Chemosphere 80 (2010) 888-893

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Perchlorate removal by acidified zero-valent aluminum and aluminum hydroxide

Hsing-Lung Lien*, Chia Ching Yu, Ya-Ching Lee

Department of Civil and Environmental Engineering, National University of Kaohsiung, Kaohsiung 811, Taiwan, ROC

ARTICLE INFO

Article history: Received 25 February 2010 Received in revised form 8 May 2010 Accepted 10 May 2010 Available online 2 June 2010

Keywords: Perchlorate Aluminum Aluminum hydroxide Adsorption Corrosion

1. Introduction

Perchlorate salts such as ammonium perchlorate have been used as oxidants in solid propellants for rockets, missiles, and fireworks (Urbansky, 2002). Widespread perchlorate contamination of groundwater and drinking water supplies in 25 US states and Puerto Rico has been reported (US EPA, 2004). Perchlorate is a health concern because it inhibits iodine uptake in the thyroid gland causing the reduced production of thyroid hormones (Urbansky, 2002). The US Environmental Protection Agency has established an official perchlorate reference dose of 0.0007 mg kg⁻¹ d⁻¹, which corresponds to a drinking water equivalent level of 24.5 ppb (US EPA, 2005).

As a strong oxidant with the high oxidation state of the chlorine, +7, perchlorate reduction is a thermodynamically favorable process under ambient conditions (Urbansky, 2002).

$$ClO_4^- + 8H^+ + 8e^- \rightarrow Cl^- + 4H_2O \quad E^o = 1.287 V$$
 (1)

However, studies have indicated a large kinetic barrier for perchlorate reduction (Gu et al., 2003; Cao et al., 2005). Because of the kinetic barrier, researchers have devoted great efforts to developing remedial technologies for perchlorate reduction using various reactive media (e.g., iron) (Gu et al., 2003; Láng and Horányi, 2003; Moore et al., 2003; Cao et al., 2005; Oh et al., 2006; Son et al., 2006; Yu et al., 2006). However, under ambient conditions, incomplete removal of perchlorate (66%) was found in 2 wk when a high iron dose (1250 g L⁻¹) was applied at neutral pH (Moore

ABSTRACT

Removal of perchlorate using either acid-washed zero-valent aluminum or aluminum hydroxide was studied in batch reactors under ambient temperature and pressure. Approximately 90–95% of perchlorate was removed within 24 h in the presence of 35 g L⁻¹ aluminum at acidic pH (4.5 ± 0.2). Although aluminum is a strong reductant, this study indicated no explicit evidence to support perchlorate reduction while it was found that an adsorption process is involved in the perchlorate removal. The adsorbed perchlorate ions were desorbed effectively using a 1.0 N MgSO₄ solution. The effective composition for the perchlorate adsorption is confirmed as aluminum hydroxide (bayerite), which is a product of the aluminum corrosion. Rapid adsorption of perchlorate was observed in the presence of aluminum hydroxide. The perchlorate adsorption by aluminum hydroxide is dependent on the solution pH. The removal mechanism can be attributed to the ion-pair formation at the aluminum hydroxide surface.

© 2010 Elsevier Ltd. All rights reserved.

et al., 2003). To effectively reduce perchlorate, reaction systems usually require incorporating with microbial reduction processes (Son et al., 2006; Yu et al., 2006) or operating under particular conditions such as an elevated temperature (Gu et al., 2003; Cao et al., 2005; Oh et al., 2006; Xiong et al., 2007), high metal doses (Moore et al., 2003), or extremely acidic conditions (Gu et al., 2003; Láng and Horányi, 2003). More recently, Wang et al. (2008) reported the use of pressurized hydrogen gas for perchlorate removal in the presence of metallic catalysts. It was found that the Ti–TiO₂ catalyst can remove more than 90% of initial perchlorate concentrations (1 ppm) in 3 d. They also reported an indirect electrochemical reduction process for effective removal of perchlorate using a titanium electrode (Wang et al., 2009).

While the chemical and microbial reduction can transform perchlorate to chloride, different approaches for perchlorate removal such as adsorption and ion exchange have also been developed (Yoon et al., 2009). It has been reported that surfactant-tailored activated carbon is capable of adsorbing perchlorate at ppb level and both perchlorate and surfactant can be destroyed during the thermal regeneration process of activated carbon (Parette and Cannon, 2005). Lehman et al. (2008) reported a combination of the exchange process with biological brine treatment to remove perchlorate from the groundwater.

Aluminum metal is a strong reducing agent ($E^{\circ} = -1.662$ V) that has a standard reduction potential more negative than zero-valent iron ($E^{\circ} = -0.43$ V). Our previous work has demonstrated that aluminum can serve as a reactive reagent for reductive degradation of chlorinated organic compounds through aluminum corrosion (Lien and Zhang, 2002; Lien, 2005; Chen et al., 2008). Electrochemical studies found the reduction of perchlorate occurs in the presence





^{*} Corresponding author. Tel.: +886 7591 9221; fax: +886 7591 9376. *E-mail address*: lien.sam@nuk.edu.tw (H.-L. Lien).

^{0045-6535/\$ -} see front matter @ 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.chemosphere.2010.05.013

of aluminum (Ujvári et al., 2002a; Láng and Horányi, 2003; Li et al., 2004; Láng et al., 2005), but the conversion ratio was very low (\sim 1.4%). On the other hand, the aluminum corrosion products such as aluminum hydroxide/oxyhydroxides are known as good adsorbents (Sposito, 1996). The use of aluminum-based drinking water treatment residual for effective adsorption of perchlorate has been reported (Makris et al., 2006).

In this study, acid-washed zero-valent aluminum was tested for perchlorate removal under ambient conditions. The use of acidification to treat aluminum is to activate its reducing power by dissolving the passive oxide layer and to create a favorable condition for perchlorate adsorption. The objective is armed at investigating removal mechanisms of perchlorate in reaction with aluminum. Both chemical reductions and surface adsorption processes are taken into consideration in this study. Characteristics of aluminum and its reactions in Al⁰–H₂O systems were systemically examined to understand the influence of aluminum corrosion on the perchlorate removal. In this study, it was found that the adsorption of perchlorate is the major removal process. In order to determine the effective composition, aluminum hydroxide, a corrosion product of the zero-valent aluminum, was therefore synthesized and tested for its capability of perchlorate adsorption under various pH conditions.

2. Materials and methods

2.1. Chemicals

Aluminum powder (325 mesh (44 μ m), 99.5%) was purchased from Alfa Aesar. Sodium perchlorate (NaClO₄, ACS reagent, 99+%) and sodium chloride (NaCl, 99.5+%) were purchased from Sigma Aldrich. Concentrated hydrochloric acid (37.5%) with trace metal grade and magnesium sulfate (MgSO₄·7H₂O, ACS reagent) obtained from J.T. Baker. Deionized water (>18 M Ω cm, ELGA LabWater) was used in all experiments.

2.2. Preparation of acid-washed aluminum and aluminum hydroxide

Concentrated HCl (13 mL) was slowly added to a 1000 mL glass beaker containing 5.0 g aluminum powder in 10 mL aqueous solution and the suspension was mixed with a magnetic stirrer in a fume hood under ambient conditions. Immediate fume evolution was observed. A small amount of deionized water was quickly added to dissipate heat and the suspension was stirred for 60 s. The acid-washed aluminum samples were then filtered and rinsed with 500 mL deionized water. After acid washing, about 3.5 ± 0.4 g (n = 5) aluminum particles were recovered in each batch preparation. Synthesized aluminum hydroxide was prepared by oxidizing acid-washed aluminum at 40 °C for 24 h. X-ray diffraction (XRD) spectra indicated it was in the form of bayerite.

2.3. Batch experiments

Batch experiments were conducted in 200 mL serum bottles (Wheaton, actual volume was approximately 220 mL) sealed with polytetrafluoroethylene-lined, butyl rubber septa and aluminum crimp caps. In a typical experiment, a desired amount of acid-washed aluminum (0.5-3.5 g) was placed in 100 mL perchlorate-contaminated water. The initial concentration of perchlorate was 10 mg L⁻¹. Because of a significant hydrogen evolution in the reaction systems containing acid-washed aluminum, the sealed reactor was connected to a 70 mL plastic syringe using Teflon tubing to release gas and monitor the production of hydrogen gas. The initial pH of the solution was about 5.2 and was adjusted with 1.0 N HCl to pH 4.5 ± 0.2 prior to perchlorate addition unless indicated

otherwise. This procedure produced an average concentration of soluble chloride at approximately $115 \pm 13 \text{ mg L}^{-1}$ (n = 4), which was considered as a background level of soluble chloride. The solution pH was measured at the beginning and end of the experiment. The serum bottles were placed on a platform shaker in horizontal position (180 rpm) at room temperature ($24 \pm 1 \text{ °C}$). Solution pH and temperature were measured with a Sension 3 laboratory pH meter (HACH Co.) equipped with a combination pH electrode and a thermocouple probe, respectively. For pH effects on the perchlorate adsorption by synthesized aluminum hydroxide, 50 g L⁻¹ aluminum hydroxide was placed in a 200-mL serum bottle containing 10 mg L⁻¹ perchlorate in 100 mL aqueous solution. The solution pH was adjusted by 1.0 N HCl or NaOH at the beginning of the reaction and monitored periodically throughout the experiment.

For repetitive cycles of adsorption–desorption of perchlorate by synthesized aluminum hydroxide, in each cycle, 10 mg L^{-1} perchlorate was added in a batch reactor containing 35 g L^{-1} aluminum hydroxide in a 100 mL aqueous solution. After perchlorate desorption, the solution was discarded and the aluminum hydroxide was carefully washed by 300 mL deionized water to remove residual perchlorate and was then resealed for the next cycle.

2.4. Analytic methods

At selected time intervals, 1 mL aqueous aliquot withdrawn by a 5 mL gastight syringe was diluted with 4 mL deionized water for ion chromatograph (IC) analysis. The total sampling volume did not exceed 10% of the total solution volume. The solution was filtered through a 0.2 μ m cellulose membrane filter (Millipore, MA) to remove particulates prior to IC analysis. Perchlorate and chloride were analyzed on a Metrohm 861 Advanced Compact IC equipped with a Metrosep A Supp 5–100/4.0 column. Eluent contained 9 mM Na₂CO₃/2.8 mM NaHCO₃ was used.

Hydrogen gas was determined by HP 4890 GC–TCD equipped with a 60/80 Carboxen-1000 column (Supelco, 457 cm \times 0.32 cm). Dissolved aluminum concentration was measured by an inductively coupled plasma-optical emission spectrometry (PerkinElmer Optima 2000DV, PerkinElmer Inc.). The wavelength of aluminum ion was set at 396.153 nm.

XRD measurements were performed using a X-ray diffractometer (Siemens D5000) with a copper target tube radiation (Cu K α 1) producing X-rays with a wavelength of 1.54056 Å. Samples were placed on a quartz plate and were scanned from 20 to 80° (2 θ) at a rate of 2° min⁻¹. The specific surface area of solids was measured by Brunauer–Emmett–Teller (BET) N₂ method using a COULTER SA 3100 surface area analyzer (Coulter Co.). Zeta potential of fresh acid-washed aluminum and synthesized aluminum hydroxide in aqueous solutions was measured by a zeta potential analyzer (ZetaPlus, Brookhaven Instruments Corporation). The solid loading was 0.2 g L⁻¹ in 10⁻² M NaCl aqueous solution. Prior to analysis, the solution pH was adjusted to desired values by adding 1.0 M HNO₃ or KOH.

3. Results and discussion

3.1. Characteristics of acid-washed aluminum and its reactions in the Al^0-H_2O system

Fig. 1 depicts XRD spectra for fresh acid-washed aluminum (Fig. 1a) and aged aluminum particles taken after reacting with 10 mg L⁻¹ perchlorate for 24 h. (Fig. 1b). The characteristic peaks of aluminum appear at 38.6°, 44.9°, 65.2°, and 78.5° where the main diffraction peak is near at the diffraction angle (2 θ) of 38.6°. The diffraction angle of peaks shown in Fig. 1a indicated that the fresh acid-washed aluminum is mainly consisted of zero-valent



Fig. 1. XRD patterns for fresh and aged acid-washed aluminum.

aluminum. Compared to the XRD pattern of fresh acid-washed aluminum, aged aluminum particles showed a significant change of their composition at the surface. The XRD pattern of aged aluminum particles revealed the diffraction peaks at diffraction peaks appeared at 20.4°, 27.9°, 36.6°, and 40.7° indicating aluminum hydroxide (bayerite, Al(OH)₃) was formed.

Surface area analyses showed that specific surface areas of the acid-washed aluminum were dramatically increased during the reaction in the aqueous solution. The fresh particles have the specific surface area about $12 \text{ m}^2 \text{ g}^{-1}$ while it increased to $70 \text{ m}^2 \text{ g}^{-1}$ after 16 h and 130 m² g⁻¹ after 24 h. As indicated by XRD analysis, zero-valent aluminum was converted to aluminum hydroxide after 24 h. Aluminum hydroxide has been known as porous media having specific surface areas greater than $100 \text{ m}^2 \text{ g}^{-1}$ (Sivaraj et al., 1986; Phambu, 2003). The high specific surface area of particles after reactions can therefore be attributed to the aluminum hydroxide formation.

The zero point of charge (pH_{zpc}) for fresh acid-washed aluminum and synthesized aluminum hydroxide particles was determined to be at pH 7.2 and 8.0, respectively. At pH below pH_{zpc} , the surface is positively charged because it adsorbs more protons; conversely, at pH above pH_{zpc} , the surface is negatively charged (Kasprzyk-Hordern, 2004). This indicated that the surface of both types of particles is positively charged under acidic conditions that may be beneficial to perchlorate removal through the electrostatic attraction since perchlorate is an anion.

In the Al^0-H_2O system, the characteristic reaction of aluminum corrosion (Eq. (2)) results in hydrogen evolution, aluminum dissolution, and increasing pH and temperature under acidic conditions (Abiola et al., 2004; Studart et al., 2005; Ishii et al., 2007).

$$Al^{0} + 3H_{2}O \rightarrow Al^{3+} + 1.5H_{2} + 3OH^{-}$$
 (2)

As shown in Fig. 2a, no hydrogen gas was produced within the first 6 h in the reaction system containing 10 mg L⁻¹ perchlorate and 17.5 g L⁻¹ acid-washed aluminum. However, the rate of hydrogen evolution increased to about 40 mL h⁻¹ within 8–13 h. During the experimental period of 16–20 h, a vigorous evolution of hydrogen was monitored at a significantly higher rate (~233 mL h⁻¹). At the end of the experiment (24 h), the rate declined to near zero. The hydrogen evolution period, a rapid increasing stage and a plateau period under both acidic and alkaline conditions has been reported (Abiola et al., 2004; Ishii et al., 2007). Similar to the hydrogen evolution, no significant change of pH was observed within the first 4 h while the solution pH quickly increased to 7 at 8 h and then remained relatively constant at 8.1 ± 0.5 throughout the experiment.

The aluminum dissolution was confirmed by the measurement of the dissolved aluminum ion concentration. Dissolved aluminum ions were found in the aqueous solution during the perchlorate removal. The aluminum concentration peaked at about 30 mg L⁻¹ at 8 h and then gradually declined to below detection limit at 16 h. The high dissolved aluminum concentration can be attributed to initial acidic conditions of the reaction system. Nevertheless, the dissolved aluminum was removed from the aqueous solution when the solution pH increased to about 8.1 during the hydrogen evolution (Eq. (2)). Under such alkaline conditions, dissolved aluminum is readily precipitated as an insoluble form of polymeric aluminum hydroxide (Deltombe and Pourbaix, 1958). This is consistent with the XRD analysis indicating the formation of aluminum hydroxide.

Aluminum corrosion is an exothermic reaction that releases heat and causes an increase in temperature. Although batch reactors were placed under ambient temperature (24 ± 1 °C), a significant increase of the solution temperature was observed (Fig. 2a). As depicted in Fig. 2a, the solution temperature rose from 24 to 40 °C at 10 h and then gradually declined to 24 °C.

3.2. Perchlorate removal using acid-washed aluminum

Studies have shown that the perchlorate reduction in the presence of various metals takes place in acidic media (Ujvári et al., 2002a,b; Li et al., 2004; Láng et al., 2005). Fig. 2b shows the perchlorate removal with acid-washed aluminum under ambient conditions at initial pH of 4.5. The metal dose used in the experiments ranged from 5 to 35 g L^{-1} in 100 mL perchlorate solutions. A lag phase was found during the perchlorate removal. The lag phase is defined as the time required removing at least 20% of the initial perchlorate concentration. For example, the lag time was 16 and $^{\circ}$ 8 h at the metal dose of 5 and 17.5 g L^{-1} , respectively. The perchlorate concentration decreased rapidly after the lag phase even at the low metal dose. The overall perchlorate removal efficiency reached to about 85–95% in all three different conditions of the metal dose. As discussed in detail later, the existence of the lag phase is in fact a consequence of the reaction time requirement for the formation of aluminum hydroxide from the aluminum oxidation.

Chloride has been widely documented as a final product in the perchlorate reduction by zero-valent iron under elevated temperature conditions (Ujvári et al., 2002b; Moore et al., 2003; Gu et al., 2003; Cao et al., 2005). As discussed above, the aluminum corrosion leads to increase temperature and produce hydrogen gas. The increase in temperature tends to enhance reaction rates and the vigorous hydrogen evolution suggests an increasing rate of electron transfer. Therefore, one could expect that perchlorate undergoes a chemical reduction to chloride (Eq. (1)) through the aluminum oxidation.

To investigate this possibility, experiments were conducted to analyze the chloride formation in this study without using HCl to adjust pH. In the batch reactor containing 10 mg L⁻¹ perchlorate and 17.5 g L^{-1} acid-washed aluminum in 100 mL aqueous solution, the initial pH was about 5.2 and the background chloride concentration was about 3 mg L^{-1} because the acid-wash step during the aluminum preparation introduced residual chloride into the reaction system. Surprisingly, instead of observing an increase in the chloride concentration, it was found that the total chloride concentration decreased along with perchlorate removal after the lag phase. The same behavior was also observed in all cases under acidic conditions. As illustrated in Fig. 2c, simultaneous disappearance of both perchlorate and chloride occurred right after the lag phase in the presence of 17.5 g L^{-1} acid-washed aluminum at pH 4.5. With pH adjustment, the initial concentration of chloride was measured about 118 mg L^{-1} while it rapidly reduced to 6 mg L⁻¹ at 16 h. Thus, attempts to verify the possibility of perchlo-



Fig. 2. (a) Hydrogen evolution, pH and temperature change during the perchlorate removal with acid-washed aluminum; (b) perchlorate removal with acid-washed aluminum at various metal doses; (c) adsorption and desorption of chloride and perchlorate ions in the perchlorate removal with acid-washed aluminum. The initial chloride concentration was measured about 118 mg L^{-1} .

rate reduction to chloride in zero-valent aluminum systems were unsuccessful.

The adsorption at the solid surface is another possible process to explain the perchlorate removal as well as the simultaneous disappearance of both perchlorate and chloride. It has been reported that chloride accelerates the pitting corrosion of aluminum by penetrating the aluminum oxide film and then is immobilized at the surface through the incorporation with oxide to form oxide-chloride complexes (Kolics et al., 1998; Branzoi et al., 2003; McCafferty, 2003). To verify whether the disappearance of chloride and perchlorate is a consequence of the surface adsorption, desorption experiments were performed. Studies have indicated that the adsorption strength of sulfate is higher than that of perchlorate and chloride at the aluminum and aluminum oxide surface (Horányi and Joó, 2000; Kolics et al., 1998). Therefore, the desorption experiment was conducted by adding sulfate ions into batch reactors. The addition of 0.5 mL MgSO₄ (1.0 N) corresponding to 240 mg L⁻¹ SO₄^{2–} was carried out when the significant disappearance of both perchlorate and chloride was achieved at 24 h. It was found that more than 99% of sulfate ions quickly disappeared with a corresponding increase in both perchlorate and chloride concentrations in the aqueous solution after 12 h of the sulfate addition (Fig. 2c). The desorbed perchlorate accounted for 96% of the total amount of perchlorate. The observation of perchlorate desorption can be attributed to the high adsorption affinity of sulfate capable of replacing the adsorbed perchlorate at the surface. Similarly, chloride was desorbed after sulfate was added. The recovery of desorbed chloride was about 98%.

Accordingly, this result demonstrates that the disappearance of perchlorate in the presence of acid-washed aluminum is mainly resulted from the surface adsorption process. It should be noted that the disappearance of sulfate is not a consequence of the sulfate reduction because sulfate was added while aluminum was oxidized.

3.3. Effective composition of aluminum for perchlorate removal

Because the adsorption is the major process for perchlorate removal in the presence of acid-washed aluminum, experiments were conducted to investigate the reactive composition of solids for perchlorate adsorption. Fig. 3 illustrates repetitive cycles of adsorption-desorption for perchlorate removal using synthesized aluminum hydroxide at initial pH 4.5. Aluminum hydroxide, confirmed by the XRD analysis, was prepared by oxidation of acidwashed aluminum at 40 °C for 24 h. For each cycle of perchlorate adsorption and desorption, 10 mg L⁻¹ perchlorate was added in a batch reactor containing 35 g L⁻¹ synthesized aluminum hydroxide in a 100 mL aqueous solution. As shown in Fig. 3, rapid adsorption of perchlorate was found in the first cycle where about 90% of perchlorate was removed within 15 min. Perchlorate was readily desorbed after the addition of 0.5 mL MgSO₄ (1 N). The desorbed perchlorate accounted for 80% of total amount of perchlorate added. Compared to the acid-washed aluminum (Fig. 2c), synthesized aluminum hydroxide shows a similar pattern for perchlorate adsorption and desorption. As depicted in Fig. 2c, acid-washed aluminum in the form of zero-valence at the first few hours showed only minor effect for perchlorate removal. The effective removal of perchlorate did not take place until the lag phase where aluminum hydroxide was formed. As a result, it is clear that aluminum



Fig. 3. Repetitive cycles of adsorption–desorption for perchlorate removal by synthesized aluminum hydroxide. The perchlorate concentration and metal loading was 10 mg L^{-1} and 35 g L^{-1} , respectively.

hydroxide is a key composition for serving as an effective adsorbent for perchlorate removal.

In this study, we conclude that perchlorate is primarily removed by aluminum hydroxide that is a product from the aluminum corrosion in the AI^0-H_2O system. The lag time of perchlorate removal shown in Fig. 2b actually reflects the length of reaction time for the oxidation of aluminum to aluminum hydroxide. It was found that increasing metal dose tends to increase the solution temperature that facilitates the aluminum oxidation. Once aluminum hydroxide is formed, perchlorate adsorption occurs. Consequently, the lag time can be reduced as increasing metal doses.

Adsorption of anions onto the aluminum hydroxide surface can undergo an ion-pair formation with positively charged surface sites (Eq. (3)) or ligand exchange with surface hydroxyls (Eq. (4)) (Sposito, 1996).

$$\equiv \text{AlOH}_2^+ + \text{A}^- \rightarrow \equiv \text{AlOH}_2^+ \text{A}^- \tag{3}$$

$$\equiv AIOH + A^{-} \rightarrow \equiv AIA + OH^{-}$$
⁽⁴⁾

where \equiv AlOH $_2^+$ and \equiv AlOH represent the surface hydroxyl (aluminol) groups and A⁻ represents an anion, which is ClO_4^- in this study. The iron-pair formation, caused by the electrostatic attraction between anions and positively charged hydroxide surface, is dependent on pH_{zpc} while the ligand-exchange reactions usually lead to increase pH.

Fig. 4 shows the effect of pH on perchlorate adsorption by synthesized aluminum hydroxide. Perchlorate adsorption on the solids increased with decreasing pH. At pH 2.0, more than 98% of perchlorate was adsorbed whereas only 20–30% of perchlorate was removed at pH 8–10. The aluminum hydroxide that has a high affinity for perchlorate at lower pH can be attributed to the ionpair formation at the positively charged surface of the solids as measured by zeta potentials. The electrostatic attraction between perchlorate and the positively charged surface occurred at lower pH whereas the electrostatic repulsion between perchlorate and the negatively charged surface took place as increased pH.

Measurements of pH change before and after the perchlorate adsorption with synthesized aluminum hydroxide were conducted. Same measurements were also carried out for a control test in which the batch reactor contained only synthesized aluminum hydroxide without perchlorate. It was found that the solution pH increased from 4.5 to about 6.0 during the perchlorate adsorption with aluminum hydroxide; however, same behavior was also observed in the control test. This indicated that the increase in pH was not caused by ligand-exchange reactions, which replace



Fig. 4. Effects of pH on the perchlorate adsorption by synthesized aluminum hydroxide. The perchlorate concentration and metal loading was 10 mg L^{-1} and 50 g L^{-1} , respectively.

hydroxyls on the surface by perchlorate. Instead, the pH increase might be due to the amphoteric nature of hydrated alumina surface (Sposito, 1996). Accordingly, this study suggested that perchlorate does not undergo ligand-exchange reactions at the surface of aluminum hydroxide.

4. Conclusions

In this study, we examined the use of acid-washed zero-valent aluminum for perchlorate removal. Perchlorate can be effectively removed after a lag phase. There is no evidence to support that the perchlorate removal is caused by the chemical reduction. A desorption experiment indicated that perchlorate undergoes primarily an adsorption process. The addition of 0.5 mL MgSO₄ (1.0 N) led to a quick desorption of perchlorate. The desorbed perchlorate accounted for 96% of the total amount of perchlorate. Aluminum hydroxide, a product of the aluminum corrosion, has been confirmed as the effective composition for the perchlorate adsorption. Synthesized aluminum hydroxide is capable of adsorbing perchlorate rapidly at slightly acidic pH and desorbing perchlorate by sulfate addition. The adsorption mechanisms can be attributed to the ion-pair formation at the aluminum hydroxide surface.

Acknowledgment

The authors would like to thank National Science Council (NSC), Taiwan ROC for the financial support through NSC Grants (NSC 95-2221-E-390-013-MY3).

References

- Abiola, O.K., Oforka, N.C., Angaye, S.S., 2004. Corrosion behaviour of aluminum in hydrochloric acid (HCl) solution containing mercaptoacetic acid. Mater. Lett. 58, 3461–3466.
- Branzoi, V., Golgovici, F., Branzoi, F., 2003. Aluminum corrosion in hydrochloric acid solutions and the effect of some organic inhibitors. Mater. Chem. Phys. 78, 122– 131.
- Cao, J., Elliott, D., Zhang, W., 2005. Perchlorate reduction by nanoscale iron particles. J. Nanopart. Res. 7, 499–506.
- Chen, L.-H., Huang, C.-C., Lien, H.-L., 2008. Bimetallic iron–aluminum particles for dechlorination of carbon tetrachloride. Chemosphere 73, 692–697.
- Deltombe, E., Pourbaix, M., 1958. Electrochemical behaviour of aluminium potential pH diagram of the system Al-H₂O at 25 °C. Corrosion 14, 496t–500t.
- Gu, B., Dong, W., Brown, G.M., Cole, D.R., 2003. Complete degradation of perchlorate in ferric chloride and hydrochloric acid under controlled temperature and pressure. Environ. Sci. Technol. 37, 2291–2295.
- Horányi, G., Joó, P., 2000. Application of the radiotracer technique for the study of the specific anion adsorption on Al₂O₃ in acidic medium. J. Colloid Interface Sci. 231, 373–378.
- Ishii, K., Ozaki, R., Kaneko, K., Fukushima, H., Masuda, M., 2007. Continuous monitoring of aluminum corrosion process in deaerated water. Corros. Sci. 49, 2581–2601.
- Kasprzyk-Hordern, 2004. Chemistry of alumina, reactions in aqueous solution and its application in water treatment. Adv. Colloid Interface Sci. 110, 19–48.
- Kolics, A., Polkinghorne, J.C., Wieckowski, A., 1998. Adsorption of sulfate and chloride ions on aluminum. Electrochim. Acta 43, 2605–2618.

- Láng, G.G., Horányi, G., 2003. Some interesting aspects of the catalytic and electrocatalytic reduction of perchlorate ions. J. Electroanal. Chem. 552, 197– 211.
- Láng, G., Inzelt, G., Vrabecz, A., Horányi, G., 2005. Electrochemical aspects of some specific features connected with the behavior of iron group metals in aqueous perchloric acid/perchlorate media. J. Electroanal. Chem. 582, 249–257.
- Lehman, S.G., Badruzzaman, M., Adham, S., Roberts, D.J., Clifford, D.A., 2008. Perchlorate and nitrate treatment by ion exchange integrated with biological brine treatment. Water Res. 42, 969–976.
- Li, L., Chen, S.-H., Yang, X.-G., Wang, C., Guo, W.-J., 2004. Pitting corrosion induced current oscillations during electrodissolution of Al in HClO₄ solutions. J. Electroanal. Chem. 572, 41–49.
- Lien, H.-L., Zhang, W., 2002. Enhanced dehalogenation of halogenated methanes by bimetallic Cu/Al. Chemosphere 49, 371–378.
- Lien, H.-L., 2005. Transformation of chlorinated methanes by zero-valent aluminum coupled with Pd/Al₂O₃. Environ. Technol. 26, 663–672.
- Makris, K.C., Sarkar, D., Datta, R., 2006. Aluminum-based drinking-water treatment residuals: a novel sorbent for perchlorate removal. Environ. Pollut. 140, 9–12.
- McCafferty, E., 2003. Sequence of steps in the pitting of aluminum by chloride ions. Corros. Sci. 45, 1421–1438.
- Moore, A.M., De Leon, C.H., Young, T.M., 2003. Rate and extent of aqueous perchlorate removal by iron surfaces. Environ. Sci. Technol. 37, 3189–3198.
- Oh, S.-Y., Chiu, P.C., Kim, B.J., Cha, D.K., 2006. Enhanced reduction of perchlorate by elemental iron at elevated temperatures. J. Hazard. Mater. B 129, 304-307.
- Parette, R., Cannon, F.S., 2005. The removal of perchlorate from groundwater by activated carbon tailored with cationic surfactants. Water Res. 39, 4020–4028. Phambu, N., 2003. Characterization of aluminum hydroxide thin film on metallic
- aluminum powder. Mater. Lett. 57, 2907–2913. Sivaraj, C., Reddy, B.P., Rao, B.R., Rao, P.K., 1986. Preparation of catalytically active
- γ-Al₂ O₃ from a basic aluminum succinate precursor precipitated from homogeneous solution. Appl. Catal. 24, 25-35.
- Son, A., Lee, J., Chiu, P.C., Kim, B.J., Cha, D.K., 2006. Microbial reduction of perchlorate with zero-valent iron. Water Res. 40, 2027–2032.
- Sposito, G. (Ed.), 1996. The Environmental Chemistry of Aluminum, 2nd ed. CRC Press, Boca Raton.
- Studart, A.R., Innocentini, M.D.M., Oliveira, I.R., Pandolfelli, V.C., 2005. Reaction of aluminum powder with water in cement-containing refractory castables. J. Eur. Ceram. Soc. 25, 3135–3143.
- Ujvári, M., Láng, G., Horányi, G., 2002a. Stability of perchlorate ions in acid medium: interaction with zinc and aluminum. J. Electroanal. Chem. 32, 581–582.
- Ujvári, M., Láng, G., Horányi, G., 2002b. Stability of perchlorate ions in acid medium: interaction with iron. J. Appl. Electrochem. 32, 1403–1406.
- Urbansky, E.T., 2002. Perchlorate as an environmental contaminant. Environ. Sci. Pollut. Res. 9, 187–192.
- US Environmental Protection Agency, 2004. Known Perchlorate Releases in the US http://www.epa.gov/fedfac/pdf/detection_with_dates_12_10_04.pdf>.
- US Environmental Protection Agency, 2005. EPA Sets Reference Dose for Perchlorate. http://yosemite.epa.gov/opa/admpress.nsf/0/c1a57d2077c4bfda-85256fac005b8b32?OpenDocument.
- Wang, D.M., Ismat Shah, S., Chen, J.G., Huang, C.P., 2008. Catalytic reduction of perchlorate by H₂ gas in dilute aqueous solutions. Sep. Purif. Technol. 60, 14–21.
- Wang, D.M., Lin, H.Y., Ismat Shah, S., Ni, C.Y., Huang, C.P., 2009. Indirect electrochemical reduction of perchlorate and nitrate in dilute aqueous solutions at the Ti–water interface. Sep. Purif. Technol. 67, 127–134.
- Xiong, Z., Zhao, D., Pan, G., 2007. Rapid and complete destruction of perchlorate in water and ion-exchange brine using stabilized zero-valent iron nanoparticles. Water Res. 41, 3497–3505.
- Yoon, I.-H., Meng, X., Wang, C., Kima, K.-W., Bang, S., Choe, E., Lippincott, L., 2009. Perchlorate adsorption and desorption on activated carbon and anion exchange resin. J. Hazard. Mater. 164, 87–94.
- Yu, X., Amrhein, C., Deshusses, M.A., Matsumoto, M.R., 2006. Perchlorate reduction by autotrophic bacteria in the presence of zero-valent iron. Environ. Sci. Technol. 40, 1328–1334.