

# Monometallic nano-catalysts for the reduction of perchlorate in water

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## ABSTRACT

Perchlorate removal in a clean, cost-effective and publicly acceptable approach is one of the important issues in current drinking water treatment practice. Catalytic membrane (CM) was prepared by coating monometallic catalysts of the nano-size onto supports by chemical or electrochemical method. The support materials were stainless steel and graphite. Nano-catalysts were made of transitional metals from the first, the second and the third row of the periodic table. The CM was characterized by surface analysis techniques including SEM, XPS and BET. The CM was used as cathode where the reduction of perchlorate occurred through hydrogen atoms that were generated on the CM surface. All experiments were performed at ambient conditions. It was found that for the first time perchlorate could be reduced readily by hydrogen atoms in the presence of catalyst. At a maximum perchlorate concentration of 100 mg/L, it is possible to achieve a > 90% removal in 8 h using nano-catalysts such as Sn, Ti, and Co. The rate constants were between 5.1 and 9.6  $\mu\text{M}\cdot\text{L}^{-1}\cdot\text{hr}^{-1}$  among the 18 different monometallic nano-catalysts tested. Chloride was the major end product, whereas a small quantity of chlorite was observed in the presence of Co catalyst. Membrane coated with metallic nano-catalysts at different mass showed different reduction rate, e.g., the optimum surface coverage for Sn was 0.6 to 0.7 mg per gram stainless steel membrane.

**Keywords:** monometallic catalyst, nano-size, perchlorate reduction, electrochemical, hydrogen atoms

## 1 INTRODUCTION

Perchlorate salts, such as ammonium, potassium, and sodium, are important national strategic chemicals [1]. Perchlorate in the environment is mostly contributed from production of explosives, pyrotechnics and blasting formulations [2, 3] in addition to naturally occurring to a limited extent [4].

Perchlorate ion persists in the environment for many years [5, 6]. It is now known that perchlorate is present in groundwater and surface water of more than 20 US states. The detection of perchlorate at elevated concentrations in drinking water supplies in Nevada, Utah, and California in the late 1990s has prompted interest and concern of this new chemical species in the environment.

Perchlorate is a stable ion that may affect humans and other animals through multiple pathways of exposures. The toxicological mechanism through which perchlorate exerts its effects have been reviewed in some detail [7, 8, 9]. The U.S. EPA named perchlorate a contaminant of concern after studies linked the chemical to thyroid disorders and other potential health problems.

Two major technologies were currently suggested for the treatment of large-volume water that contains perchlorate: ion exchange and biological processes or their combinations. Other emerging or studied technologies such as membrane separation, electrodialysis, adsorption and chemical process are not being applied at field treatment facilities.

None of these treatment technologies is feasible for real-world applications due to process cost, operation difficulties, relatively low removal efficiency, difficult in maintenance, low process flexibility, low public acceptance and subsequently low political buyout. More researches are needed for a cost-effective, high efficient and public-acceptable removal process.

## 2 EXPERIMENTAL

### 2.1 Materials

Perchlorate solution was synthesized by dissolving proper perchlorate salt into distilled water. Distilled water was prepared in the laboratory by a water-purification system (Mega-Pure System, Model MP-290). Sodium perchlorate (> 95%), ammonium perchlorate (> 98%), potassium chlorate (> 98%), sodium chloride (> 80%) and sodium chloride (> 99.5%) were purchased from Sigma-Aldrich (Allentown, PA). All chemicals used for the preparation of catalytic membranes, were supplied by different companies, namely, cadmium (II) perchlorate hydrate (> 99.9%), chromium (III) perchlorate hexahydrate, cobalt (II) nitrate (> 98%), cupric sulfate (> 99%), lead chloride (> 98%), manganese chloride (> 97%), molybdenum (II) acetate (> 98%), palladium chloride (> 98%), platinum chloride (> 98%), rhodium (III) chloride hydrate (> 99%), ruthenium chloride hydrate (> 98%), scandium perchlorate (40%), stannous (II) chloride (> 99%), titanium(III) oxide (> 99.9%), vanadium (II) chloride (95%), zirconium(IV) chloride (> 99.5%) from Sigma-Aldrich Company (Allentown, PA); Nickel (II) perchlorate (> 99%) from Johnson Matthey Company, (Wayne, PA) and zinc

chloride (> 99%) from the Fisher Scientific International Inc.. All chemicals were used as received.

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

## 2.2 Preparation of Catalytic Membrane

The raw membrane was first cut into small pieces (40 mm x 40 mm) upon receive in the laboratory. The membranes were then hanging one by one on a mixing motor rotating at a low speed of < 100 rpm while being immersed in the sulfuric solution of 0.01M for cleaning. After cleaning, the membranes were rinsed with DIW water. Each membrane was dried in a dryer for 1 hour and weighted before coating of catalyst. The metal ion solutions were prepared by dissolving the appropriate chemicals in DIW water at a concentration range of 0.01 mM to 0.1 M depending on the solubility. The washed membrane was hung again on the same motor, and immersed in the metal ion solution completely. An electroplating system was set up with the membrane as cathode and graphite as anode. When the motor began to rotate at a speed of 20 rpm, the potential was applied on the system with a constant current of 20 to 100 mA. After electroplating, the catalytic membrane was washed and dried before weighing. The catalyst density was determined from the amount of metal deposited on the membrane and the weight of the tare membrane. The images of the catalytic membrane was observed using SEM (JOEL 7400F) as to reveal the morphology and the degree of surface coverage of the metallic catalysts on surface of the inorganic membrane.

## 2.3 Reduction of perchlorate on membrane system

The main reduction chamber of the system was a glass connector (ACE Glass Company, Wilmington, DE). The catalytic membrane was attached at the opening bottom of the glass connector. The catalytic membrane behaved as a cathode, which was prepared according to procedures described above. An anode (e.g., iron rod) was placed in the glass connector as a counter electrode. The electrochemical reaction producing hydrogen atoms was driven by a power supply (Model FB1000, Fisher Scientific International Inc., USA). A second power supply (Model WP705B, Vector-VID) was used to facilitate the transport of perchlorate ion from the bulk to the catalytic membrane. The first power supply supplied the constant current for the generation of hydrogen atoms at the cathodic catalytic membrane and the second power supply provided constant potential for perchlorate ion transport.

**Reduction of perchlorate.** The reaction system described above was used with the addition of an ion-exchange membrane outside the catalytic membrane. The

purpose of the ion-exchange membrane adjacent to the catalytic membrane at the opening bottom of the glass connector was to increase the concentration of perchlorate at the vicinity of the catalytic membrane. The volume between these two membranes was estimated to be one mL. The initial concentration of perchlorate was 10 ppm, and the experiment was performed at ambient conditions.

**Effect of catalyst mass weight.** Effect of surface coverage of catalysts was performed by investigating the difference of perchlorate removal for different mass weight of catalyst coated on unit weight of support. As described in section 2.2, catalytic membranes with different weight of catalysts per unit weight of support were prepared by applying different electroplating time (0.5 to 10 minutes) at the same constant current. Surface of the membranes was pictured by SEM instrument (JOEL 7400F).

**Effect of catalyst type.** In order to identify the effective catalysts, different catalytic membranes were prepared using metals from the first, the second, and the third row of the periodic table. A total of 18 monometallic catalysts of the transition metal in the periodic table were coated on the stainless steel mesh support. Fifty liters of perchlorate solution (10 mg/L) was used as the initial solution after purging with hydrogen gas for 30 minutes. The volume of the solution for each experiment was 1.2 liter during the screening of catalysts. The changes in perchlorate concentrations in addition to reaction intermediates, namely chlorate, chlorite and especially chloride were monitored and pH values recorded.

## 2.4 Analytical methods

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. The separation part was a 4-mm Dionex AS-16 anion-exchange analytical column and guard column. The flow rate of sodium hydroxide effluent was  $1.20 \text{ mL-min}^{-1}$  with a concentration gradient to assure satisfying separation and detection limit. For all experiments with an initial perchlorate concentration of larger than 0.001 mM, a 25- $\mu\text{L}$ -injection loop was used for perchlorate analysis. For concentration of less than 0.001 mM, the injection loop was changed to a 1000-  $\mu\text{L}$ .

# 3 RESULTS AND DISCUSSION

## 3.1 Surface analysis of the membrane

Figure 1 shows clearly that the surface of morphology of catalysts is different. For catalysts such as Sn and Mn, the surface area is supposed to be small due to its layered-structure on the membrane. For catalysts such as Sc, Co, Cu and Cr, the spongy structure will yield a large surface that provides active sites for the reaction. In the mean time,

catalysts such as Pd and Mo may not have enough active sites due to the lack of mass on the membrane.

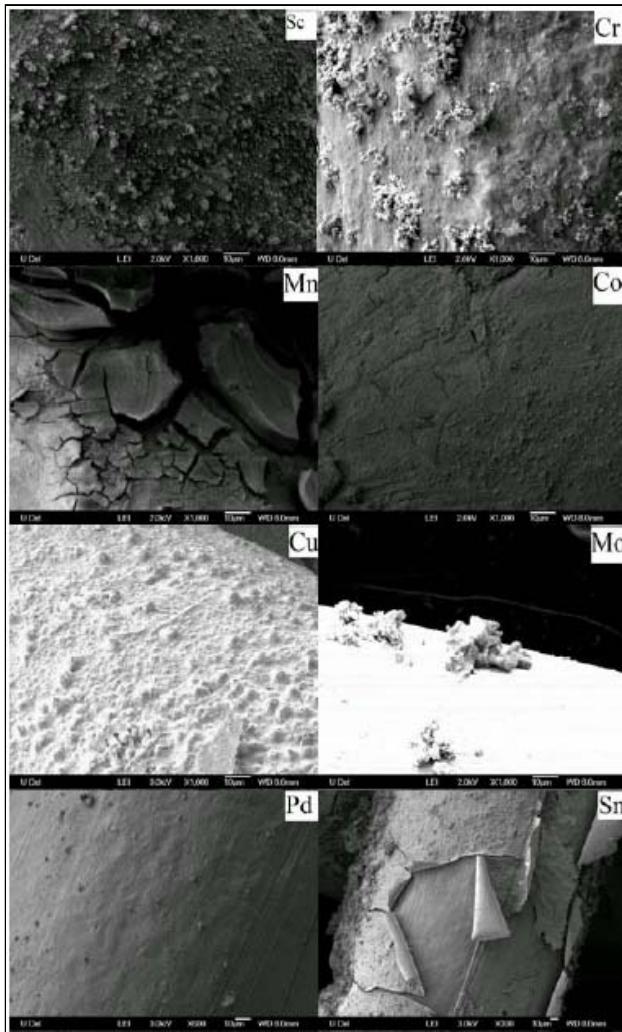


Figure 1 SEM images of different catalytic membranes.

## 3.2 Reduction of perchlorate

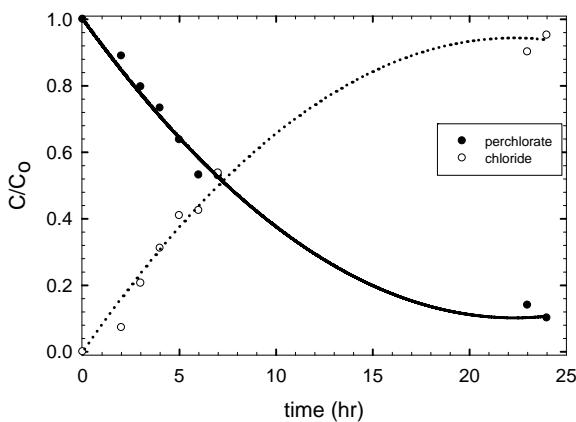


Figure 2 Reduction of perchlorate by catalytic membrane.

The reduction of perchlorate was obvious as shown in Figure 2. This is the first time that perchlorate can be reduced by hydrogen at reasonable rates. The decrease of the concentration of perchlorate was sharply at the first several hours indicated the reduction rate was rapid. It can be found it was a zero order reduction at high concentration of perchlorate. With the concentration became low, the rate turned out to be a first order.

From the analysis of the chemicals in the solution, chloride was the main end product of the reduction. However, both chlorate and chlorite were the intermediate since their peak appeared in the ion chromatography during the analysis. Their concentrations were so low that cannot be shown in Figure 2.

## 3.3 Effect of catalyst mass

It is speculated that the amount of catalyst on the stainless steel mesh support can also affect the rate of perchlorate reduction. As shown in Figure 3, the surface coverage of catalyst on the membranes was totally different at different amount of surface catalyst, e.g., Sn.

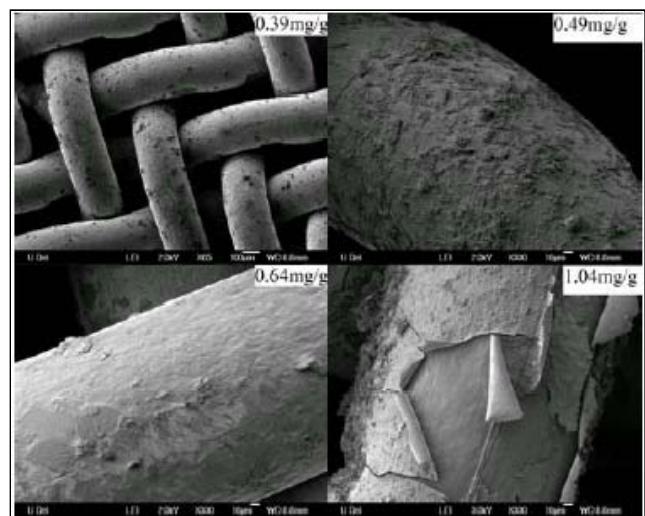


Figure 3 SEM images of catalytic membranes coated with different mass of Sn.

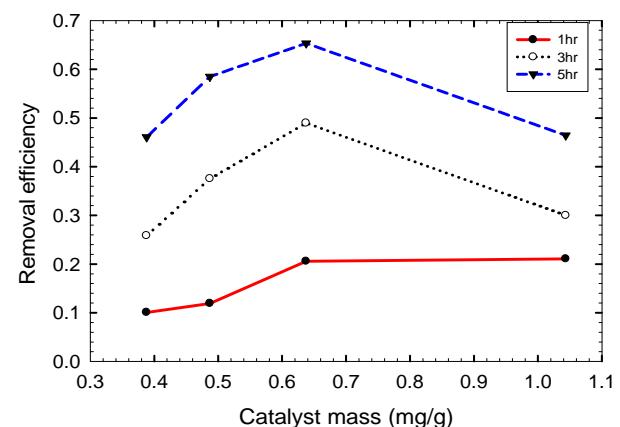


Figure 4 Remove efficiency with different catalyst mass.

Results shown in Figure 4 clearly indicate that there was an optimal catalyst density range at 0.6 to 0.7 mg/g as exemplified by Sn. The perchlorate removal efficiency increased with the increase in the catalysts density till 0.65 mg/g, but decreased abruptly as the catalyst density became greater than 0.7 mg/g. Further study is necessary to gain insight into the mechanisms of catalyst density on the perchlorate removal efficiency.

### 3.4 Effect of catalyst type

The abundance of electrons in the d orbital renders the transition metals good catalytic properties. It is well known that the bonding strength is closely related to the number of d electrons. The bonding strength plays an important role in the catalytic activities of a catalyst. In general, the catalytic activity of these metals can be correlated with the electronic configuration of the d-orbital as "percentage d characteristic" of the metallic bond based on Pauling's valence bond theory or with the strength of the metal adsorbate bond.

Element		Z	d - electron	$k^{\#}$ $\mu\text{M}\cdot\text{L}^{-1}\cdot\text{hr}^{-1}$	$k'^{*}$ $\text{mM}\cdot\text{L}^{-1}\cdot\text{hr}^{-1}\cdot\text{mg}^{-1}$
IIIA	Sc	21	1	5.9	11.8
IVA	Ti	22	2	11.0	2.5
	Zr	40	2	5.5	1.5
VA	V	23	3	7.4	2.6
VIA	Cr	24	5	9.9	16.5
	Mo	42	5	9.3	13.5
VIIA	Mn	25	5	7.0	2.2
VIIIA	Co	27	7	10.4	1.4
	Ni	28	8	6.8	1.8
	Ru	44	7	9.2	3.4
	Rh	45	8	7.3	4.6
	Pd	46	10	7.6	2.9
	Pt	78	10	7.6	18.2
IB	Cu	29	10	8.6	1.0
IIB	Zn	30	10	6.6	2.3
	Cd	48	10	8.9	22.2
IVB	Sn	50	10	9.8	3.4
	Pb	82	9	5.1	0.7

Table 1 List of Electron Characteristics and Rate constants.

Table 1 lists the atomic number (Z), d-electron, rate constants and specific rate constants. From Table 1, it is seen that among the 18 metallic catalysts tested, Sc, Ti, Cr, Mo, Pt and Cd were the most promising.

### 4 SUMMARY

On-site hydrogen atoms produced electrochemically by using membrane coated with monometallic catalysts can readily reduce the perchlorate to chloride. The reduction

rate was different for different catalyst and/or mass weight of the catalysts.

### 5 ACKNOWLEDGEMENT

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