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Electrodialytically assisted catalytic reduction (EDACR) of perchlorate in dilute aqueous solutions

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Abstract

Perchlorate is an emerging contaminant that has received much attention among the public and private sectors in water purification. There is need for innovative technology to remove perchlorate from dilute aqueous solutions at reasonable reaction rate and to reduce it to potentially benign states such as chloride simultaneously. This study investigated the removal of perchlorate using hydrogen as the major electron donor using an electrodialytically assisted electrocatalytic process. The process superimposes an electrodialysis process on a catalytic medium that functions as a cathode. The electrodialysis system facilitates the transport of anionic perchlorate toward the cathodically charged catalytic medium and brings about an accumulation of perchlorate at the vicinity of the catalytic medium surface. The catalytic medium is a stainless steel mesh coated with nano-sized metallic catalysts. Upon the application (at constant current) of a cathodic current, hydrogen atoms are generated which react rapidly with the weakly adsorbed perchlorate on the surface of catalysts. Results indicated that the electrodialytically assisted catalytic reduction (EDACR) system was able to reduce perchlorate at low concentrations (i.e., 10–100 ppm) in synthetic solutions. The reduction reaction can be described by the Langmuir–Hinshelwood kinetics with an observed rate constant (k'_{obs}) of 2.4×10^{-4} M/h. Under ultra-low perchlorate concentrations, i.e., <1 ppm, the reaction is limited by the surface concentration of perchlorate. Improvement of the perchlorate reduction can be made by the addition of multivalent metal ions, such as Ti^{4+}. The presence of Ti^{4+} ions enhances the accumulation of perchlorate at the catalytic medium surface, which greatly facilitates perchlorate reduction. The perchlorate reduction was rapid following a first-order kinetics with rate constant of $5.33\,\mathrm{d}^{-1}$ (or $0.22\,\mathrm{h}^{-1}$). The concentration of perchlorate decreased drastically from 1000 to 120 ppb in 9 h, or an 88% removal in this EDACR system.

Keywords: EDACR system; Perchlorate removal; Catalytic reduction

1. Introduction

Perchlorate salts are of important national strategic concern [1]. The production of explosives, pyrotechnics, and blasting formulations for military applications contribute mostly to the occurrence of perchlorate in the environment [2,3]. To a limited extent, perchlorate also occurs naturally in the Chilean caliche and has been detected in the fertilizer derived from the nitrate mineral [4]. Perchlorate ion is extremely persistent in the environment [1–3]. Recent surveys by the US EPA and American Water Works Association (AWWA) indicate that perchlorate is present in groundwater and surface water at harmful concentrations in more than 26 states in USA [5,6]. Perchlorate may affect human and animal health through multiple pathways of exposures. The toxicological mechanism of perchlorate has been reviewed in some details [7,8]. Perchlorate can competitively inhibit iodide uptake, reduce thyroid hormone production and further affect normal metabolism, growth, and development of organisms [7–11]. The National Academy of Engineers has currently recommended an RfD of $0.0007\,\mathrm{mg\,kg^{-1}\,d^{-1}}$, which yields a drinking water equivalent limit of 24.5 ppb assuming a relative source contribution (RSC) of 100% and a 2.0-L daily water intake for a 70-kg adult. In summary, there is a current national interest and concern about this emerging contaminant in drinking water among the public and the private sectors.

Currently ion-exchange and biological processes and their combinations are the major practices in perchlorate remediation/treatment [12]. Other emerging technologies such as membrane separation, electrodialysis, adsorption, and chemical reduction are in the development stage [13]. It has been reported that perchlorate ion can be biologically reduced to chloride completely [14–18]. Logan and LaPoint studied the reduction of perchlorate with hydrogen gas as the electron donor and reported a degradation rate constant of ca. $0.7\,\mathrm{d}^{-1}$ [19]. In another study,

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Logan et al. observed the microbial reduction of perchlorate in high-salinity solutions that was produced from the treatment of perchlorate by ion-exchange approach [20]. Also, Cang et al. reported the perchlorate reduction in high salt solutions by cultured activated sludge [21]. In spite of the effectiveness, the biological technology has suffered from low public acceptance when it is applied to the treatment of drinking water. Currently ion-exchange process has been successfully demonstrated also. However, the process cannot decompose perchlorate and the exhausted resins must be regenerated [22–25]. Likewise, membrane separation such as nano-filtration and reverse osmosis can effectively remove perchlorate from water but cannot transform it chemically [26]. Fouling and inherent high treatment cost are major technological challenges of the membrane separation technology [26]. Adsorption is another alternative. Adsorbent such as granular activated carbon (GAC) is one of the most common perchlorate sorbers [27–29]; nonetheless, it does not bring about degradation. Thermal decomposition or radiolysis can transform perchlorate to its reduced states specifically chloride [30,31]. However, it is impractical due to its large energy consumption and extreme reaction conditions.

Electrochemical reduction of perchlorate is practically appealing. There have been efforts to reduce perchlorate electrochemically since the early 1900s [32–46]. Electrochemical reduction is an easy operation and has high public acceptance. Unfortunately, the chemical inertness of perchlorate makes the reaction rate extremely slow. In order to facilitate the rate of electrochemical reduction of perchlorate, extreme experimental conditions such as high perchlorate concentrations (e.g., >100 ppm) and acidic pH (e.g., <2–3) are needed [32,35–38,41,45].

In conclusion, none of current treatment technologies provides effective removal and destruction of perchlorate at low concentrations and under ambient conditions. The objectives of this study were (1) to verify the hypothesis that catalytically generated hydrogen can contribute to effective perchlorate reduction, (2) to study the feasibility of enhancing perchlorate reduction assisted by the electrodialytic ion transport, and (3) to assess the technical capability of the electrodialytically assisted catalytic reduction at low perchlorate concentrations, e.g., <1000 ppb under ambient conditions.

2. Materials and methods

2.1. Chemicals and materials

Deionized water was prepared in the laboratory using a water-purification system (Mega-Pure System, Model MP-290) and was used in all experiments. Perchlorate acid (67–71%), sodium perchlorate (>95%), ammonium perchlorate (>98%), potassium chlorate (>98%), sodium chlorite (>80%), and sodium chloride (>99.5%) were purchased from Sigma–Aldrich (Allentown, PA). All chemicals used for the preparation of catalytic media, including platinum chloride (>98%), stannous (II) chloride (>99%), titanium (III) oxide (>99.9%), cobalt (II) nitrate (>98%), rhodium (III) chloride hydrate (>99.9%), and ruthenium chloride hydrate (>99.98%) were purchased from Sigma–Aldrich Company (Allentown, PA). Titanium sulfate (>80%) was purchased from the Fisher Scientific Company (Pittsburgh, PA). All chemicals were used as received.

Stainless mesh (openings 0.1 mm, thickness 0.25 mm) was purchased from InterNet (Anoka, MN). Ion-exchange membrane (AMX, CMX) was purchased from Tokuyama Soda Inc. (Burlingame, CA).

2.2. Preparation of catalytic media (CM)

The raw stainless steel mesh was cut into small pieces (e.g., 40 mm × 40 mm) upon receipt in the laboratory. The materials were washed with sulfuric acid solution (0.01 M) by being immersed in the cleaning solution while being hung on a mixing motor, which was rotated slowly at a speed of <10 rpm. After 2 min, the medium was rinsed with DIW water for three successive times. Each mesh pieces was dried in an oven at 50 °C and weighed before being coated of metallic catalyst. The metal ion solutions were prepared by dissolving the appropriate chemicals in DIW water at a concentration in the range of 0.01 mM to 0.1 M depending on the solubility of the metal salts. The acid-washed mesh medium was hung again on the same motor, and immersed in the appropriate metal ion solution for the coating of metallic catalyst. An electroplating system was set up with mesh as the cathode and graphite as the anode. When the motor began to rotate at a speed of 20 rpm, a dc potential was applied to provide a constant current of 20–100 mA. The coating time was between 1 and 20 min dependent on the metal ion concentration and current density used. After electroplating, the catalytic medium was washed at least three consecutive times with DIW before drying in an oven. The final weight of each catalytic medium was recorded after drying. The surface density of the catalyst was determined by the weight difference before and after electroplating.

2.3. Reduction of perchlorate in the catalytic medium-only system

Perchlorate solution was prepared by dissolving a suitable amount of ammonium perchlorate into a given volume of deionized water. About 50 L of perchlorate solution with a concentration of 10 ppm was prepared. For each reduction experiment, a total of 1.5 L of the perchlorate solution was used. The main configuration of the reactor consists of a glass vessel with the catalytic medium placed in its bottom section. The catalytic medium was the cathode and the anode was an iron rod. A power supply (Model FB1000, Fisher) was used to drive the electrocatalytic reduction under constant current operation. This system was termed as catalytic medium (CM)-only system as shown in Fig. 1a.

2.4. Electrodialytic concentration of perchlorate

In order to prove that perchlorate was successfully transported toward the catalytic medium, experiments were conducted using a one-membrane electrodialysis system. A perchlorate solution at an initial concentration of 40 ppm was