 48–55.
- [27] H. Huang, G.A. Sorial, Perchlorate remediation in aquatic systems by zero valent iron, *Environ. Eng. Sci.* 24 (7) (2007) 917–926.
- [28] W. Zhang, Nanoscale iron particles for environmental remediation: an overview, *J. Nanopart. Res.* 5 (2003) 323–332.
- [29] A.M. Moore, T.M. Young, Chloride interactions with iron surfaces: implications for perchlorate and nitrate remediation using permeable reactive barriers, *J. Environ. Eng.* 131 (6) (2005) 924–933.
- [30] Y. Furukawa, J.W. Kim, J. Watkins, R.T. Wilkin, Formation of ferrihydrite and associated iron corrosion products in permeable reactive barriers of zero-valent iron, *Environ. Sci. Technol.* 36 (24) (2002) 5469–5475.
- [31] X. Yu, C. Amrhein, M.A. Deshusses, M.R. Matsumoto, Perchlorate reduction by autotrophic bacteria in the presence of zero-valent iron, *Environ. Sci. Technol.* 40 (4) (2006) 1328–1334.
- [32] H. Zeng, B. Fisher, D.E. Giammar, Individual and competitive adsorption of arsenate and phosphate to a high-surface-area iron oxide-based sorbent, *Environ. Sci. Technol.* 42 (2008) 147–152.
- [33] D. Rickard, The solubility of FeS, *Geochim. Cosmochim. Acta* 70 (2006) 5779–5789.
- [34] U.R. Evans, Use of soluble inhibitors, *Ind. Eng. Chem.* 37 (1945) 703–705.
- [35] Y. Roh, S.Y. Lee, M.P. Elless, Characterization of corrosion products in the permeable reactive barriers, *Environ. Geol.* 40 (1–2) (2000) 184–194.
- [36] V.L. Snoeyink, D. Jenkins, *Water Chemistry*, John Wiley & Sons, Inc., New York, 1980.
- [37] U. Kurt, M. Yasar Avsar, G. Talha, Treatability of water-based paint wastewater with Fenton process in different reactor types, *Chemosphere* 64 (9) (2005) 1536–1540.
- [38] H.S. Son, J.K. Im, K.D. Zoh, A Fenton-like degradation mechanism for 1,4-dioxane using zero-valent iron(Fe<sup>0</sup>) and UV light, *Water Res.* 43 (5) (2009) 1457–1463.

- [39] M.E. Morgada, I.K. Levy, V. Salomone, S.S. Farías, G. López, M.I. Litter, Arsenic (V) removal with nanoparticulate zerovalent iron: effect of UV light and humic acids, *Catal. Today* 143 (3–4) (2009) 261–268.
- [40] G.L. Devi, S.G. Kumar, K.M. Reddy, C. Munikrishnappa, Photo degradation of methyl orange an azo dye by advanced fenton process using zero valent metallic iron: influence of various reaction parameters and its degradation mechanism, *J. Hazard. Mater.* 164 (2009) 459–467.
- [41] C. Su, R.W. Puls, Significance of iron(II,III) hydroxycarbonate green rust in arsenic remediation using zero valent iron in laboratory column tests, *Environ. Sci. Technol.* 38 (19) (2004) 5224–5231.