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Cathodic reduction of hexavalent chromium coupled with electricity generation achieved by reverse-electrodialysis processes using salinity gradients

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ABSTRACT

A new approach for the simultaneous generation of electric energy and the treatment of waters contaminated by recalcitrant pollutants using salinity gradients was proposed. Reverse electrodialysis allows for the generation of electric energy from salinity gradients. Indeed, the utilization of different salt concentrations gives a potential difference between the electrodes which allows the generation of electric energy by using suitable electrolytes and an external circuit. The simultaneous generation of electric energy and the treatment of waters contaminated by Cr(VI) was successfully achieved for the first time by reverse electrodialysis processes using salinity gradients and proper redox processes. The effect on the process of many operative parameters, such as the extent of the salinity gradient, the number of membrane pairs in the stack, the initial concentration of Cr(VI), the concentration of the supporting electrolyte and the flow rates of the solutions fed in the stack, was also investigated.

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1. Introduction

Chromium compounds are widely used in metal plating, paints and pigments, leather tanning, textile dyeing, printing inks and wood preservation [1]. As a consequence, relevant amounts of wastewaters containing chromium, as Cr(VI) and Cr(III), are discharged by industries and have to be properly treated. Trivalent chromium is relatively harmless and plays an essential role in biological processes, whereas hexavalent chromium is about 100–1000 times more toxic [2]. It is limited in groundwater by a World Health Organization provisional guideline value of $0.05\,mg\,L^{-1}$ [3]. Chemical and electrochemical reduction of toxic Cr(VI) into the less toxic Cr(III) (eq. (1)) is an effective approach widely studied in literature [4–9] for the treatment of such solutions. Direct electrochemical reduction on carbon electrodes (such as carbon felt or reticulated vitreous carbon) allowed to achieve an almost total conversion of Cr(VI) in Cr(III) under proper operative conditions [4]. Other approaches such as ion-exchange resins and filtration are also reported [2,10]. However, these technologies can require high energy inputs and/or generate secondary polluted by-products. Recently, it has been shown that microbial fuel cells can be used for wastewater treatment [11] and, also, for

the cathodic reduction of Cr(VI) to Cr(III) [12], thus avoiding the necessity to supply energy to the system. The anode side contained electrochemically active microorganisms that worked as biocatalysts using various organic substrates to produce electrons while the Cr(VI) abiotic reduction took place at the cathode.

$$Cr_2O_7{}^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \qquad (1)$$
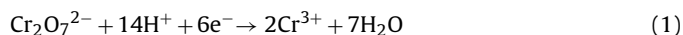
However, this approach presented quite low current and power densities and a slow rate of removal of Cr(VI). As an example, Wang. et al. [12] reported the effective reduction of Cr(VI) (initial concentration 25 mg/L) on a carbon felt cathode in 60 h with the generation of a power density lower than $0.2\,W/m^2$.

We want to propose here for the first time another sustainable technology for wastewater treatment and simultaneous generation of electric energy based on the utilization of salinity gradients and reverse electrodialysis processes. Reverse electrodialysis (RED) is a process for direct electricity production from salinity gradients, based on the use of many pairs of anion and cation exchange membranes situated between two electrodes [13–20]. The energy that theoretically can be generated per each m^3 of river water is 1.7 MJ when mixed with a large surplus of sea water [21]. It has been recently proposed to use salinity gradients obtained by thermolytic solutions such as ammonium bicarbonate (NH_4HCO_3) [22] that can be concentrated with waste heat (< 80 °C) or with solar energy with conventional technologies such as vacuum distillation [22,23]. Pilot-plants are now under construction in Italy and

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Holland [24]. The electromotive force for a stack assembly of N membrane pairs fed with water solutions of NaCl can be estimated by eq. (2) [15,16,25].

$$E = 2\,N\alpha RT\ln(a_c/a_d)/F \qquad (2)$$

where R is the gas constant, T the absolute temperature, α is the average permselectivity of the membrane pair, F the Faraday constant and a_c and a_d the solute activities in concentrated and diluted solutions, respectively.

In recent papers, some authors have shown that a proper selection of redox species and electrode materials is of paramount relevance in order to develop the RED process on an applicative scale [21,26,27]. Other authors recently studied the possible utilization of capacitive electrodes for RED processes [28] while the group of Logan proposed the utilization of bacterial oxidation of organic matter and oxygen reduction in the presence of Pt-based cathodes to increase the energy capture in RED stack [22]. In this paper, the possible utilization, in the frame of RED, of a redox process for the wastewater treatment, namely the cathodic reduction of Cr(VI) to Cr(III), was widely studied in order to evaluate the possible utilization of RED for the simultaneous generation of electric energy and the treatment of wastewaters resistant to conventional biological processes, thus enhancing the perspectives of both processes. Thus, from the point of view of RED, the redox processes would be no more a penalty but an opportunity to increase the value of the process that could be used for both electric generation and water treatment. At the same time electrochemical remediation processes carried out in a RED would not need external electric energy which is up to now one of the more relevant limitations to the practical application of such tools.

2. Experimental

2.1. Experiments in stack

Two similar home made lab scale stacks were used (Fig. 1) with different dimensions. The stack consists of n number (n = 9, 39 or 49) of anion and n + 1 number of cation-exchange membranes (Fuji), gasket integrated with spacers (Deukum, 0.28 mm thickness) and two external membranes to separate electrodic compartments and side ones, creating n + 1 (10, 40 or 50) pairs of alternating high concentrated (HC) and low concentrated (LC) chambers. A cationic (Nafion) and an anionic (Selemion) external membranes were used in contact with cathodic and anodic compartments, respectively (Table S1 in the electronic supporting information). The two electrode chambers contained a carbon felt cathode (Carbone Lorraine) choosen according to the pertaining literature [29-31] and a titanium meshes coated with Ti/IrO$_2$-Ta$_2$O$_5$ anode (Magneto). The area of each electrode and of each membrane was 28 and 100 cm^2 for the small and the large stack, respectively. The HC solution entered from the cell next to the anode chamber and flowed in parallel through the HC cells in the stack, exiting from the cell next to the cathode chamber. The LC stream entered in the RED stack near the cathode and flowed in parallel through the LC cells in the stack, exiting from the cell next to the anode chamber. Two peristaltic pumps (General Control SpA) continuously fed the HC and LC solutions. Two closed-loop hydraulic circuits were used for electrodic solutions. The two electrodic solutions were continuously recirculated to the electrodic compartments and to two different reservoirs by two peristaltic pumps (General Control SpA). During power density curve experiments, fresh HC and LC solution were pumped through the RED stack with the effluents collected in separate vessels.

Solutions used in HC and LC compartments were prepared by dissolving NaCl (analytical grade Sigma-Aldrich) into deionized
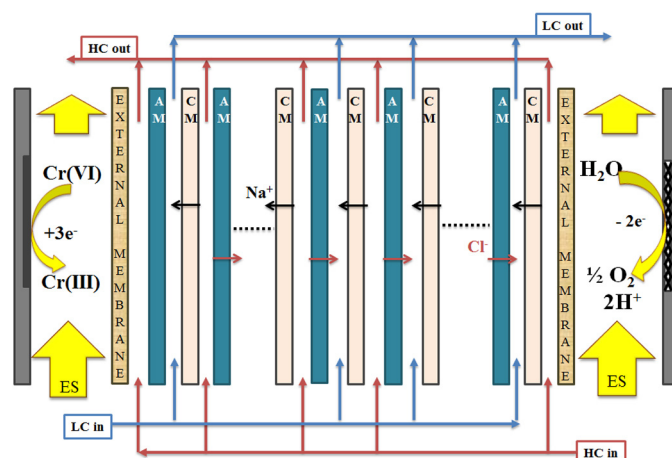

Fig. 1. Scheme of RED stack. The figure illustrates how anionic (AM) and cationic membranes (CM) are used to selectively drive the flow of positive ions to the left (toward the cathode) and the negatively charged ions to the right (toward the anode). The flow of these charged ions is converted in a flow of electrons at electrodes that sustain current production and cathodic reduction of Cr (VI). The stack is fed with high concentrated (HC) and low concentrated (LC) saline solutions and with electrolyte solutions (ES). The HC solution entered from the cell next to the anode chamber and flowed in parallel through the HC cells in the stack, exiting from the cell next to the cathode chamber. The LC stream entered in the RED stack near the cathode and flowed in parallel through the LC cells in the stack, exiting from the cell next to the anode chamber.

water. Experiments were performed with two separated solutions (250 mL each) flowing in the electrodic compartments:

- anodic solution containing 0.1 M Na$_2$SO$_4$ (Sigma-Aldrich) and H$_2$SO$_4$ (pH = 2)
- cathodic solution containing Cr(VI) (grade Sigma-Aldrich) with an initial concentration of 2, 25 or 50 mg/L, 0.1 or 0.5 M Na$_2$SO$_4$ (grade Sigma-Aldrich) as supporting electrolyte at a pH = 2 (H$_2$SO$_4$).

Experiments were repeated at least twice with an error usually lower than 5%.

2.2. Analyses

Power production was studied by measuring both the potential drop across a variable external resistance (range 4.6–163.6 Ω) and the current intensity by a multimeter Simpson. The overall external resistance was given by the contribution of a variable resistance (range 1–160 Ω) and that of cables and an amperometer (with an estimated resistance of about 3.6 Ω). Power was calculated by multiplying the electrical current and the total cell potential. Power density can be computed by the ratio between the power and the total area of all membranes or the total area of cationic membranes (W per m^2 of membrane pair) or the geometric area of the electrode. In the paper we reported the power density P as the ratio between the power and the geometric area of the electrode. Only in the last section the power density per membrane area was also cited. Power production during batch recycle experiments was measured in the same way across a fixed external resistance of the value of about 4.6 Ω. The removal of Cr(VI) was monitored by using Agilent Cary 60 UV Spectrophotometer. Cr(VI) was detected at λ = 540 nm, after treatment with 1,4-diphenylcarbazide and its concentration was determined after proper calibration using the Lambert Beer law. The lower detection limit for Cr(VI) was 0.01 ppm.