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Energy generation and abatement of Acid Orange 7 in reverse electrodialysis cells using salinity gradients

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ABSTRACT

The simultaneous generation of electric energy and the treatment of wastewaters contaminated by an organic pollutant resistant to conventional biological processes, Acid Orange 7 (AO7), was achieved for the first time using proper redox processes by reverse electrodialysis using salinity gradients. The stack was fed with two aqueous solutions with different concentrations of NaCl and a synthetic wastewater contaminated by AO7. Various electrochemical approaches including electro-Fenton, electrogeneration of active chlorine (IOAC) and coupled process were performed in a stack equipped with 40–60 cell pairs and studied by focused electrolyses. The effect of the number of cell pairs and of the NaCl concentration of saline solutions was also investigated.

1. Introduction

Wastewater treatment technology is undergoing a transformation due to more restrictive regulations governing the discharge and disposal of hazardous pollutants [1]. Electrochemical based technologies are very promising methods for treating wastewaters containing organic pollutants resistant to biological processes or toxic for microorganisms [1–3] or for disinfection purposes [4]. These methods present numerous advantages including the utilization of a green reagent such as the electron, very high removal of numerous recalcitrant pollutants, efficient disinfection, high flexibility and no necessity to transport or stock chemical oxidants or reductants [1]. On the other hand, a wide utilization of such methods is likely to be limited by the cost of electric energy necessary to drive electrode reactions, for some applications by the cost of electrode materials, and for wastewaters with low conductibility by the necessity to add a supporting electrolyte [5].

Reverse electrodialysis (often named in literature with SGP-RE or RED acronyms) 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 [6–11]. Salinity gradient energy can be obtained from seawater and freshwater sources in estuarine or coastal areas, from salt ponds and seawater/river water or using thermolytic solutions [12] that can be concentrated with waste heat (>40 °C) energy [13] with conventional technologies such as vacuum distillation. The supply of solutions with different salt concentration in the RED stack gives rise to a potential difference between the electrodes that can be used to produce electric energy by adopting suitable redox processes. The interest in the utilization of RED for the production of electric energy from salinity gradients increased in the last years since RED seems closer to a possible application due mainly to the development of cheap and more effective membranes. The net power density achieved for RED (i.e., the power density obtained by the stack minus the power density needed to pump the solutions) increased in the last few years from 0.7 to 1.2 W/m^2 (computed as the power per membrane area) using seawater and river water and reached values of about 2–2.5 W/m^2 using water from salt pond and seawater [14,15]. Drastic further increase is furthermore expected in the next few years because of research on spacers and membranes. Quite high powers are expected for industrial plants (involving thousands of cell pairs) according to computations made by industries (as an example, for a 200 m^3/s flow rate, with NaCl concentrations of 30 g/L and 1 g/L, a power of 200 MW was recently estimated by FujiFilm [16]). Pilot-plants are now under construction in Italy and Holland [17]. In order to generate electric energy by RED the following components are necessary [9,18]:

(1) anion-exchange membranes (AEMs) and cation-exchange membranes (CEMs) used to selectively drive the flow of positive ions in one direction (toward the cathode) and the negatively charged ions in the opposite direction (toward the anode) (Figs. 1 and 2);

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(2) solvents, which make a continuum for ion transport;
(3) electrolytes, i.e. the current carriers between cathode and anode;
(4) electrodes, where electron transfer reactions occur to allow the transformation of the charge carrier from ion to electron. Indeed, the utilization of different salt concentrations at both sides of the membranes gives a potential difference between the electrodes which allows the generation of electric energy by using suitable redox processes and an external circuit;
(5) end membranes to confine the special ions of the electrolyte (e.g. H^+);
(6) spacers, to ensure the feed of the stack with the low and high concentrated solutions.

In some recent papers, it was shown that a proper selection of redox species and of electrode materials is of paramount relevance in order to develop the RED process on an applicative scale [9,18,19]. In particular, some of the authors studied in detail the possible utilization of various redox processes such as reduction/oxidation of iron species, oxidation and reduction of water, oxidation of chloride and reduction of water [18,19]. Vermaas et al. studied the possible utilization of capacitive electrodes for RED processes [20]. Most of proposed redox systems give rise to a significant economic penalty for the process due to energy necessary to drive the redox processes coupled with the cost of electrodes and electrolytes. Recently, it has been proposed to select the redox processes with the aim of adding value to the overall process. Cusik et al. proposed the utilization of bacterial oxidation of organic matter to increase the energy capture in RED stack [12,21] and for hydrogen generation [22] while some of the authors showed for the first time that RED can be used for the simultaneous generation of electric energy and the cathodic treatment of a wastewater contaminated by Cr(VI) [23].

In this frame, as a continuation of previous researches, we have studied the possible utilization of a RED stack for the simultaneous generation of electric energy and the treatment of wastewaters contaminated by organic pollutants resistant to conventional biological processes, by a proper selection of redox processes. Such coupled process could enhance the perspectives of both RED process and electrochemical treatment of organics. Thus, the electrochemical treatment of waters contaminated by organics would no more need a supply of electric energy and the RED process could allow also the wastewater treatment. In this frame, one has to consider that industrial plants, that generates liquid effluents, very often produce waste heat that can be used to easily generate salt gradients or use diluted waters that can be used for RED with seawater if plants are located near the sea.

To test the possible utilization of RED for the simultaneous treatment of wastewaters contaminated by organic pollutants and the generation of electric energy, we examined the decoloration of an aqueous solution contaminated by a model organic recalcitrant compound, the Acid Orange 7 (AO7), a largely used azoic dye resistant to biological processes, that can be effectively treated, according to the literature, by various electrochemical processes [24–26]. Very large amounts of synthetic dyes are

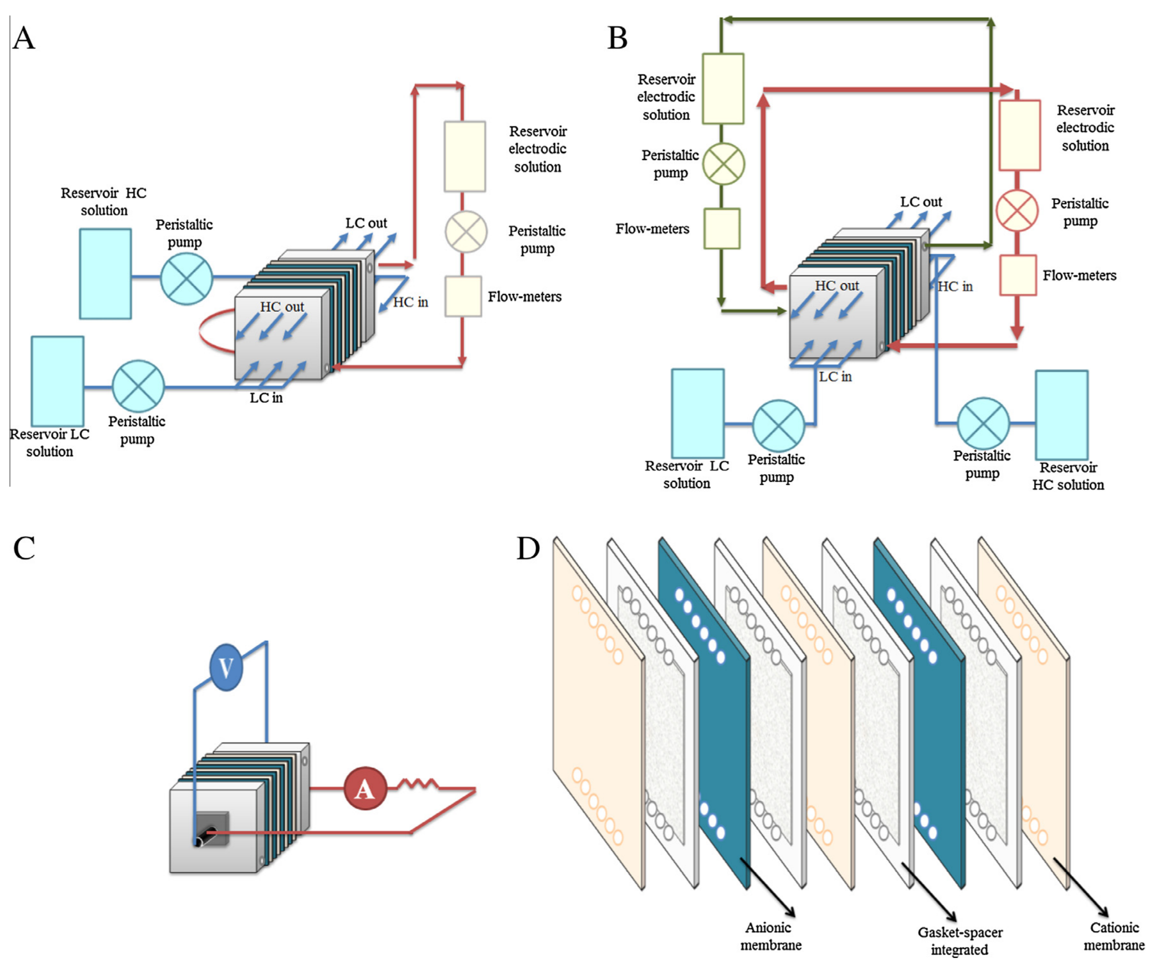

Fig. 1. Main components of the system for an undivided (1A) and two separated (1B) electrodic patterns. (C) Reports the circuit containing a load (resistor), an amperometer and a voltmeter. (D) Reports the main components of the cell pairs.