

Chromium(VI) Reduction in Aqueous Medium by means of Catalytic Membrane ReactorsV. Pinos^{a, b, c}A. Dafinov^{a, *}

anton.dafinov@urv.cat

F. Medina^aJ. Sueiras^a^aChemical Engineering Department, Rovira I Virgili University, Av Paisos Catalans 26, 43007 Tarragona, Spain^bDepartamento de Recursos Hídricos y Ciencias Ambientales, Dirección de Investigación (DIUC), Universidad de Cuenca, Av Victor Manuel Albornoz, Campus Quinta Balzain, Cuenca, Ecuador^cFacultad de Ciencias Química, Universidad de Cuenca, Av 12 de Abril, Cuenca, Ecuador

*Corresponding author.

Abstract

A novel method for catalytic reduction of chromium (VI) to 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.

Keywords: Catalytic membrane reactors; Chromate reduction; Pd and Pd/CeO₂/Fe₂O₃ active phases

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(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 HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. The equilibrium between both ions depends on their 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 to 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(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 to 10 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 to 10 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) 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 μm 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 350 °C for 3 h. In the case of the CMRs with only palladium or transitions metals solely the corresponding part of the procedure was developed.

Three different CMRs were prepared: a) 0.9 w/w-% of Pd b) 2.1 w/w-% of Pd b) 2.1 w/w-% of Fe_2O_3 and 2.1 w/w-% of CeO_2 and c) 1.5 w/w-% of Fe_2O_3 , 1.5 w/w-% of CeO_2 and 0.3 w/w-% of Pd. In all cases, the amount of deposited active phases was calculated by the weight difference between the original membrane and the modified membrane.

The compositions of the prepared three catalytic membrane reactors are presented in Table 1. It also includes a membrane reactor without an active phase used for blank tests.

Table 1 Composition of the prepared catalytic membrane reactors.

Catalytic membrane reactor	% Fe_2O_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

The void volume of the CMRs was calculated by the weight differences between dry and wet reactors. The length of the reactors was 15 cm with 13 cm^2 effective external surface area.

2.4 Catalytic membrane reactor characterization

Environmental Scanning Electron Microscopy (ESEM), JEOL JSM-6400 was used to study the bulk and surface structure of the membrane. Both the inner and outer membrane surfaces were characterized.

Transmission electron microscopy (TEM), JEOL model 1011, was employed to determine the mean size of palladium particles deposited into the CMRs. In this process, a piece of the CMRs was crushed and the powder was dispersed in ethanol. The sizes of the observed Pd particles were determined using the software ITEM by Olympus. Scanning Electron Microscopy in back-scattering mode (BSE) was used to determine the distribution of the active phases on the membrane. Analysis was performed over a several pieces of CMRs.

XRD measurements were performed using a Bruker-AXS D8-Discover diffractometer equipped with a parallel incident beam (Göbel mirror), a vertical θ - θ goniometer, an XYZ motorized stage and a General Area Diffraction System (GADDS). Samples were placed directly on the sample holder and the area of interest was selected with the aid of a video-laser focusing system. An X-ray collimator system allowed the analysis of areas of 500 μm . The X-ray diffractometer was operated at 40 kV and 40 mA to generate $\text{CuK}\alpha$ radiation. The GADDS detector was a HI-STAR (multiwire proportional counter of 30 × 30 cm with a 1024 × 1024 pixel) placed 15 cm away from the sample. We collected one frame (2D XRD patterns) covering 2 θ –56°–2 θ –56°–2 θ . The exposure time was 900 s per frame and it was chi-integrated to generate the conventional 2 θ vs. intensity diffractogram. Image scale: small lines separation corresponds to \approx 100 μm . The mean area analyzed was represented by an ellipsoid centered in the cross with a constant short axis of 0.5 mm (N-S direction) and a variable long axis (from 1.5 to 0.6 mm in the W-E direction). The analyses of the XRD diffractogram were performed by the ICDD database (release 2007) using Diffracplus Evaluation software (Bruker 2007).

2.5 Experimental setup

The catalytic membrane reactors were tested in a semi-batch mode of operation. A schematic diagram of the reaction setup is presented in Fig. 1.

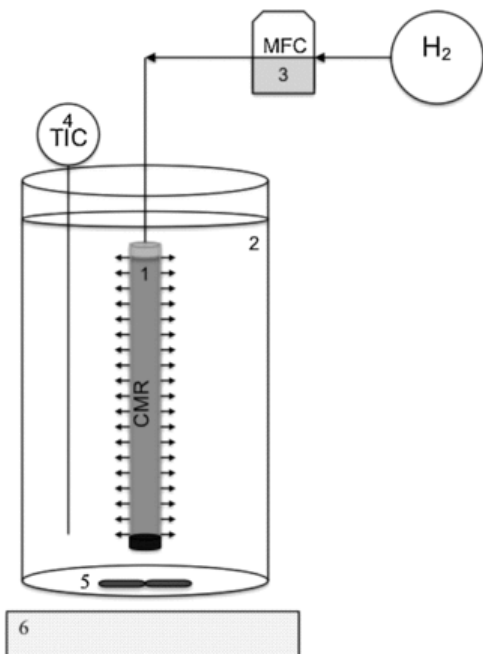


Fig. 1 Experimental setup; 1 catalytic membrane reactor, 2 reaction vessel, 3 mass flow controller, 4 temperature indicator and controller, 5, 6 magnetic stirrer and controller.

alt-text: Fig. 1

The hydrogen flow was adjusted using a mass flow controller and supplied to one end of the reactor whilst the other end was kept closed. The CMR was submerged into a glass reactor containing 100 ml of water polluted with Cr(VI) ions. The hydrogen crossed the membrane wall reaching the water on the external surface. All the tests were performed at room temperature. The hydrogen supply was maintained at $10 \text{ cm}^3/\text{min}$ in all experiments. Different experiments were performed for a variety of chromate concentrations in the range of 0.5 to 18 mg L^{-1} . The pH of the water solution was varied between 3 and 7. Thereafter, it was maintained at 3 in all experiments. Two types of water were used in the tests. Initially, Milli-Q water was used. Later in order to check the practical applicability of the proposed method the experiments were performed using mineral water with composition as described above. In order to quantify the chromate reduction, samples were withdrawn from the reaction vessel during the experiments.

3 Results and discussion

3.1 Catalytic membrane reactor characterization

The ESEM analysis of the CMRs revealed that no obstructions of the original pore structure of the corundum fibers occurred by the active catalytic phases. Homogeneous catalytic phase's distribution over the entire membranes was observed. In order to examine the Pd particles on the CMRs, pieces of the reactors were grinded to a fine powder. After the proper pretreatment of these powder samples they have been observed with TEM. A representative picture corresponding to CMR3 is shown in [Fig. 2](#).

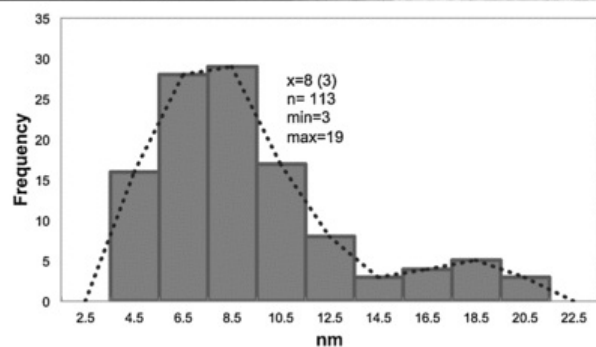
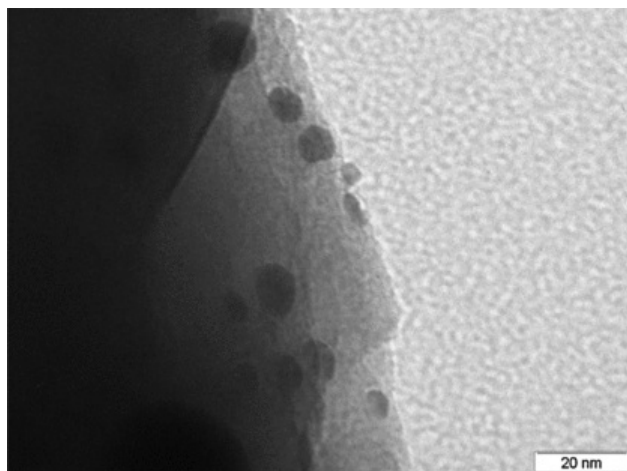
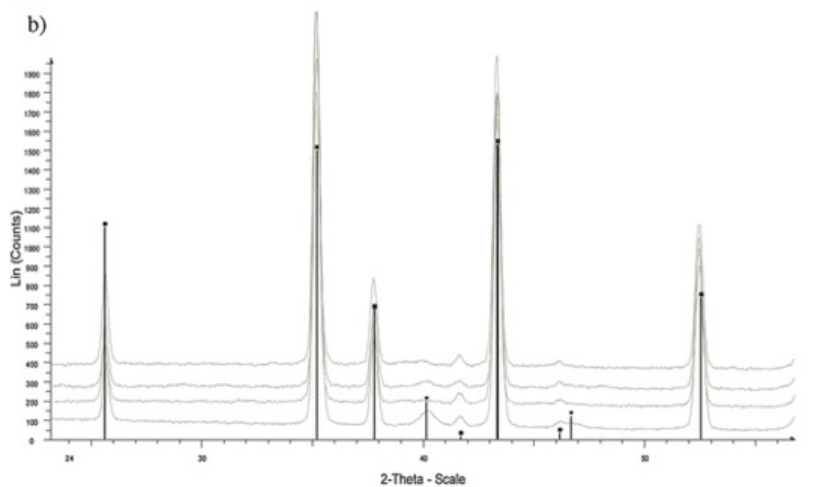
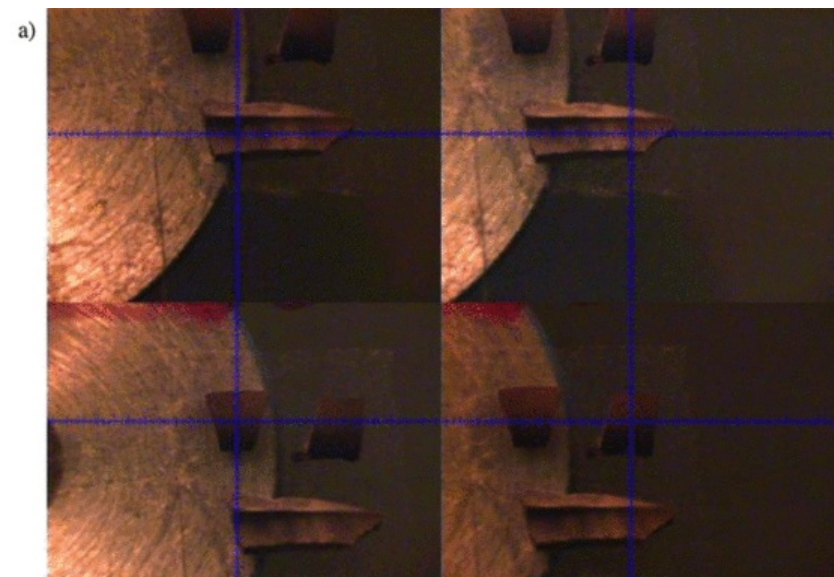


Fig. 2 TEM of catalytic membrane reactor of CMR3 (0.3% Pd, 1.5% Fe₂O₃, 1.5% CeO₂).

alt-text: Fig. 2

The Pd particle size distribution was determined after counting more than 113 particles. The obtained particle mean size was 8 nm with a standard deviation of 4 nm. The minimum size was 3 nm and the maximum 19 nm. Fig. 2 also shows a histogram for the Pd particle size distribution obtained in this analysis. No differences in particle size and distribution were observed between CMR1 and CMR3.

The XRD analysis of the CMRs pieces confirmed a homogeneous active phase distribution across the entire membranes. A representative example of the obtained results, an image of the CMR piece and diffractograms at different points, are presented in Fig. 3 for the case of CMR1. A piece of the membrane reactor is placed under the beam and the reflected rays are collected at specific angles. The registered patterns correspond to the area of 500 μm² and 20 μm depth. The diffraction patterns are obtained from two zones of each side of the membrane reactors. The results demonstrate that the active phases are homogeneously distributed over the entire membrane. More detailed discussion was presented in our previous works where the membrane reactors were prepared following similar procedure [31,32]. The registered diffraction patterns on the outer and the inner membrane surfaces are shown in Fig. 3a. The obtained diffractograms for this case can be seen in Fig. 3b. As stated before they confirm that the active phases are homogeneously distributed through the entire catalytic membrane. The diffractogram corresponding to CMR3 presented also homogeneous palladium distribution.



Y + 40.0 mm - (OUT), 500um, 15cm, 900s - Type: Detector - Start: 23.200 ° - End: 56.800 ° - Temp.: 25 °C (Room) - 2-Theta: 23.200 ° - Step: 0.020 °
 Y + 45.0 mm - (OUT), 500um, 15cm, 900s - Type: Detector - Start: 23.160 ° - End: 56.800 ° - Temp.: 25 °C (Room) - 2-Theta: 23.160 ° - Step: 0.020 °
 Y + 50.0 mm - (IN), 500um, 15cm, 900s - Type: Detector - Start: 23.160 ° - End: 56.860 ° - Temp.: 25 °C (Room) - 2-Theta: 23.160 ° - Step: 0.020 °
 Y + 55.0 mm - (IN), 500um, 15cm, 900s - Type: Detector - Start: 23.290 ° - End: 56.850 ° - Temp.: 25 °C (Room) - 2-Theta: 23.290 ° - Step: 0.020 °
 ■ 01-083-2080 (A) - Corundum, syn - Al₂O₃ - WL: 1.54056 - Rhombo.H.axes
 ▼ 00-046-1043 (*) - Palladium, syn - Pd - WL: 1.54056 - Cubic

Fig. 3 a) Pieces of CMR1 (0.9% Pd) measured at four points, two on the inner and two on the outer surface. b) X-ray diffractogram obtained for the four points.

alt-text: Fig. 3

3.2 Catalytic activities of the CMRs

The first tests were performed with CMR3, the model solution was Milli-Q water containing 5.4 mg L⁻¹ of Cr(VI) without any pH adjustment. The hydrogen supply was fixed to 10 cm³/min. No chromate reduction was observed in this case. It is well known that the redox potential of the Cr(VI)/Cr(III) depends on the pH of the aqueous medium and it increases at higher acidity. At neutral pH the Cr(VI) mainly exists as CrO₄²⁻. As a next step, the pH of the solution was decreased to 3 by adding hydrochloric acid. For the

chosen Cr(VI) concentration at pH of 3 the predominant form of Cr(VI) is HCrO_4^- and traces of H_2CrO_4 are probably also present. It is well known and broadly studied that at low concentrations and pH lower than 6.8 the predominant species is HCrO_4^- ($\epsilon_0 = 1.20 \text{ V}$) followed by $\text{Cr}_2\text{O}_7^{2-}$ ($\epsilon_0 = 1.33 \text{ V}$); when the pH is above 6.8 the predominant species is CrO_4^{2-} ($\epsilon_0 = -0.13 \text{ V}$) [3,8,34]. After acidifying the water the chromate concentration decreased steadily during the experiment. The results are presented in Fig. 4.

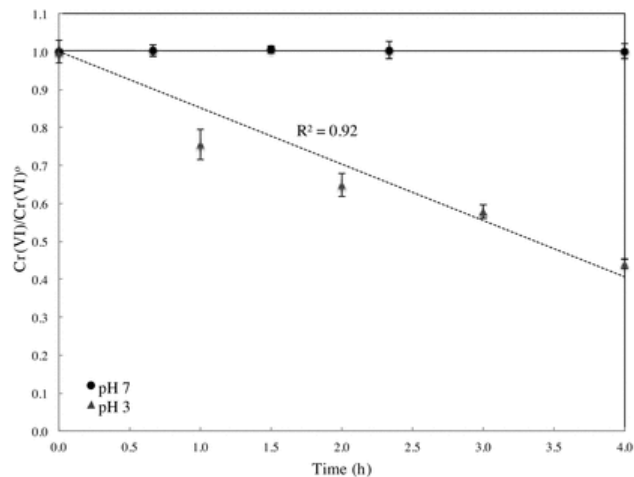


Fig. 4 Cr(VI) reduction in milli-Q water with CMR3 (0.3% Pd, 1.5% Fe_2O_3 , 1.5% CeO_2) at pH 3 or 7, and $10 \text{ cm}^3/\text{min}$ of H_2 supply, 5.4 mg L^{-1} Cr(VI) at room temperature.

alt-text: Fig. 4

It is important to note that the amount of hydrogen supplied is much higher than the one consumed in the reaction (e.g. $1 \text{ cm}^3/\text{min H}_2/\text{h}$). There are mainly two reasons, which made necessary to use such high excess of hydrogen:

Firstly, the hydrophilic nature of the catalytic membrane reactors imply that the hydrogen must be supplied at higher pressure in order to overcome the capillary pressure of the water occupying the porous structure of the membrane.

Secondly, the non-uniform pore size distribution requires the application of pressures higher than the bubble point of the main part of the pores.

This ensures that the hydrogen could reach practically the entire outer surface of the reactor where the reaction takes place. All experiments were performed at room temperature and due to the same initial nominal pore size of the ceramic fibers, $1.4 \text{ }\mu\text{m}$, the hydrogen reached pressures between 1.2 and 1.5 barg in the inner part of the CMRs.

The proposed reaction mechanism is depicted in Fig. 5. The hydrogen flows from the inner CMRs side through the pore structure reaching the outer surface. Part of it is activated on the Pd domains loaded uniformly into the reactor. The activated hydrogen reduces the two forms of chromate forming Cr(III). The reaction takes place predominantly at the solid-liquid-gas contact line. The porous membranes create a triple-point interface between the three different phases (gas, liquid, and the solid catalyst on the membrane) [33].

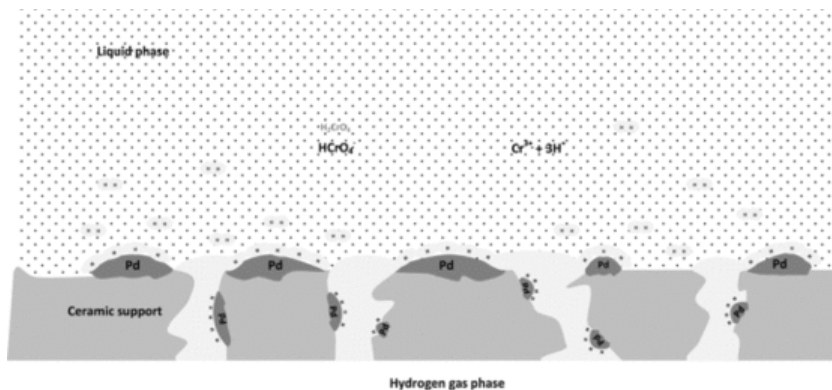


Fig. 5 Reaction mechanism of reduction of chromium(VI) to chromium(III).

alt-text: Fig. 5

After this initial screening of the activity of the CMRs for chromate reduction, the rest of the experiments were carried out with a hydrogen supply fixed at $10 \text{ cm}^3/\text{min}$ and pH of the water medium adjusted to 3.

In order to check whether any specific adsorption of the different forms of Cr(VI) occurred on the ceramic reactors at different pH, additional experiments were performed with catalytic membrane reactors that did not contain palladium. The tests were done with CMR0, which was free from an active phase, as well as with CMR2, which only contained a mixture of iron and cerium oxides. For both reactors no change in the Cr(VI) concentration was observed for 8 h under the experimental conditions.

On the other hand, experiments with CMR1 and CMR3 were performed at pH 3 simulating heterogeneous catalytic system. In those experiments the reactor was submerged into the reaction vessel supplying the hydrogen to the solution by bubbling. No activity for Cr(VI) reduction has been observed.

CMR1 contained only palladium as an active phase. Chromium reduction with this reactor was performed using two types of water, Milli-Q and mineral. The initial Cr(VI) concentration was 8 mg L^{-1} . For the two types of water the chromate concentration steadily decreased to below 0.03 mg L^{-1} (the low detection limit of the used analytical method). The results are presented in Fig. 6. In the graphs are included also error bars that were calculated from the repetitive runs.

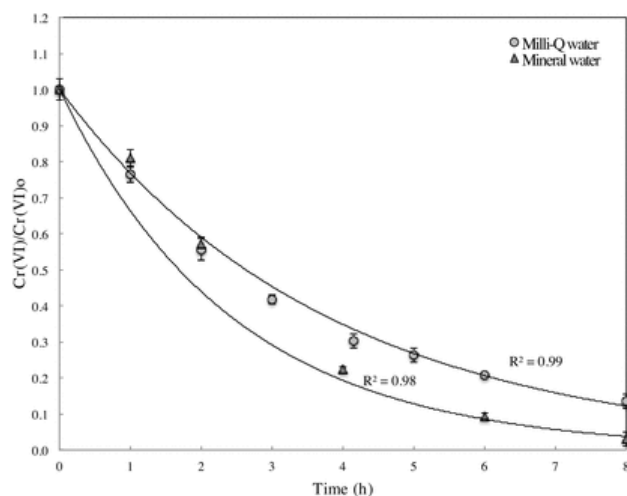


Fig. 6 Cr(VI) reduction in milli-Q or mineral water with CMR1 (0.9% Pd) at pH 3 and $10 \text{ cm}^3/\text{min}$ of H_2 supply, 8 mg L^{-1} Cr(VI) at room temperature.

alt-text: Fig. 6

The reaction proceeds most likely as a first order reaction in respect to the chromium concentration as can be seen from the exponential fits and the corresponding regression coefficients. As mentioned before we assumed that the hydrogen concentration does not vary during the reaction. In order to compare the performance of CMRs for chromate reduction, the first 4 h of the experiments have been used assuming linear trends. The rate for chromium reduction is estimated to be $1.6 \text{ mg L}^{-1} \text{ Cr(VI)}/\text{h}$ for the test with mineral water. It is important to note that the chromium reduction by the proposed system is not affected by the presence of other ions as demonstrated by the tests with mineral water. It is worth noticing that CMR1 was tested in consecutive experiments and no decrease of its activity was observed. No special activation procedures were performed between the different tests with either Milli-Q or mineral water.

As described in the experimental section, cerium and iron oxides were loaded in CMR3 before palladium deposition. It is well known that in the cerium oxide part of the Ce is in the 3+ oxidation state [35]. The proportion between Ce(III) and Ce(IV) depends on different factors. In the present case, due to the near contact between the oxide, the palladium and the activated hydrogen on its surface, it can be expected that the presence of Ce(III) will be rather high. Therefore the aim of the preparation of CMR3 was to verify whether the activity of the catalytic membrane reactors would be increased with the incorporation of the mixed oxides and whether this would also increase the efficiency of hydrogen use. At the same time the amount of the noble metal was reduced three times compared to CMR1. Fig. 7 presents the obtained results for the chromate reduction in two different aqueous media, Milli-Q and mineral water.

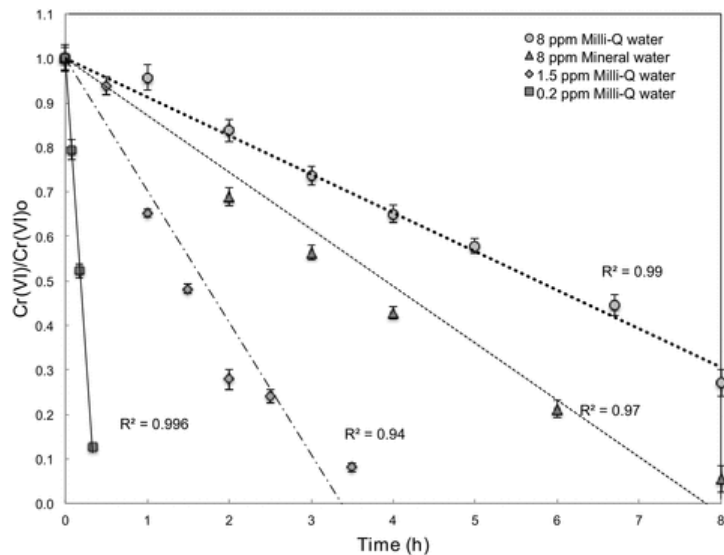


Fig. 7 Cr(VI) reduction in milli-Q or in mineral water with CMR3 (0.3% Pd, 1.5% Fe₂O₃, 1.5% CeO₂) at pH 3 and 10 cm³/min of H₂ supply at room temperature.

alt-text: Fig. 7

Similarly to the tests with CMR1, this reactor was used in nine consecutive experiments and no decrease of activity was observed.

CMR3 reduced the chromate efficiently in the two types of water at pH 3 and room temperature as can be seen in Fig. 7. As in the case of CMR1, here also the results show that the activity of the CMR is slightly higher when the Cr(VI) reduction occurs in mineral water. More investigation is required in order to reach a plausible explanation for the observed behaviour. Contrary to the results obtained with CMR1, a linear trend of Cr(VI) concentration decrease with time over the entire range of the test is observed (see also the reported regression coefficients). The linear trend of chromate reduction is also indication that the reaction is most likely to be zero order with respect to the chromate. For the full duration of the experiment, the rate of Cr(VI) reduction can be roughly estimated at 1 mg L⁻¹ Cr(VI)/h. Compared to CMR1 it is somewhat lower but it should be remembered that the Pd content in the CMR3 is three times lower compared to CMR1.

For the case of CMR3 an additional test was performed with an initial concentration of Cr(VI) of 0.2 and 1.5 mg L⁻¹. As can be seen in Fig. 7 it was confirmed that at lower concentration the reaction rate decreases, e.g. 1.1 mg/L h vs 0.5 and 0.4 mg/L-h vs 0.5 and 0.4 mg/L-h of Cr(VI) reduction for high and low concentrations, respectively.

Taking into account the prolonged linear trend of Cr(VI) reduction as well as the higher activity of CMR3 compared to CMR1, it can be speculated that the Ce(III)/Ce(IV) pair participates in the chromate reduction. However it is too premature at this stage to draw definitive conclusions.

Table 2 are summarises the experimental conditions and the results obtained in the different tests.

Table 2 Experimental conditions and results obtained with the different CMRs in Cr(VI) reduction tests.

alt-text: Table 2

	CMR											
	CMR0		CMR1		CMR2		CMR3					
Cr(VI), mg L ⁻¹	8.0	8.0	8.0	8.0	8.0	8.0	5.4	5.4	0.2	1.5	8.0	8.0
pH	3	3	3	3	3	3	3	7	3	3	3	3
H ₂ flow, cm ³ /min	10	10	10	10	10	10	10	10	10	10	10	10
Type of water	MQ	M	MQ	M	MQ	M	MQ	MQ	MQ	MQ	MQ	M

Cr(VI) reduction, mg/Lh first 4 h	0.0	0.0	1.4	1.6	0.0	0.0	0.7	0.0	0.4	0.5	0.7	1.1
Cr(VI) reduction, mg/h g of Pd	–	–	9.2	10.4	–	–	15.2	0.0	8.6	10.9	15.2	23.9
Cr(VI) reduction, mg/h m ² of membrane	0.0	0.0	109	115	0.0	0.0	53	0.0	30	38	53	84

* MQ Milli-Q water, M mineral water.

The catalytic membrane reactors without palladium did not possess any activity for Cr(VI) reduction as can be seen from Table 2. It is also important to mention that at neutral pH no chromate reduction occurred. Table 2 summarizes the results for Cr(VI) reductions starting at different initial concentrations as well the tests for the two types of water. In all cases the results indicate that the process is faster in mineral water than in model solutions. At this stage it is rather difficult to give a plausible explanation for this finding. More tests are planned in order to investigate the effects of other anions presented in the water, with special attention to sulfates, phosphates and nitrates. In order to compare the performance of different CMRs for chromium reduction the rates are calculated for the first 4 h of reaction assuming linear trends for all cases. As mentioned before, for CMR3 containing cerium and iron oxides, the trend of Cr(VI) was linear for the entire duration of the experiment in all tests. With respect to the activity as a function of the amount of palladium contained by catalytic membrane reactors (see the penultimate row in the table), it appears that CMR3 is above two times more active than CMR1. It can be suggested that this is due to the Ce³⁺/Ce⁴⁺ contribution to the reaction by increasing the number of active sites involved in the reaction. Full characterisation of the processes related to the catalytic reduction of Cr(VI) described in this paper call for additional research to evaluate the effects of parameters such as hydrogen flow rate and composition of catalyst as a means of optimising the performance of the reactors. As mentioned above a new set of experiments is under consideration in order to address this issue. The modular nature of the catalytic membrane reactors allows the proposed process to be scaled up easily. The data representing the capacity for Cr(VI) reduction expressed per one square meter of catalytic membrane reactor is shown in the last row of the table. No loss of catalytic activity was registered in repetitive runs and during the entire period the experiments were performed, i.e. for more than 4 months.

Additional experiments were performed in order to check whether full elimination of the chromium ions from the solution is possible at these relatively low concentrations. The final solution after the Cr(VI) reduction was separated and its pH was adjusted to 8 by sodium hydroxide solution. At this pH the Cr³⁺ precipitates forming Cr(OH)₃. Thereafter the solution was filtered using standard laboratory 0.45 µm filter. After filtration the filter was washed with 5% HCl solution and the liquid kept. The content of chromium was measured in both solutions (the filtrate and the washing solution) using the ICP apparatus. The measured concentration of chromium (unreduced Cr(VI)) in the filtrate confirmed the results obtained by the photometric method. The measured amount of chromium in the acidic solution is the same as the amount of Cr(VI) reduced during the reaction.

4 Conclusions

The present work demonstrates an efficient method for Cr(VI) reduction in the concentration range between 0.2 and 8 mg L⁻¹ using specially prepared catalytic membrane reactors in aqueous medium. The presence of palladium as an active phase in the CMRs is required for the reaction to take place. Also the water solution must be acidified to pH of 3.

The proposed reaction system using CMRs can also be used very efficiently to reduce chromate present at low concentrations in model and real water sources using only hydrogen as a reagent. Remarkably, the proposed CMRs did not present any loss of catalytic activity in repetitive runs. By a final pH adjustment to 8 the chromium can be eliminated completely from the contaminated aqueous source after filtration. Due to the modular character of the starting commercial ceramic membranes used in the present study, the process is easily scalable. From practical point of view the obtained results are promising and encourage further work in this direction.

Conflict of interest

None.

Acknowledgments

Pinos wants to express her gratitude for the economic support given by the doctoral scholarship from SENESCYT, convocatoria abierta 2012, I fase. As well as the Universities of Cuenca and Rovira I Virgili.

References

[1]

J. Barnhart, Occurrences, [Uses, and Properties of Gases, and properties of chromium](#), *Regul. Toxicol. Pharmacol.* **26**, 1997, S3–S7, <http://dx.doi.org/10.1006/rtph.1997.1132>.

[2]

D.A. Vander Griend, J.S. Golden and C.A. Arrington, Kinetics and [Mechanism of Chromate Reduction with Hydrogen Peroxide in Base](#), *Inorg. Chem.* **41**, 2002, 7042–7048,

<http://dx.doi.org/10.1021/ic0257975>.

[3]

F.A. Cotton, S.G. Wilkinson, Química inorgánica avanzada, Editorial Limusa S.A. De C.V., (1986).

[4]

WHO, Guidelines for ~~drinking-water~~ Drinking-water Quality—Volume 1: Recommendations, WHO, 2015, (accessed 28.04.14) http://www.who.int/water_sanitation_health/dwq/gdwq3rev/en/.

[5]

O. US EPA, *Basic Information about Chromium in Drinking Water* 2015, (accessed 28.04.14) <http://water.epa.gov/drink/contaminants/basicinformation/chromium.cfm>.

[6]

L.-Y. Chang, Chromate reduction in wastewater at different pH levels using thin iron wires—A laboratory study, *Environ. Prog.* **24**, 2005, 305–316, <http://dx.doi.org/10.1002/ep.10082>.

[7]

H. Mekatel, S. Amokrane, B. Bellal, M. Trari and D. Nibou, Photocatalytic reduction of Cr(VI) on nanosized Fe₂O₃ supported on natural Algerian clay: ~~E~~ characteristics, kinetic and thermodynamic study, *Chem. Eng. J.* **200–202**, 2012, 611–618, <http://dx.doi.org/10.1016/j.cej.2012.06.121>.

[8]

F. Burriel, F. Lucena, S. Arribas and J. Hernández, Química Analítica Cualitativa, 18th ~~ed.~~, 2008, Paraninfo S.A.; Madrid Espana.

[9]

U. Divrikli, A.A. Kartal, M. Soylak and L. Elci, Preconcentration of Pb(II), Cr(III), Cu(II), Ni(II) and Cd(II) ions in environmental samples by membrane filtration prior to their flame atomic absorption spectrometric determinations, *J. Hazard. Mater.* **145**, 2007, 459–464, <http://dx.doi.org/10.1016/j.jhazmat.2006.11.040>.

[10]

S.E. Fendorf and G. Li, Kinetics of ~~Chromate Reduction by Ferrous I~~chromate reduction by ferrous iron, *Environ. Sci. Technol.* **30**, 1996, 1614–1617, <http://dx.doi.org/10.1021/es950618m>.

[11]

D.L. Sedlak and P.G. Chan, Reduction of hexavalent chromium by ferrous iron, *Geochim. Cosmochim. Acta.* **61**, 1997, 2185–2192, [http://dx.doi.org/10.1016/S0016-7037\(97\)00077-X](http://dx.doi.org/10.1016/S0016-7037(97)00077-X).

[12]

M. Doyle, R.J. Swedo and J. Rocek, Effect of cerium(III) and cerium(IV) on chromic acid oxidations. Elimination of the chromium(IV)-alcohol oxidation, *J. Am. Chem. Soc.* **95**, 1973, 8352–8357.

[13]

M. Celebi, M. Yurderi, A. Bulut, M. Kaya and M. Zahmakiran, Palladium nanoparticles supported on amine-functionalized SiO₂ for the catalytic hexavalent chromium reduction, *Appl. Catal. B Environ.* **180**, 2016, 53–64, <http://dx.doi.org/10.1016/j.apcatb.2015.06.020>.

[14]

S.-S. Chen, B.-C. Hsu and L.-W. Hung, Chromate reduction by waste iron from electroplating wastewater using plug flow reactor, *J. Hazard. Mater.* **152**, 2008, 1092–1097, <http://dx.doi.org/10.1016/j.jhazmat.2007.07.086>.

[15]

S.-S. Chen, C.-Y. Cheng, C.-W. Li, P.-H. Chai and Y.-M. Chang, Reduction of chromate from electroplating wastewater from pH 1 to 2 using fluidized zero valent iron process, *J. Hazard. Mater.* **142**, 2007, 362–367, <http://dx.doi.org/10.1016/j.jhazmat.2006.08.029>.

[16]

E.M.N. Chirwa and Y.-T. Wang, Hexavalent ~~Chromium Reduction by Bacillus sp. in a Packed-Bed B~~chromium reduction by bacillus sp. in a packed-Bed bioreactor, *Environ. Sci. Technol.* **31**, 1997, 1446–1451,

<http://dx.doi.org/10.1021/es9606900>.

[17]

L.E. Eary and D. Rai, Chromate removal from aqueous wastes by reduction with ferrous ion, *Environ. Sci. Technol.* **22**, 1988, 972–977, <http://dx.doi.org/10.1021/es00173a018>.

[18]

A. Fiúza, A. Silva, G. Carvalho, A.V. de la Fuente and C. Delerue-Matos, Heterogeneous kinetics of the reduction of chromium(VI) by elemental iron, *J. Hazard. Mater.* **175**, 2010, 1042–1047, <http://dx.doi.org/10.1016/j.jhazmat.2009.10.116>.

[19]

M. Gheju and A. Iovi, Kinetics of hexavalent chromium reduction by scrap iron, *J. Hazard. Mater.* **135**, 2006, 66–73, <http://dx.doi.org/10.1016/j.jhazmat.2005.10.060>.

[20]

J.P. Gould, The kinetics of hexavalent chromium reduction by metallic iron, *Water Res.* **16**, 1982, 871–877, [http://dx.doi.org/10.1016/0043-1354\(82\)90016-1](http://dx.doi.org/10.1016/0043-1354(82)90016-1).

[21]

H.-T. Hsu, S.-S. Chen, Y.-F. Tang and H.-C. Hsi, Enhanced photocatalytic activity of chromium(VI) reduction and EDTA oxidization by photoelectrocatalysis combining cationic exchange membrane processes, *J. Hazard. Mater.* **248–249**, 2013, 97–106, <http://dx.doi.org/10.1016/j.jhazmat.2012.12.058>.

[22]

Y. Ishibashi, C. Cervantes and S. Silver, Chromium reduction in *Pseudomonas putida*, *Appl. Environ. Microbiol.* **56**, 1990, 2268–2270.

[23]

V.V. Konovalova, G.M. Dmytrenko, R.R. Nigmatullin, M.T. Bryk and P.I. Gvozdyak, Chromium(VI) reduction in a membrane bioreactor with immobilized *Pseudomonas* cells, *Enzyme Microb. Technol.* **33**, 2003, 899–907, [http://dx.doi.org/10.1016/S0141-0229\(03\)00204-7](http://dx.doi.org/10.1016/S0141-0229(03)00204-7).

[24]

A.R. Pratt, D.W. Blowes and C.J. Ptacek, Products of ~~Chromate Reduction on Proposed Subsurface Remediation M~~[chromate reduction on proposed subsurface remediation](#) material, *Environ. Sci. Technol.* **31**, 1997, 2492–2498, <http://dx.doi.org/10.1021/es9607897>.

[25]

H. Wang, X. Wu, Y. Wang, Z. Jiao, S. Yan and L. Huang, Simultaneous ~~Removal of Phenol and Cr(VI) by TiO₂ Nanotube Array Photoelectrocatalysis: Simultaneous Removal of Phenol and Cr(VI) by TiO₂ Nanotube Array P~~[removal of phenol and Cr\(VI\) by TiO₂ nanotube array photoelectrocatalysis: simultaneous removal of phenol and Cr\(VI\) by TiO₂ nanotube array](#) photoelectrocatalysis, *Chin. J. Catal. Chin. VERSION.* **32**, 2011, 637–642, <http://dx.doi.org/10.3724/SP.J.1088.2011.01246>.

[26]

Z. Wang, R.T. Bush, L.A. Sullivan and J. Liu, Simultaneous ~~Redox Conversion of Chromium(VI) and Arsenic(III) under Acidic C~~[redox conversion of Chromium\(VI\) and Arsenic\(III\) under acidic c](#)onditions, *Environ. Sci. Technol.* **47**, 2013, 6486–6492, <http://dx.doi.org/10.1021/es400547p>.

[27]

Y.-T. Wang and H. Shen, Bacterial reduction of hexavalent chromium, *J. Ind. Microbiol.* **14**, 1995, 159–163, <http://dx.doi.org/10.1007/BF01569898>.

[28]

K. Wrobel, A.R. Corrales Escobosa, A.A. Gonzalez Ibarra, M. Mendez Garcia, E. Yanez Barrientos and K. Wrobel, Mechanistic insight into chromium(VI) reduction by oxalic acid in the presence of manganese(II), *J. Hazard. Mater.* **300**, 2015, 144–152, <http://dx.doi.org/10.1016/j.jhazmat.2015.06.066>.

[29]

E.C. Thornton and R.L. Jackson, Laboratory and Field Evaluation of the Gas Treatment Approach for In-situ Remediation of Chromate-Contaminated Soils, 1994, Westinghouse Hanford Co.; Richland, WA (United States) <http://www.osti.gov/scitech/biblio/10161217>.

[30]

Apha, AWWA, Wef, Standard Methods for the Examination of Water and Wastewater, 22nd ed., 2012, Amer Water Works Assn; Washington, DC.

[31]

O. Osegueda, A. Dafinov, J. Llorca, F. Medina and J. Suerias, In situ generation of hydrogen peroxide in catalytic membrane reactors, *Catal. Today*. **193**, 2012, 128–136, <http://dx.doi.org/10.1016/j.cattod.2012.01.040>.

[32]

O. Osegueda, A. Dafinov, J. Llorca, F. Medina and J. Sueiras, Heterogeneous catalytic oxidation of phenol by in situ generated hydrogen peroxide applying novel catalytic membrane reactors, *Chem. Eng. J.* **262**, 2015, 344–355, <http://dx.doi.org/10.1016/j.cej.2014.09.064>.

[33]

M. Sanchez J and T.T. Tsotsis, Catalytic ~~membranes and membrane~~ Membranes and Membrane Reactors, 2016, Wiley-VCH; 2002.

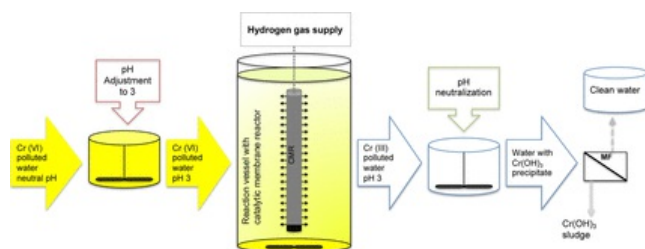
[34]

C. de, G. Sampaio, L.S. Frota, H.S. Magalhães, L.M.U. Dutra, D.C. Queiroz, R.S. Araújo, et al., Chitosan/mangiferin particles for Cr(VI) reduction and removal, *Int. J. Biol. Macromol.* **78**, 2015, 273–279, <http://dx.doi.org/10.1016/j.ijbiomac.2015.03.038>.

[35]

F. Zhang, P. Wang, J. Koberstein, S. Khalid and S.-W. Chan, Cerium oxidation state in ceria nanoparticles studied with X-ray photoelectron spectroscopy and absorption near edge spectroscopy, *Surf. Sci.* **563**, 2004, 74–82, <http://dx.doi.org/10.1016/j.susc.2004.05.138>.

Graphical abstract



Highlights

- Catalytic membrane reactors (CMRs) with Pd and Pd/CeO₂/Fe₂O₃ active phases.
- Reduction of Cr-(VI) to Cr-(VI) to Cr(III) with hydrogen by means of CMRs.
- Chromate reduction in synthetic and real mineral waters.
- Complete elimination of chromium after pH adjustment and filtration.
- Steadily performance of the CMRs in the chromate reduction.

Queries and Answers

Query: The author names have been tagged as given names and surnames (surnames are highlighted in teal color). Please confirm if they have been identified correctly

Answer: The authors names are correct

Query: “Your article is registered as a regular item and is being processed for inclusion in a regular issue of the journal. If this is NOT correct and your article belongs to a Special Issue/Collection please contact s.natarajan.2@elsevier.com immediately prior to returning your corrections.”

Answer: It is correct, the article is for inclusion in a regular issue.

Query: Please check the section conflict of interest and correct if necessary.

Answer: There is no conflict of interest.

Query: Please check the presentation of table 2 and correct if necessary.

Answer: The Table 2 is correct.