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Short communication

Enhanced reduction of perchlorate by elemental iron at elevated temperatures

Seok-Young Oh[a], Pei C. Chiu[a], Byung J. Kim[b], Daniel K. Cha[a,*]

[a] *Department of Civil and Environmental Engineering, University of Delaware, Newark, DE 19716, USA*
[b] *U.S. Army Engineering Research and Development Center, Champaign, IL 61826-9005, USA*

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Abstract

Kinetics of perchlorate reduction by elemental iron was examined at elevated temperatures using microwave heating and conventional block heating. It was hypothesized that increasing the solution temperature may accelerate the reduction of perchlorate by overcoming the high activation energy barrier. Results from microwave heating study showed that 98% of aqueous perchlorate was removed in 1 h at 200 °C. Similar results observed in control experiments with a block heater indicated that the enhancement in the extent and rate of perchlorate removal by elemental iron was mostly due to heat energy at high temperature. The rapid and complete reduction of perchlorate by elemental iron at elevated temperatures suggests that iron reduction process at elevated temperature may be an option to consider for complete removal of perchlorate from industrial discharges.

Keywords: Perchlorate; Reduction; Elemental iron; Temperature

1. Introduction

Perchlorate salts (e.g., ammonium perchlorate) have been used as an oxidizer in solid propellants for rockets and missiles [1]. Perchlorate is known to have detrimental effect on human health because it interferes with iodine uptake, which is necessary for the production of thyroid hormones [2,3]. California Department of Health Services has recently lowered the action level for perchlorate in drinking water from 18 to 6 μg/L [3].

Aqueous perchlorate is known to be highly stable under ambient conditions and, because of its high solubility in water, the conventional treatment techniques such as carbon adsorption and ultrafiltration are found to be ineffective in removing perchlorate from discharges. On the other hand, thermodynamics predicts that perchlorate is unstable under ambient conditions and should readily be transformed to chloride in the presence of metals such as zero-valent iron (Fe(0)). However, recent researches demonstrate that these reduction reactions occur very slowly under ambient conditions, indicating that the kinetic barriers to perchlorate reduction are very large [4,5].

Iron metal has been receiving a great deal of attention as a strong reducing agent for soil and groundwater remediation because it is inexpensive, abundant, and easy to handle. Despite extensive research and knowledge of its many potential applications, the feasibility of applying iron technology to perchlorate treatment has been questioned due to the slow kinetics of iron–perchlorate reaction under ambient conditions [6]. Moore et al. [7] reported that 66% of perchlorate was reductively removed by elemental iron in 2 weeks at neutral pH. They suggested that, due to the slow reaction rate, the elemental iron may not be applicable immediately as a remediation technology for perchlorate removal. However, such kinetic hindrance may be overcome by increasing the temperature. Recently, Gu et al. [8] observed a complete decomposition of perchlorate in 60 min at 195 °C with ferrous ions as the reducing agent. Reported activation energy for the perchlorate reduction was 120 ± 5 kJ/mol. The rate of perchlorate reduction by ferrous ion, a weak reductant relative to Fe(0), increased by 3 orders of magnitude when the temperature was raised from 110 to 195 °C [8]. Horányi and co-workers [9–12] also reported that the reduction of perchlorate to chloride by Fe(0) in acidic media was enhanced by increasing

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* Corresponding author. Tel.: +1 302 831 2435; fax: +1 302 831 3640.
E-mail address: cha@ce.udel.edu (D.K. Cha).

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proton concentration and temperature [9–12]. They showed that elemental iron reduced approximately 18% of perchlorate in 1 M $HClO_4$ solution to chloride in 5 h. The extent of reduction was enhanced by about 15% with increasing temperature from 25 to 45 °C [9,10]. Láng and Horányi [11] concluded that the initial reduction of perchlorate to chlorate was a rate-limiting step.

In this study, the feasibility of using elemental iron to reduce aqueous perchlorate at elevated temperatures was examined. We hypothesized that increasing the temperature will accelerate the reduction of perchlorate by overcoming the kinetic barrier of high activation energy. Both microwave heating and conventional block heating were shown to be effective in enhancing the rate and extent of perchlorate reduction by elemental iron.

2. Materials and methods

2.1. Chemicals

Sodium perchlorate monohydrate ($NaClO_4 \cdot H_2O$, ∼100%) and sodium chlorate ($NaClO_3$, >99%) were purchased from Fisher Scientific (Pittsburgh, PA) and Aldrich (Milwaukee, WI), respectively, for perchlorate and chlorate stock solutions. HEPES [*N*-(2-hydroxyethyl)piperazine-*N*′-(ethanesulfonic acid)] was obtained from Sigma (St. Louis, MO). The elemental iron used in this study was cast iron obtained from Master Builders, Inc. (Aurora, OH) and was used without pretreatment. The specific surface area of the Master Builders iron was 1.29 m^2/g [13].

2.2. Batch reduction experiments

The procedures and conditions for the batch reduction experiments were described in detail in previous publications [14,15]. All experimental reactors were prepared in an anaerobic glove bag ($I^2R^®$, Cheltenham, PA) filled with N_2. Replicate Pyrex® vials (12 mL) contained 1 g of elemental iron and 10 mL of perchlorate/chlorate solution. Initial concentrations of perchlorate and chlorate were 0.5 and 1.3 mM, respectively. Each vial was deoxygenated by purging with N_2 for 30 min. The pH of the solution was buffered at 7.4 using 0.1 M HEPES. The vials were placed on a platform shaker in horizontal position and rotated at 100 rpm. At selected time intervals, replicate vials were sacrificed and the solution was immediately filtered through a 0.22-μm cellulose membrane filter (Millipore, MA) for the perchlorate and chlorate determination.

2.3. Batch reduction experiments at elevated temperature

In order to examine the perchlorate reduction by iron at elevated temperatures, a 500 W microwave digester (Milestone, Monroe, CT) was initially used to heat the contents of batch reactors. Teflon® test vessels contained 50 g of Master Builders cast iron and 20 mL of 0.5 mM perchlorate solution. The pH of test solution was buffered at 7.4 with 0.1 M HEPES. The reactors were sealed with gas-tight screw caps and slowly rotated in the digester oven at 30 rpm. The microwave digester was equipped with automated temperature control system and temperature of batch reactor was maintained at desired levels (125–200 °C) by intermittently applying microwave. The total times of microwave applications for 125, 150, 175, and 200 °C were approximately 30, 45, 60, and 80 min, respectively, for each 2-h experiment. At selected time intervals, replicate reactors were sacrificed and solutions were filtered through 0.22-μm cellulose membrane filter (Millipore, MA) for perchlorate analysis. A COD block heater (HACH, Loveland, CO) was also used to heat the batch reactor contents to examine the potential role of microwave radiation on perchlorate reduction reaction. Pyrex® vials (12 mL) containing 10 g of elemental iron and 3 mL of 0.5 mM perchlorate solution in 0.1 M HEPES buffer were heated in the block heater at 100–150 °C. The heater was pre-heated at adjusted temperature before placing the vials. At each sampling time, replicate vials were sacrificed and analyzed for perchlorate.

2.4. Chemical analysis

Perchlorate and chlorate were analyzed by an ion chromatograph (Dionex, Sunnyvale, CA) equipped with a Dionex Ionpac AS11 column [16]. NaOH solution (100 mM for perchlorate, 1 mM for chlorate) was used as the eluent and the injection volume was 10 μL.

3. Results and discussion

3.1. Reduction of perchlorate/chlorate with elemental iron

As expected, perchlorate removal by elemental iron in pH-buffered solution was slow and incomplete at room temperature (20 ± 1 °C). Only 50.8% of initial perchlorate was removed after 3 weeks (Fig. 1a). Pseudo-first-order rate constant for the perchlorate removal was estimated to be $0.032 \pm 0.001\ h^{-1}$ ($R^2 = 0.996$). Using surface area concentration of the iron (129 m^2/L), surface area-normalized rate constant was calculated as $1.03 \pm 0.04 \times 10^{-7}\ L\ m^{-2}\ h^{-1}$. This value is compared to the rate constant ($10^{-7}\ L\ m^{-2}\ h^{-1}$) reported by Moore et al. [7].

On the other hand, chlorate removal was rapid and complete as 100% of initial chlorate disappeared from solution in 2 h (Fig. 1b). The calculated pseudo-first-order rate constant of $0.0262 \pm 0.003\ min^{-1}$ ($R^2 = 0.986$) was similar to the value estimated by Westerhoff [17] using the data obtained from an iron column experiment. Láng and Horányi [11] reported that the initial reductive transformation of perchlorate to chlorate by two-electron transfer may be the rate-determining process in the overall reduction of perchlorate by elemental iron.

3.2. Reduction of perchlorate by elemental iron at elevated temperatures

To enhance the iron reduction of perchlorate, we evaluated the microwave heating of iron–water system up to 200 °C using a microwave digester. At 125 °C, 40% of initial perchlorate was removed from solution after 2 h (Fig. 2). The rate and extent of perchlorate disappearance in the presence of elemental iron