



Chromium(VI) reduction in aqueous medium by means of catalytic membrane reactors



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ABSTRACT

A novel method for catalytic reduction of chromium(VI) to chromium(III) in model and real water is proposed in this work. Hydrogen was used as a reducer. Three different catalytic membrane reactors were prepared and employed in the studied reaction. The catalytic membrane reactors were prepared using commercial corundum hollow fiber membranes. The active phases, palladium, cerium oxide, iron oxide or combinations of them, were incorporated by incipient wetness impregnation of the corresponding water-soluble salts followed by calcination and reduction. The catalytic tests were performed in semi-batch mode at ambient conditions. A mass flow controller was used to supply hydrogen to one end of the membrane whilst the other end was kept closed. The reactors were submerged into a vessel containing the chromate solution. The concentration of the chromate was continuously monitored following a standard analytical method. The initial chromate concentration was varied between 0.5 and 18 mg L⁻¹. In order to completely reduce the Cr(VI) to Cr(III), it was necessary to decrease the pH of the solution to 3. In the end of the tests the final solutions were neutralized to pH 8 and filtered. The content of chromium in the final solutions and in the precipitates was determined by inductively coupled plasma (ICP) technique. It was demonstrated that for the studied reaction the presence of palladium is essential. In all experiments, with synthetic and real water adjusted to pH 3, the catalytic membrane reactors containing palladium (0.3–0.9 w/w%) effectively reduced the chromium to levels below 0.03 mg L⁻¹ without losing activity in repetitive runs. The results from ICP analyses demonstrated that the chromium can be completely eliminated from the water after neutralization and filtration.

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1. Introduction

Chromium, the 21st most abundant element in the earth's crust, is a metallic element found naturally in rocks and soil. Although it exists in several oxidation states, the zero, trivalent, and hexavalent states are the most common [1]. In water, chromium is commonly found in (III) or (VI) oxidation state [2]. The chromium (IV) and (V) are transient intermediates during the reduction of hexavalent chromium; both are unstable in water, forming chromium(III) or (VI) [3]. Trivalent chromium has very low solubility and reactivity at neutral pH resulting in low mobility in the environment and low toxicity in living organisms. In fact, chromium(III) is considered essential for living organisms [1].

Hexavalent chromium however is very soluble in water and it is considered to be the most toxic form of the metal. In drinking water, according to a number of studies, the soluble Cr(VI) compounds may cause cancer [4]. EPA has an enforceable drinking water standard for total chromium of 0.1 mg L⁻¹, which includes chromium(VI) and chromium(III) [5]. WHO recommended a maximum allowable concentration of 0.05 mg L⁻¹ of hexavalent chromium [4]. The wastewater contaminated with chromium(VI) must be treated before discharge or reuse. The conventional treatment process generally involves two steps: (1) reduction of Cr(VI) to Cr(III) and (2) precipitation of Cr(III), for total removal of the chromium after filtration [6].

In aqueous medium and depending on the pH and the concentration, hexavalent chromium occurs in oxy anions such as HCrO₄⁻; Cr₂O₇²⁻ or CrO₄²⁻ with the chromate ion being predominant in basic medium [7]. At values of pH below 6, chromate ion accepts protons and converts into HCrO₄⁻ and Cr₂O₇²⁻. The equilibrium between both ions depends on their

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concentration. In concentrated solutions, dichromate is predominant while, in dilute solutions, hydrogen chromate ion is predominating [8]. The dichromate is well known as a very strong oxidant in acid medium while a less oxidant chromate predominates in basic solutions [3]. When reducing agents are present in the aqueous solution, these oxyanions are reduced to trivalent chromium. The trivalent chromium at pH values between 8–10 forms $\text{Cr}(\text{OH})_3$ that has very low solubility in water and precipitates [9]. Thus, the trivalent chromium hydroxide can be removed by filtration.

The most common way to reduce hexavalent chromium in aqueous medium is with iron and ferrous ions used as electron donors while the chromium is the electron acceptor [6]. The reduction from Cr(VI) to Cr(III) occurs through the formation of pentavalent and tetravalent chromium as intermediate states [10,11]. It is suggested that the presence of cerium(III) accelerates the conversion of Cr(IV) to Cr(III) acting as one-electron reducing agent [12].

Several studies have been developed to reduce Cr(VI) to Cr(III) in aqueous medium [6,7,10–28]. Most of them used iron or ferrous ions as reducing agent [6,7,10,11,14,15,17–19]. The majority of the studies were performed with synthetic wastewater with hexavalent chromium while a few deal with wastewater from electroplating industry with Cr(VI) concentration over 400 mg L^{-1} [14,15]. Other ways to address the problem are the use of biological agents to reduce hexavalent chromium in synthetic wastewater [16,22,23,27]. The photo catalytic reduction of chromium presented in synthetic water and in wastewater polluted with chromium and EDTA from printed circuit boards [21] has also studied. The redox reaction between chromium(VI) and arsenic(III) from acid mine drainage (AMD) wastewater in presence of H_2O_2 as promoter also was studied [26]. Recently, it was reported that the Cr(VI) can be reduced by formic acid using specially designed catalyst with incorporated Pd nanoparticles [13]. Moreover, it was proposed the Cr(VI) reduction by oxalic acid in the presence of Mn (II) [28].

Previous studies have shown that in situ gas treatment has significant potential for the remediation of Cr(VI) contaminated settings; some of these studies showed that hydrogen sulfide can immobilize >90% of Cr(VI) present in contaminated soils [29]

Only few of the studies focused on chromium(VI) reduction at low concentration, e.g. in the range $5\text{--}10 \text{ mg L}^{-1}$. In those cases, different proposals have been made e.g. reduction with iron wires, packed-bed bioreactors and by the use of photoelectrocatalysis with nanotube array electrodes. In the former case, the process involves simultaneous reduction of chromium combined with phenol oxidation in synthetic wastewater [6,16,25].

This work proposes a novel method for Cr(VI) to Cr(III) reduction using hydrogen gas as reducer. In order to accomplish the final goal, contactor catalytic membrane reactors (CMRs) were developed and prepared. The active phases, Pd or Pd/CeO₂, Fe₂O₃ were deposited to the commercial ceramic hollow fiber membranes by impregnation of water-soluble salts. Thereafter they have been activated by calcination followed by reduction steps. The experiments were performed in semi batch mode. The hydrogen was supplied to the one end of the reactor whilst the other was kept closed. The CMR was submerged to the water solution

containing Cr(VI) ions. The Cr(VI) can be reduced to Cr(III) and after pH adjustment of the final solution to pH 8 and filtration the chromium can be completely removed from the water. The tested catalytic membrane reactors showed a steady performance during the Cr(VI) reduction without losing activity in repetitive runs.

2. Materials and methods

2.1. Preparation of the chromate containing water

A stock solution containing $179 \text{ mg L}^{-1} \text{CrO}_4^{2-}$ was prepared from K_2CrO_4 salt, Panreac. An aliquot part of this solution was added to Milli-Q or mineral water in order to obtain 0.5, 3.4, 12 or 18 mg L^{-1} of CrO_4^{2-} solutions corresponding to 0.2, 1.5, 5.4 or 8 mg L^{-1} of Cr(VI), respectively.

The composition of the mineral water as stated by the supplier (Bezoya, 2015; <http://www.bezoya.es>) was: dry residue 28 mg L^{-1} , 21 mg L^{-1} bicarbonates, 0.6 mg L^{-1} chlorides, 5.26 mg L^{-1} calcium, 0.91 mg L^{-1} magnesium and 1.36 mg L^{-1} sodium.

2.2. Chromate analysis

The chromate concentration in the withdrawn samples was measured with a Jasco V–630 spectrophotometer. Samples were prepared in accordance with the standards methods 3500-Cr: Colorimetric Method for the examination of water and wastewater [30]. 1,5 biphenyl carbazide was added to the samples as an indicator and its absorbance was measured at 540 nm. A calibration curve in the range $0.05\text{--}10 \text{ mg L}^{-1}$ of Cr(VI) for the chromium(VI) determination was prepared using standard solutions according to the standard method. Following the above standard method the low detection limit for the chromium(VI) was 0.03 mg L^{-1} . This value is lower than the maximum limit allowed according to the WHO, 0.05 mg L^{-1} .

Once the reaction was finished, the pH of the solution was adjusted to 8 by sodium hydroxide. The solution was then filtered using $0.45 \mu\text{m}$ cellulose acetate filter. The filter was washed with 5% HCl acid in order to recover the Cr(III). The amount of chromium was measured in both solutions, the acidic containing the Cr(III) and the filtrate containing the unreacted Cr(VI). The measurements were performed using inductively coupled plasma spectroscopy, Spectro.

2.3. Preparation of the catalytic membrane reactors

Commercial corundum hollow fibers for micro-filtration were used for the preparation of the catalytic membrane reactors. The details of the manufacture process of the membranes and the preparation of the catalytic membrane reactors are described in detail in our previous works [31,32]. In the present case we used fibers with $1.4 \mu\text{m}$ nominal pore size. The length of the fibers was 15 cm. The active phases were impregnated by incipient wetness technique starting from water soluble precursors, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 99.9% from Aldrich, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 99% from Sigma–Aldrich and palladium(II) chloride 59.83% metal content from Johnson Matthey. The catalytic membrane reactor (CMR) containing transitional metal oxides and Pd were prepared in two stages, first the iron and cerium precursors were impregnated from water solution, dried and calcined at 450°C for 6 h. Then the palladium precursor solution was impregnated. Once the impregnation was finished the membranes were dried in a special vessel under vacuum for 30 min. During this step the fibers were rotated along the axis in order to avoid preferential deposition of the salts onto the ceramic support. Further the membranes were dried at 120°C for 5 h and finally calcined at 450°C overnight. The CMRs containing palladium were reduced under flowing hydrogen at

Table 1
Composition of the prepared catalytic membrane reactors.

Catalytic membrane reactor	% Fe ₂ O ₃	% CeO ₂	% Pd	% Porosity
CMR0 (blank)	–	–	–	15
CMR1	–	–	0.9	15
CMR2	2.1	2.1	–	15
CMR3	1.5	1.5	0.3	15

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