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# Electrodiallytically 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 electrodiallytically 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 electrodiallytically 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 ( $k'_{\text{obs}}$ ) of  $2.4 \times 10^{-4}$  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  $\text{Ti}^{4+}$ . The presence of  $\text{Ti}^{4+}$  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  $5.33 \text{ d}^{-1}$  (or  $0.22 \text{ h}^{-1}$ ). The concentration of perchlorate decreased drastically from 1000 to 120 ppb in 9 h, or an 88% removal in this EDACR system.

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**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  $0.0007 \text{ mg kg}^{-1} \text{ d}^{-1}$ , 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.  $0.7 \text{ d}^{-1}$  [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)

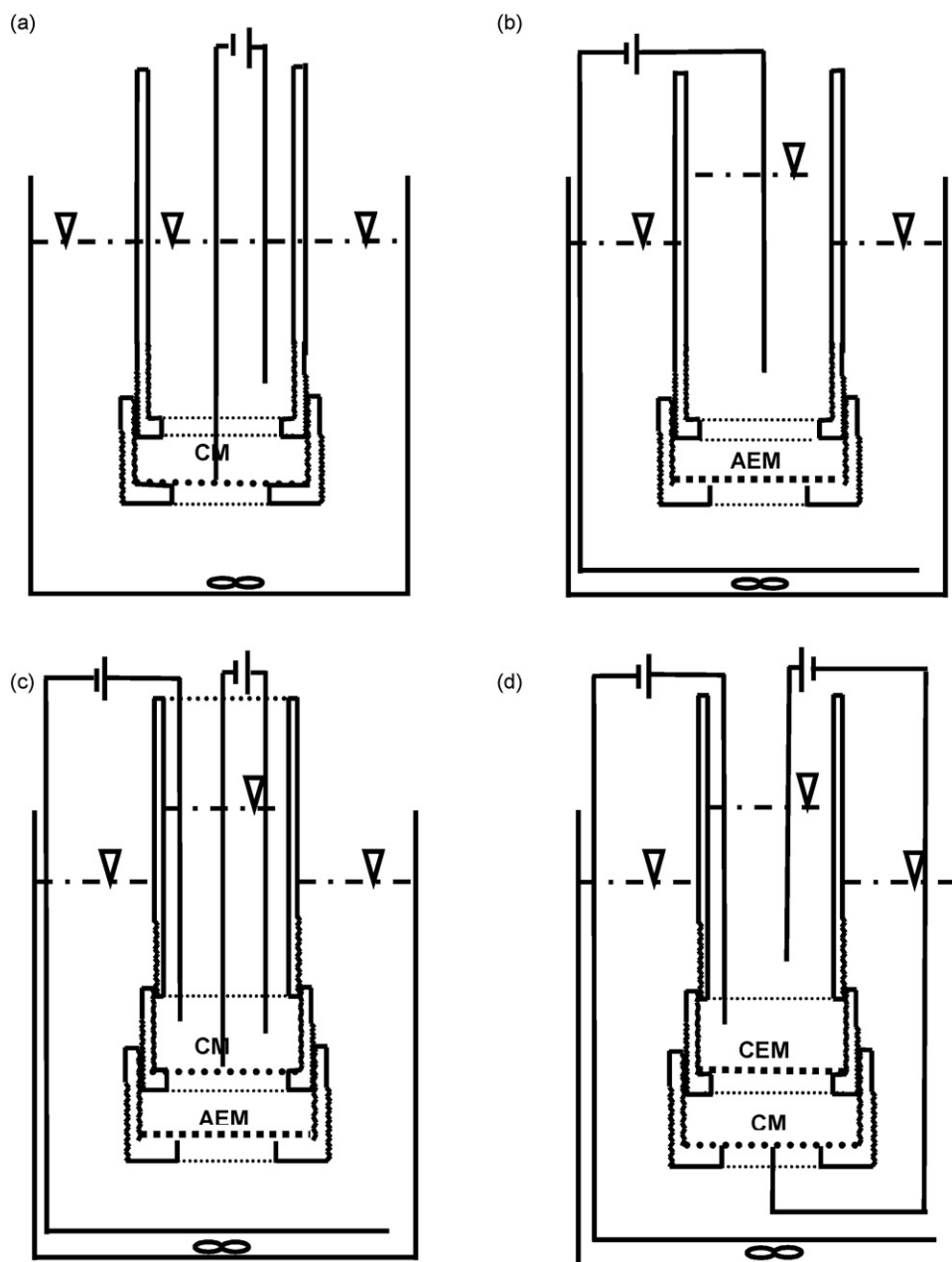
The raw stainless steel mesh was cut into small pieces (e.g., 40 mm × 40 mm) upon receipt in the laboratory. The materials were washed with sulfuric acid solution (0.01 M) by being immersed in the cleaning solution while being hung on a mixing motor, which was rotated slowly at a speed of <10 rpm. After 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



prepared and introduced into the container. The reactor was filled with the supporting electrolyte of NaOH solution at a concentration of 0.01 M. The system was termed as ED-AEM as shown in Fig. 1b. Both the concentration of perchlorate ions in the reactor and the container were monitored.

The electrodiallytically assisted catalytic reduction system consists of three major components: the container, the reactor, and the power supply units. The container was a reaction flask made of Pyrex glass with a volume of 2 L. The reactor

was made of plastic (ID = 7.5 cm;  $H$  = 20 cm) with a catalytic medium and an anion-exchange membrane installed at its bottom section. The catalytic medium (CM) functioned as a cathode as described above. An anode (e.g., iron rod) was placed in the reactor as a counter electrode. The anion-exchange membrane (AEM) together with the applied electrical field functioned as a single-membrane electrodialysis unit that separated the bulk solution in the container and the reactor. A power supply (Model WP705B, Vector-VID) provided a constant potential to facilitate the transport of perchlorate ion from the bulk to the catalytic membrane was used. The volume between the CM and the AEM was less than 1 mL. The electrocatalytic reduction reaction was driven by a separated power supply (Model FB1000,

Fisher Scientific Company, USA), which supplied constant current for the generation of hydrogen atoms at the catalytic medium surface. This experimental setup was termed an A-EDACR system. Fig. 1c shows the corresponding sketch of the laboratory A-EDACR system.

## 2.6. Reduction of perchlorate at different concentrations

Reduction of perchlorate was conducted at initial perchlorate concentrations in the range of 8.3–79.2 ppm. The ambient conditions were kept constant throughout the experiments. Perchlorate solution with a volume of 1500 mL was added to the container first. Then the reactor was placed in the container. The distance between the bottom of the reactor and that of the container was about 6 cm. The reactor was then added 50 mL of supporting electrolyte (0.01 M of NaOH). The electrocatalytic reduction reaction was initiated by turning on both power supplies. Table 1 lists the detailed experimental conditions of all experiments.

## 2.7. Reduction of perchlorate at low concentrations in the presence of $Ti^{4+}$ species

It is speculated that the presence of multivalent metal ions such as  $Ti^{4+}$  may promote the accumulation of perchlorate on the catalytic and enhance the perchlorate reduction especially when the perchlorate concentration was low. In order to test the hypothesis,  $Ti^{4+}$  species were selected mainly because Ti was the catalyst, although this is not the major criterion.  $Ti^{4+}$  has good affinity toward perchlorate and the Ti surface, which will promote reaction. Moreover,  $Ti^{4+}$  is non-toxic. The catalytic perchlorate reduction experiments were conducted at initial perchlorate concentration of 1.0 ppm. A cationic instead of anionic membrane was used and the polarity of the electric field was reversed accordingly. For this experiment, as indicated above, the catalytic medium was coated with Ti and was brought into direct contact with the bulk solution. Due to the acidic pH in the reactor compartment, the cation-exchange membrane was used to separate the bulk solution from the supporting electrolyte. The pH of bulk solution and supporting electrolyte are 5.6 and 0.7,

respectively. The supporting electrolyte was  $Ti(SO_4)_2$  solution at a concentration of 0.01 in 0.1 M sulfuric acid. The applied field strength was constant at 1 V/cm. This experimental device was termed the C-EDACR system as shown in Fig. 1d. Table 1 lists the detailed experimental conditions.

## 2.8. Sampling and chemical analysis

Samples were collected from the “container” with 10-mL disposable syringes. All samples were filtered through the membrane filter (<0.2  $\mu$ m, Fisher Scientific, CA) to remove any solid particles that might be present in the solution. Perchlorate, chlorate, chlorite, and chloride were analyzed using a Dionex ion chromatograph system with a GP50 pump, conductance detector, and an EG 40 effluent generator. Ion separation was brought by a 4-mm Dionex AS-11 anion-exchange analytical column. For experiments with initial perchlorate concentration greater than 1 ppm, a 25- $\mu$ L injection loop was used for perchlorate analysis and a 1000- $\mu$ L injection loop was used instead when the initial perchlorate concentration was less than 1 ppm. The detection limits for this system were 1, 10, 10, and 20 ppb for chloride, perchlorate, chlorite, and chlorate, respectively.

# 3. Results and discussion

## 3.1. Reduction of perchlorate in CM-only system

Fig. 2 shows the reduction of perchlorate using the CM-only system in the presence of various bimetallic catalysts, namely, Co–Rh, Co–Cr, and Co–Ru at an initial perchlorate concentration of 10 ppm. The reduction of perchlorate took place on the cathode (i.e., catalytic medium) surface where hydrogen atoms were being generated. The end products varied depending on the type of catalysts present on the SS mesh. For example, the percent perchlorate reduction was near 40% in 12 h for the Co–Rh coated medium and the predominant end product was chlorite. The release of gaseous chlorine rendered the chlorine mass imbalanced. For the Co–Cr coated SS mesh, the end product was chlorite but the rate was slower than that of the Co–Rh catalyst whereas the mass balance condition was well main-

Table 1  
Experimental conditions using the EDACR systems

Condition	Fig. 4	Fig. 5	Fig. 6
System	A-EDACR	A-EDACR	C-EDACR
Container volume (L)	2	2	2
Diameter of reactor (cm)	~3	~5	~5
Reactor volume (mL)	100	300	300
ED membrane	Anion-exchange	Anion-exchange	Catalytic-exchange
Supporting electrolyte	0.01 M NaOH	0.01 M NaOH	0.01 M $Ti(SO_4)_2$
Perchlorate concentration (ppm)	8.3–79.2	2.3	1.0
Anode	Iron rod	Iron rod	Iron rod
Cathode	Sn (CM)	Pt–Ti (CM)	Pt–Ti (CM)
Temperature ( $^{\circ}$ C)	25	25	25
pH	5.6–6.0	5.6	5.6
Current (mA)	10	10	5
Potential (V)	~10	~20	~10

CM: catalytic medium, e.g., SS mesh coated with catalysts.

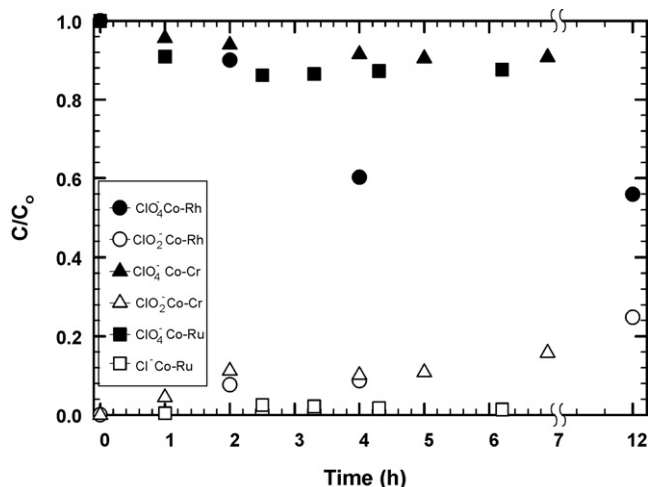


Fig. 2. Reduction of  $\text{ClO}_4^-$  in CM-only system. Experimental conditions—perchlorate concentration: 10 ppm; temperature: 25 °C; pH 5.6; anode: Fe; cathode: SS mesh coated with catalysts; voltage applied: ~20 V; current: 10 mA.

tained. However, for the Co–Ru coated SS mesh the predominant end product was chloride and there was imbalance of chlorine mass.

Results clearly indicated the capability of perchlorate reduction at the catalytic medium surface. Apparently, the lowering of activation energy in the presence of catalysts promotes the perchlorate reduction. However, the slow reaction rate makes the process impractical for common water treatment. Low perchlorate concentration at the negatively charged (cathodic) catalytic medium could cause the slow reduction rate. Intuitively the reduction of perchlorate in aqueous solutions would be dependent on the perchlorate concentration [32,47–49].

### 3.2. Electrodialytic concentration of perchlorate

In order to enhance the reaction rate, attempt was made to increase the perchlorate concentration at the catalytic SS medium surface by electrodialysis (ED). It is expected that the ED system will provide transport mechanism for the perchlorate ion. Fig. 3 shows the increase in perchlorate concentration by the one-membrane ED system. It can be seen that the single-membrane ED system can transport the perchlorate from the “container” to the “reactor” in 8 h under an electric field of 2 V/cm readily. It is interesting to note that the perchlorate concentration decreased exponentially in the “container”. However, perchlorate disappeared from the “container” did not show up in the “reactor” immediately; rather there was a lag (ca. 1 h) in the transport of perchlorate across the anionic membrane. Apparently the anionic membrane retained the perchlorate ions briefly before releasing them to the solution. Once the perchlorate was freed from the anionic membrane, the perchlorate concentration increased exponentially. A 100% of perchlorate transport was possible. Electrodialytic transport can play a key role in the perchlorate reduction reaction.

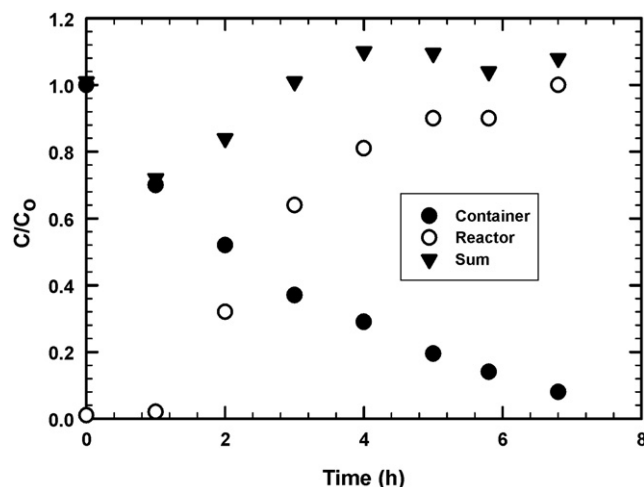


Fig. 3. Concentration of perchlorate ions by single-membrane electrodialysis. Experimental conditions—perchlorate concentration: 40 ppm; ion-exchange membrane: anion membrane; temperature: 25 °C; pH 5.6; anode: Fe; cathode: Fe; ED voltage applied: ~10 V; current: ~10 mA.

### 3.3. Reduction of perchlorate at different concentrations

Based on the above results it is expected that by superimposing the electrodialysis over the catalytic reduction, it is possible to improve the perchlorate removal rate. This is the electrodialytically assisted catalytic reduction (EDACR) system. Fig. 4a shows the change in perchlorate concentration with time at various initial perchlorate concentrations using the A-EDACR system. Results indicated significant increase in perchlorate reduction compared with the CM-only system (Fig. 2). The higher the initial concentration, the greater was the removal efficiency. The initial reaction rates were 6.9, 22.9, 61.3, and 76.5 M/h for the initial perchlorate concentration of 8.3, 23.1, 61.3, and 79.2 ppm, respectively. Further analysis of the rate constants revealed that the perchlorate reduction could be described by the Langmuir–Hinshelwood equation, i.e.

$$-\left(\frac{dC}{dt}\right)_o = r_o = k_{\text{obs}} \frac{\Gamma_m C}{K + C} \quad \text{or} \quad r_o = k'_{\text{obs}} \frac{C}{K + C}, \quad (1)$$

where  $k_{\text{obs}}$ ,  $k'_{\text{obs}}$ ,  $\Gamma_m$ ,  $K$ , and  $C$  are the observed rate constant, apparent observed rate constant, perchlorate adsorption density at the monolayer level, adsorption constant, and residual perchlorate concentration, respectively. A linearized plot of the Langmuir–Hinshelwood equation (Fig. 4b) yields slope and intercept from which the value of  $(k_{\text{obs}} \Gamma_m)$  and  $K$  were obtained ( $2.4 \times 10^{-4}$  M/h and  $1.9 \times 10^{-3}$  M, respectively). From the adsorption constant, the free energy of perchlorate adsorption on the catalytic medium was calculated to be ca. 15.0 kJ/mol. This is a small value, which implies that the perchlorate adsorption onto the catalytic medium surface was rather weak. The excellent fit of the rate constant with the Langmuir–Hinshelwood equation clearly indicated that the reduction reaction was limited by the surface concentration of perchlorate.

The rate constant,  $k_{\text{obs}}$ , can be estimated from separated perchlorate adsorption experiments. Several researchers have reported the adsorption of perchlorate on various electrodes.



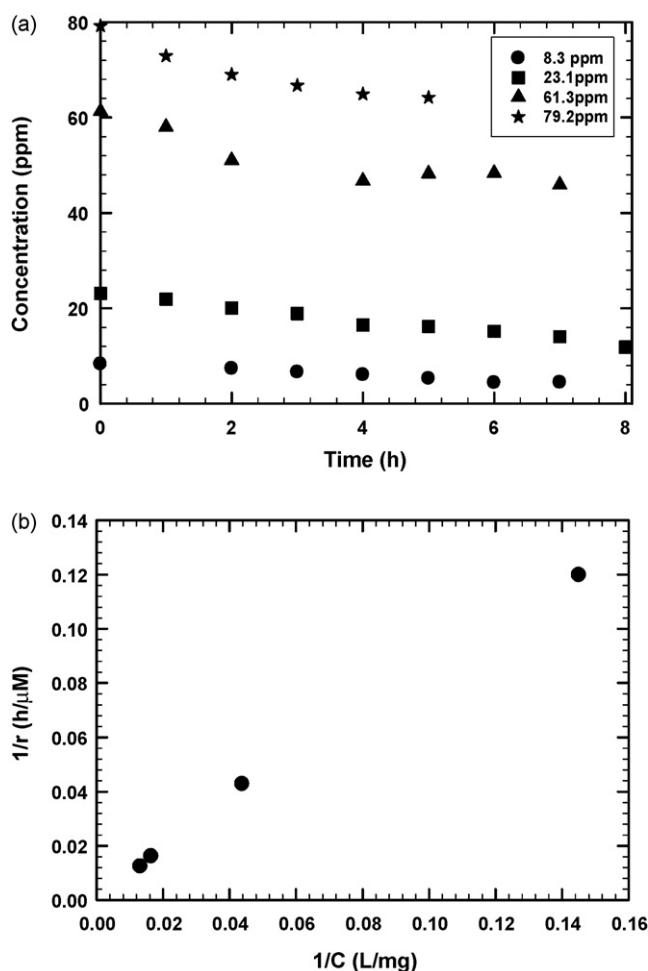


Fig. 4. Removal of  $\text{ClO}_4^-$  at various initial perchlorate concentrations anionic-electrodiallytically assisted catalytic reduction (A-EDACR) process. Experimental conditions—perchlorate concentration: 8.3–79.2 ppm; temperature: 25 °C; pH 5.6–6.0; anode: Fe; cathode: SS mesh coated with Sn; voltage applied:  $\sim 10$  V; current: 10 mA. ED voltage applied: 10 V. (a) Change of perchlorate concentration as a function of reaction time and (b) the Langmuir–Hinshelwood plot.

Goodrich and Schmid studied the adsorption of perchlorate on Au electrode [50]. Naneva et al. investigated the specific adsorption of perchlorate, nitrate, and nitrite ions on crystalline Cd surface and reported that perchlorate ion was the weakest among all oxyanions studied [51]. Niaura and Malinauskas compared the adsorption of perchlorate and sulfate on Cu electrode and reported that perchlorate was nonspecifically adsorbed [52]. It was commonly agreed that the adsorption density of perchlorate at the surface of electrode was insignificant. With an assumed  $\Gamma_m$  value of  $10^{-8}$  mol/cm<sup>2</sup> (i.e., each adsorbed perchlorate will occupy a surface area of  $10 \text{ \AA}^2$ ), the  $k_{\text{obs}}$  would be  $6 \times 10^{-7} \text{ cm}^{-1} \text{ s}^{-1}$ . (Note: The observed rate constant has the unit of specific surface area of the electrode per volume solution per time, i.e.,  $\text{cm}^2 \text{ cm}^{-3} \text{ s}^{-1}$ .)

Results clearly demonstrated that the superimposition of the single-membrane electrodialysis over the catalytic reduction process greatly enhanced the accumulation of perchlorate on the negatively charged catalytic medium surface, which in turn significantly enabled the perchlorate reduction at low concentration

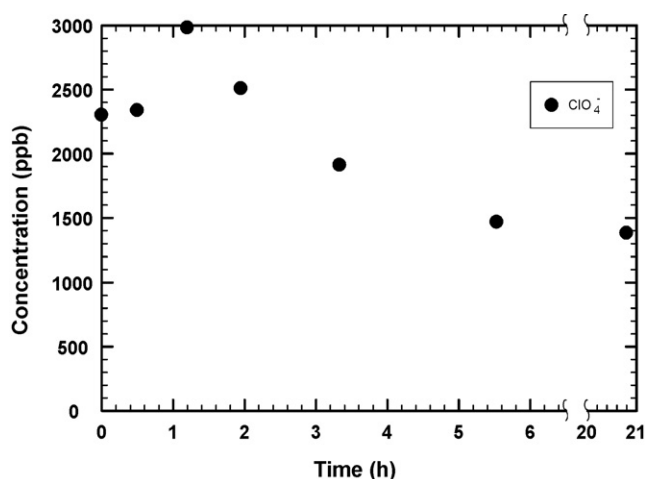


Fig. 5. Reduction of  $\text{ClO}_4^-$  at low concentrations using the anionic-electrodiallytically assisted catalytic reduction (A-EDACR) process. Experimental conditions—perchlorate concentration: 2300 ppb; CM: SS mesh coated with Pt and Ti; ion-exchange membrane: anion membrane; temperature: 25 °C; pH 5.6; anode: Fe; cathode: CM; voltage applied:  $\sim 20$  V; current: 10 mA. ED voltage: 10 V.

and under ambient conditions. If a high concentration of perchlorate at the vicinity of the catalytic medium can be maintained, perchlorate can be readily reduced to chloride eventually. The electrodiytically assisted catalytic reduction (EDACR) system provides an excellent solution to the removal of perchlorate under ambient conditions and low perchlorate concentrations, specifically, 10–100 ppm or greater.

### 3.4. Perchlorate reduction in the presence of $\text{Ti}^{4+}$ species

The perchlorate treatability of the EDACR system was further assessed at extremely low perchlorate concentration of 2.3 ppm (Fig. 5). Results indicated that the perchlorate concentration increased from 2.3 to 3.15 ppm quickly during the first hour then decreased sharply from 3.15 to 1.4 ppm at the end of 21 h following a first-order reaction and a rate constant of ca.  $0.16 \text{ h}^{-1}$  or  $3.84 \text{ d}^{-1}$  during the initial 1–6 h. The reaction then became slow and eventually stopped with concentration remaining low at ca. 1.4 ppm.

To deal with such circumstance, it is necessary to decrease the activation energy further and to increase the perchlorate concentration at the catalytic medium surface. To this end, multivalent metal species, specifically,  $\text{Ti}^{4+}$  was added to the “reactor”. Fig. 6 shows results of perchlorate reduction using the C-EDACR system in the presence of  $\text{Ti}^{4+}$  ions. (Note: In order to facilitate the transport toward and subsequent accumulation of  $\text{Ti}^{4+}$  at the cathode, a cation, instead of anion, selective membrane must be used.) It can be seen that the perchlorate reduction was rapid following first-order kinetics and with a rate constant of  $0.22 \text{ h}^{-1}$  or  $5.33 \text{ d}^{-1}$ . The concentration of perchlorate decreased drastically from 1000 to 120 ppb in 9 h, or an 88% removal. This is a drastic improvement over the A-EDACR system. The chloride concentration increased immediately following the rapid reduction of perchlorate then decreased when the reaction by-products such as chlorite ( $\text{ClO}_2^-$ ) and chlorate ( $\text{ClO}_3^-$ ) appeared. The total

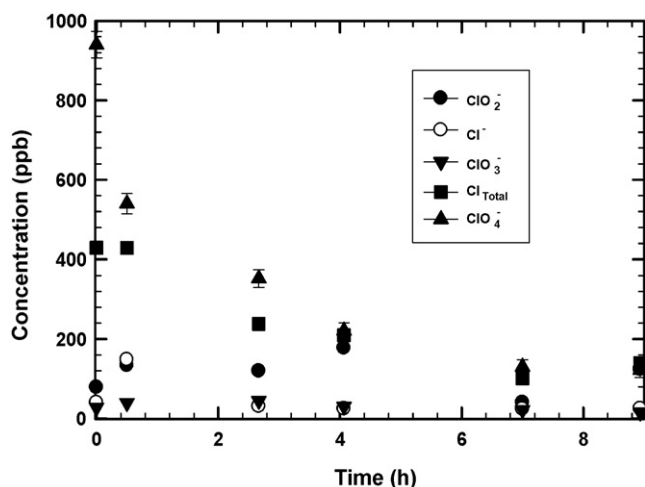


Fig. 6. Reduction of  $\text{ClO}_4^-$  at ultra-low concentration using the C-EDACR system. Experimental conditions—perchlorate concentration: 1000 ppb; CM: SS mesh coated with Pt–Ti; ion-exchange membrane: cation membrane; supporting electrolyte (in the reactor): 0.01 M of  $\text{Ti}(\text{SO}_4)_2$  in 0.1 M sulfuric acid solution; temperature: 25 °C; pH 5.6; anode: Fe; cathode: CM; voltage applied: ~10 V; current: 5 mA.

chlorine concentration, that is the sum of all chlorine containing species, decreased with reaction time. This can be attributed to the adsorption and/or doping onto solid product, which was not included in IC analysis. (Note: About 4% chlorine was found by examine the element composition of residual solid by-product using SEM/EDX.)

The accumulation of  $\text{Ti}^{4+}$  species at the catalytic medium also brought additional perchlorate reduction via the reaction between the  $\text{Ti}^{3+}$  (produced at cathode by reducing  $\text{Ti}^{4+}$ ) species and perchlorate in addition to reduction via atomic hydrogen. As indicated in Fig. 4, the A-EDACR system (Fig. 1c) failed to bring about rapid reduction of perchlorate during the first hour and the rate constant was slightly smaller than that of the C-EDACR system, i.e., rate constant of  $3.84 \text{ d}^{-1}$  versus  $5.33 \text{ d}^{-1}$ .

It must be mentioned that the surface property at the vicinity of the catalytic SS medium was improved in the presence of  $\text{Ti}^{4+}$  ions. The  $\text{Ti}^{4+}$  ions arrived at the catalytic SS medium surface after passing through the cation-exchange membrane (CEM). As a result, the surface of the catalytic SS medium can be rendered positive, i.e., charge reversal due to specific  $\text{Ti}^{4+}$  adsorption. These positively charged sites would facilitate the adsorption of perchlorate ions, which could increase the sticky coefficient between the perchlorate ions and the catalyst. Finally,  $\text{Ti}^{4+}$  ions, in addition to enhancing the adsorption of perchlorate ions on the catalyst surface, could contribute to the perchlorate reduction reaction when they were reduced to  $\text{Ti}^{3+}$  or  $\text{Ti}^{2+}$  species on the cathodic medium surface. The reaction between  $\text{Ti}^{3+}$  and/or  $\text{Ti}^{2+}$  species and adsorbed perchlorate ions was fast. Consequently, the catalytic medium surface was renewed quickly, which readied it for resuming the perchlorate reduction activity, which is essential to the situation of extremely low initial perchlorate concentrations, i.e., <1 ppm.

However, as shown in Fig. 6, the perchlorate reduction reached a steady state at the perchlorate concentration of about 100 ppb. This could be attributed to the diffusion-limiting. When

the perchlorate concentration in the bulk solution was ultra-low, the presence of electrical double layer of the catalytic medium surface hindered the approach of perchlorate ions. Ultra-low perchlorate concentrations at the catalytic medium decreased the reduction rate. This situation can be drastically improved by the increase the concentration of inert electrolyte of non-perchlorate type such as chloride as to decrease the Deby length. The capability of the C-EDACR system in the presence of  $\text{Ti}^{4+}$  to reduce perchlorate at an initial concentration of 1000 ppb under ambient conditions represents a significant advance. None current process is able to reduce perchlorate at this low concentration and under ambient conditions, however.

#### 4. Conclusion

The electrodialectically assisted catalytic reduction (EDACR) process was developed and assessed successfully for the reduction of perchlorate in dilute aqueous solutions. The EDACR system incorporates the conventional electrodialysis and the electrocatalytic reaction. Results indicated that it is possible to reduce perchlorate to chloride at initial perchlorate concentrations of 10–100 ppm under ambient conditions. Catalytic medium alone, the reduction of perchlorate was very sluggish even in presence of catalysts due to the large activation energy. In order to arrive at reasonable reduction rate, it is necessary to increase the concentration of perchlorate at the vicinity of the catalytic SS medium. This can be accomplished by superimposing the electrocatalytic process with conventional electrodialysis. The deployment of the single-membrane electrodialysis greatly increased the concentration of perchlorate at the vicinity of the catalytic medium. A high reaction rate can be achieved accordingly. Furthermore, the selectivity of ion-exchange membrane (or other barrier) will determine the transport rate of the contaminant involved. Although only perchlorate removal was investigated in this research, it is believed that the A-EDACR system can be applied to other contaminants, such as nitrate.

The perchlorate reduction in the electrodialectically assisted catalytic reduction (A-EDACR) system is a multiple-step reaction including the transfer, the accumulation, and the reduction of perchlorate. The cathodically generated hydrogen atoms reduced the surface perchlorate following a step-by-step fashion to chloride ultimately. The end product, i.e., chloride eventually diffuses into the bulk solution. The EDACR system enables the lowering of the activation energy and the increase in perchlorate ions at the catalyst surface and brings about rapid perchlorate reduction.

Under extremely ultra-low perchlorate concentration, i.e., ~1 ppm, the reduction reaction reached its minimum apparently limited by the low surface concentration of perchlorate. The addition of multivalent metal ions, specifically  $\text{Ti}^{4+}$ , enabled the rapid and effective degradation of perchlorate. The first-order reduction constant increased from 3.5 to  $5.3 \text{ d}^{-1}$  for the EDACR system in the absence and the presence of  $\text{Ti}^{4+}$  ions, respectively. The reduction constants compared favorably against any current biological de-perchlorate systems, which have average rate constant in the order of  $0.76 \text{ d}^{-1}$ .



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## References

- [1] E.T. Urbansky, Perchlorate chemistry: implications for analysis and remediation, *Biorem. J.* 2 (2) (1998) 81–95.
- [2] E.T. Urbansky, Perchlorate as an environmental contaminant, *Environ. Sci. Pollut. Res. Int.* 9 (3) (2002) 187–192.
- [3] MADEP, the occurrence and sources of perchlorate in Massachusetts, available at: [http://www.swrcb.ca.gov/rwqcb4/html/perchlorate/05\\_0805\\_perchlorate-sources.pdf](http://www.swrcb.ca.gov/rwqcb4/html/perchlorate/05_0805_perchlorate-sources.pdf), 2005.
- [4] S. Susarla, T.W. Collette, A.W. Garrison, N.L. Wolfe, S.C. McCutcheon, Perchlorate identification in fertilizers, *Environ. Sci. Technol.* 33 (19) (1999) 3469–3472.
- [5] US EPA, national perchlorate detections, available at: [http://www.epa.gov/swerrfr/documents/perchlorate\\_map/nationalmap.htm](http://www.epa.gov/swerrfr/documents/perchlorate_map/nationalmap.htm), 2004.
- [6] P. Brandhuber, S. Clark, Perchlorate Occurrence Mapping, American Water Works Association, Washington, DC, 2005, available at: [http://www.awwa.org/Advocacy/govtaff/issues/Issue07\\_Perchlorate.cfm/AWWAOccurrenceStudy](http://www.awwa.org/Advocacy/govtaff/issues/Issue07_Perchlorate.cfm/AWWAOccurrenceStudy).
- [7] J.J.J. Clark, Toxicology of perchlorate, *Environ. Sci. Res.* 57 (2000) 15–29.
- [8] A.B. Kirk, Environmental perchlorate: why it matters, *Anal. Chim. Acta* 567 (1) (2006) 4–12.
- [9] J. Fisher, P. Todd, D. Mattie, D. Godfrey, L. Narayanan, K. Yu, Preliminary development of a physiological model for perchlorate in the adult male rat: a framework for further studies, *Drug Chem. Toxicol.* 23 (1) (2000) 243–258.
- [10] C. Bradford, J. Rinchard, J.A. Carr, C. Theodorakis, Perchlorate affects thyroid function in eastern Mosquitofish (*Gambusia holbrooki*) at environmentally relevant concentrations, *Environ. Sci. Technol.* 39 (14) (2005) 5190–5195.
- [11] M.A. Greer, G. Goodman, R.C. Pleus, S.E. Greer, Health effects assessment for environmental perchlorate contamination: the dose response for inhibition of thyroidal radioiodine uptake in humans, *Environ. Health Perspect.* 110 (9) (2002) 927–937.
- [12] US EPA, perchlorate treatment technology update, available at: <http://www.epa.gov/tio/download/remed/542-r-05-015.pdf>, 2005.
- [13] ITRC, perchlorate: overview of issues, status and remedial options, available at: [http://www.itrcweb.org/gd\\_Perch.asp](http://www.itrcweb.org/gd_Perch.asp).
- [14] E. Hackenthal, W. Mannheim, R. Hackenthal, R. Becher, Reduction of perchlorate by bacteria. I. Intact cells, *Biochem. Pharmacol.* 13 (2) (1964) 195–206.
- [15] B.E. Logan, Assessing the outlook for perchlorate remediation, *Environ. Sci. Technol.* 35 (23) (2001) 482A–487A.
- [16] P.M. Sutton, Bioreactor configurations for ex-situ treatment of perchlorate: a review, *Water Environ. Res.* 78 (13) (2006) 2417–2427.
- [17] D.C. Herman, W.T. Frankenberger, Microbial-mediated reduction of perchlorate in groundwater, *J. Environ. Qual.* 27 (4) (1998) 750–754.
- [18] H. Attaway, M. Smith, Reduction of perchlorate by an anaerobic enrichment culture, *J. Ind. Microbiol.* 12 (6) (1993) 408–412.
- [19] B.E. Logan, D. LaPoint, Treatment of perchlorate- and nitrate-contaminated groundwater in an autotrophic gas phase, packed-bed bioreactor, *Water Res.* 36 (14) (2002) 3647–3653.
- [20] B.E. Logan, J. Wu, R.F. Unz, Biological perchlorate reduction in high salinity solutions, *Water Res.* 35 (12) (2001) 3034–3038.
- [21] Y. Cang, D.J. Roberts, D.A. Clifford, Development of cultures capable of reducing perchlorate and nitrate in high salt solutions, *Water Res.* 38 (14–15) (2004) 3322–3330.
- [22] A.R. Tripp, D.A. Clifford, The treatability of perchlorate in groundwater using ion-exchange technology, *Environ. Sci. Res.* 57 (2000) 123–134.
- [23] B. Gu, Y. Ku, G.M. Brown, Sorption and desorption of perchlorate and U(VI) by strong-base anion-exchange resins, *Environ. Sci. Technol.* 39 (3) (2005) 901–907.
- [24] B. Gu, G.M. Brown, L. Maya, M.J. Lance, B.A. Moyer, Regeneration of perchlorate ( $\text{ClO}_4^-$ ) loaded anion exchange resins by a novel tetrachloroferrate ( $\text{FeCl}_4^-$ ) displacement technique, *Environ. Sci. Technol.* 35 (16) (2001) 3363–3368.
- [25] T. Gillogly, S. Lehman, A. Lee, D. Clifford, D. Roberts, X. Lin, Brine treatment and reuse: demonstrating the options during perchlorate removal by ion-exchange, in: *Proc-Annual Conference, Am. Water Works Assoc.*, 2003, pp. 229–236.
- [26] Y.A. Yoon, G. Amy, S. Liang, J. Cho, Treatability of perchlorate by nanofiltration and ultrafiltration, in: *Proc-Annual Conference, Am. Water Works Assoc.*, 1999, pp. 1855–1860.
- [27] C. Na, F.S. Cannon, B. Hagerup, Perchlorate removal via iron-preloaded GAC and borohydride regeneration, *J. Am. Water Works Assoc.* 94 (11) (2002) 90–102.
- [28] 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.
- [29] R. Parette, F.S. Cannon, The removal of perchlorate from groundwater by activated carbon tailored with cationic surfactants, *Water Res.* 39 (16) (2005) 4020–4028.
- [30] E.E.I. Hackman, Detection of species resulting from condensed phase decomposition of ammonium perchlorate, *J. Phys. Chem.* 70 (24) (1972) 3545–3554.
- [31] D. Katakis, A.O. Allen, The radiolysis of aqueous perchloric acid solutions, *J. Phys. Chem.* 68 (11) (1964) 3107–3115.
- [32] G.P. Haight, W.F. Sager, Evidence for preferential one-step divalent changes in the molybdate-catalyzed reduction of perchlorate by stannous ion in sulfuric acid solution, *J. Am. Chem. Soc.* 74 (23) (1952) 6056–6059.
- [33] G.P. Haight, Mechanism of the tungstate catalyzed reduction of perchlorate by stannous chloride, *J. Am. Chem. Soc.* 76 (18) (1954) 4718–4721.
- [34] G. Horanyi, G. Vertes, Reduction of perchlorates by molecular hydrogen in presence of tungsten carbide, *Inorg. Nucl. Chem. Lett.* 10 (9) (1974) 767–770.
- [35] F. Betpera, B. Jaselskis, Reduction of perchlorate at the dropping mercury-electrode in presence of molybdate, *Electrochim. Acta* 30 (2) (1985) 217–221.
- [36] F. Colom, M.J. Gonzaleztejera, Reduction of perchlorate ion on ruthenium electrodes in aqueous-solutions, *J. Electroanal. Chem.* 190 (1–2) (1985) 243–255.
- [37] G.M. Brown, The reduction of chlorate and perchlorate ions at an active titanium electrode, *J. Electroanal. Chem. Interf. Electrochem.* 198 (2) (1986) 319–330.
- [38] C.K. Rhee, M. Wasberg, G. Horanyi, A. Wieckowski, Strong anion surface interactions-perchlorate reduction on Rh(100) electrode studied by voltammetry, *J. Electroanal. Chem.* 291 (1–2) (1990) 281–287.
- [39] I. Bakos, G. Horanyi, S. Szabo, E.M. Rizmayer, Electrocatalytic reduction of perchlorate ions at an electrodeposited rhenium layer, *J. Electroanal. Chem.* 359 (1–2) (1993) 241–252.
- [40] G. Horanyi, I. Bakos, The electrocatalytic reduction of perchlorate ions in aqueous-solutions, *Ach-Models Chem.* 131 (1) (1994) 25–41.
- [41] F.A. Fernandez, M.S. Cruz, Electrochemical reduction of perchlorate ion at Ir electrodes-ion concentration and solution pH effects, *Anales De Quimica Serie a: Quimica Fisica Y Quimica Tecnica* 81 (3) (1995) 388–390.
- [42] M. Wasberg, G. Horanyi, The Reduction of  $\text{ClO}_4^-$  ions on Rh electrodes, *J. Electroanal. Chem.* 385 (1) (1995) 63–70.
- [43] C.M.V.B. Almeida, B.F. Giannetti, T. Rabockai, Electrochemical study of perchlorate reduction at tin electrodes, *J. Electroanal. Chem.* 422 (1–2) (1997) 185–189.
- [44] T.L. Theis, A.K. Zander, X. Li, J. Sene, M.A. Anderson, Electrochemical and photocatalytic reduction of perchlorate ion, *J. Water Supply Res. Technol.-Aqua* 51 (7) (2002) 367–374.
- [45] G. Lang, G. Inzelt, A. Vrabec, G. Horanyi, Electrochemical aspects of some specific features connected with the behavior of iron group metals in aqueous perchloric acid/perchlorate media, *J. Electroanal. Chem.* 582 (1–2) (2005) 249–257.
- [46] M.Y. Rusanova, P. Polaskova, M. Muzikar, W.R. Fawcett, Electrochemical reduction of perchlorate ions on platinum-activated nickel, *Electrochim. Acta* 51 (15) (2006) 3097–3101.

- [47] F.R. Duke, P.R. Quinney, The kinetics of the reduction of perchlorate ion by Ti(III) in dilute solution, *J. Am. Chem. Soc.* 76 (14) (1954) 3800–3803.
- [48] T.W. Kallen, J.E. Earley, Reduction of perchlorate ion by aquoruthenium(II), *Inorg. Chem.* 10 (6) (1971) 1152–1155.
- [49] M.M. Abu-Omar, Effective and catalytic reduction of perchlorate by atom transfer reaction kinetics and mechanisms, *Comments Inorg. Chem.* 24 (1) (2003) 15–37.
- [50] J.D. Goodrich, G.M. Schmid, Adsorption of perchlorate ions on gold, *J. Electrochem. Soc.* 113 (6) (1996) 626–627.
- [51] R. Naneva, T. Vitanov, N. Dimitrov, V. Bostanov, A. Popov, Adsorption of perchlorate, nitrite and nitrate on the (0 0 0 1) face of a cadmium single crystal, *J. Electroanal. Chem.* 328 (1–2) (1992) 287–293.
- [52] G. Niaura, A. Malinauskas, Adsorption of perchlorate and sulfate ions on copper electrode from acid aqueous solutions as studied by SERS, *Chemija* 4 (1991) 14–32.