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Investigation of batch electrodialysis process for removal of lead ions from aqueous solutions

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HIGHLIGHTS

- Separation of Pb(II) ions by batch electrodialysis.
- Effect of operating parameters on Pb(II) separation by electrodialysis.
- Very good separation and energy performances under optimal conditions selected.
- Effective removal of lead ions and obtaining of non-toxic diluate.
- High concentration of metal in concentrate suitable for further recovery.

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ABSTRACT

Lead is a highly polluting and toxic heavy metal, whose removal from wastewater is an important problem in specific industries. The present paper reports the feasibility of removal and concentration of Pb(II) ions from model aqueous solutions in a batch electrodialysis system, in order to comply with toxicity limit and with the regulations limit for discharging the wastewaters. For process optimization, the effects of applied potential, flow rate, temperature and initial metal concentration in feed on the separation performance, and also on the current efficiency (*CE*) and energy consumption (*EC*) were investigated. It was observed that the increasing of applied voltage, flow rate and process temperature decrease the duration of the ED process, but also decrease the cell performance in terms of *CE* and *EC*. Increasing feed concentration increases the *CE* to a maximum value for feed containing 500 mg Pb/L, and further decreases it. The optimum operating conditions selected are: applied potential of 10 V, flow rate and temperature of 70 L/h and 25 °C, respectively, and feed solutions containing 500–1000 mg Pb/L. Under these selected conditions very low final concentrations of diluate (1–2 mg Pb/L) are obtained, the metal is concentrated 5-fold in the concentrate compartment, and at the same time the *CE* is very high. The batch ED process investigated proved to be able to perform an effective removal of lead ions under advantageous energy-efficiency conditions, also leading to non-toxic wastewaters having metal concentrations very close to the limit suitable for discharges into the environment. The concentrate solution resulted after ED is adequate for further metal recovery.

1. Introduction

A wide range of wastewaters containing heavy metals is generated by various industrial activities which can cause critical environmental problems as heavy metals are extremely toxic, non-biodegradable and tend to accumulate in living organisms. Among them, lead is a highly toxic metal that can cause neurological disorders, elevated body blood pressure, anaemia and gastrointestinal diseases when present in the human body. Such effects were observed even at very small lead concentrations of only 0.01–5.0 mg/L [1]. Lead contamination originates from discharging of untreated wastewaters from electroplating, printing pigments, textile and fuel industry, mining, battery manufacturing, explosives manufacturing, automotive and building construction. The industrial wastewaters are generally acidic (pH = 1.5–6) and therefore contain soluble Pb^{2+} in a wide concentration range which has significant variations in types and also on specific sources [2]; thus, some examples of typical lead concentrations in polluted industrial waters are: metal finishing industry (0.02–42 mg Pb/L) [2], mining (15 mg Pb/L) [3,5], landfill

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leachates (2–5 mg Pb/L) [4], plating industry (20–140 mg Pb/L) [5], various metal production by smelting and refining (0.02–53 mg Pb/L) and battery industry (7–2000 mg Pb/L) [2]. Therefore, the treatment of wastewaters for removal of heavy metals before discharging them is a problem of critical importance [1,6]. According to the USEPA environmental regulations, the toxicity threshold level is 5.0 mg Pb/L in wastewaters [3], and the maximum acceptable concentration of lead for the discharging of wastewaters in the surface waters stipulated by the Czech regulations is 0.5 mg Pb/L [7].

The conventional methods developed for the removal of Pb(II) ions from wastewaters include solvent extraction [8], chemical precipitation [9], ion exchange [10] and adsorption on solid sorbents [11–14]. Some limitations and disadvantages of those methods are the high capital and regeneration costs, long operation time and the fact that they can be considered as polluting methods themselves due to the use of chemical additives. Membrane-based processes are non-polluting separation techniques that compete with the above mentioned methods for the removal of heavy metals; liquid membranes [15–18], pressure driven membrane processes like reverse osmosis (RO) [19] and nanofiltration (NF) [4,19–24] proved that they can be used for obtaining highly purified effluents, being at the same time faster and cheaper than conventional separation techniques. However, in NF and RO the concentration polarization and the osmotic pressure make difficult the achievement of a high level of concentration of the metal in the retentate.

Electrodialysis (ED) is an electromembrane technique that has some important advantages like selective desalination, low use of other chemicals and high water recovery. ED is based on the transport of ions through ion-exchange membranes under the influence of an electrical potential difference as the driving force. The basic principles of ED are reviewed in the literature [25,26]. The solution to be treated is circulated through an ED stack, which consists of a series of alternating parallel anion exchange membranes (AEM) and cation exchange membranes (CEM) which are fixed between two electrodes, the anode and the cathode. Under an electrical potential difference between the electrodes, the cations move towards the cathode and the anions migrate to the anode by permeating the oppositely charged membranes and being retained by the ion-exchange membranes with the same charge. In this way, the ions are depleted in one compartment (diluate compartment) and concentrated in the adjacent compartment (concentrate compartment). Thus, the feed stream entering the ED stack (wastewater to be treated) is separated into a concentrate stream (referred as concentrate) and a dilute stream (referred as diluate). An individual ED cell (a repeating unit from the ED stack) consists of an anion- and a cation exchange membrane, a diluate and a concentrate compartment. ED has proven high performance in a wide area of applications like sea/brackish/ground water and brine desalination [27–30], energy generation [31], desalting of whey [32] and treatment of the pressure-driven membrane concentrates [33]. Furthermore, the suitability of ED for removal of various polluting heavy metals (copper, chromium, lead, zinc, nickel, silver) has been supported by a number of studies [34–42]. The ED processes can be operated in continuous mode (one pass flow), feed and bleed mode (partial recirculation) and in batch mode [25,26,43]. As in the continuous ED processes the wastewater is passing through the membrane stack/cell once, the metal removal and concentration, and also the current efficiency (*CE*) that can be achieved are not very high [25]. Therefore, continuous ED is used in large systems that contain several ED stacks in series, and thus separation is more efficient; at the same time, such big units have disadvantages like pressure loss in the stacks and high costs for pumping, maintenance and membranes [25,43]. The batch ED is an alternative of the continuous process, and it is used in industry in order to achieve a high degree of desalination and concentration and thus to meet the required end product qualities [25]; also, batch ED is the usual operation mode of small and middle ED plants in the isolated area where the supply of water and electricity is difficult and costly [27]. Some of such applications of batch ED are: demineralization of whey [44], removal of nitrate [45], seawater desalination in an island [46] or in a tank [47], wastewater treatment [48], desalination of brackish groundwater [49]. Batch ED processes are attractive in such of applications due to the fact that the maintenance of the unit (membrane cleaning, replacing of severely fouled or damaged membranes and electrodes) can be realized between batch operations [50]. Besides the industrial applications, batch ED is a very useful tool for simulating the pilot and industrial scale operations and for fast optimization of their operating parameters [51,52]. In this respect, investigations about batch ED processes performed in laboratory units like removal of heavy metals (chromium, silver) [34,41], sea/brackish/ground water and brine desalination [27–30], desalination of whey [32] or sodium sulfate removal [53], treatment of RO concentrates [51,52] were also published in the literature. If these batch process investigations are carried out under operating conditions close to those in the real applications, *i.e.* laboratory units with ED stacks similar to those in the pilot/industrial units, the same membranes and thickness of the spacer like in the pilot/industrial units and similar flow rates, the results obtained can be used for upscaling the processes [51,52].

To our knowledge, up to now the studies devoted to Pb(II) removal by ED have investigated the continuous ED processes in a single laboratory ED cell [35,38,39,42] or using an ED unit containing 110 cells [36,37]. These investigations were carried out in conditions which are not close to those in the real ED units, *i.e.* a unique small cell with thick compartments (3–4 mm), without spacers, and using very low flow rates of 0.07–1.2 mL/s [35,38,39,42]; other investigations were performed in an ED unit equipped with 2 stacks of 55 cells each, but using very low flow rates in the range of 2–10 L/h [36,37]. These studies were not achieving a very low concentration in diluate, reported low *CE* values [36,38] or no information about this key parameter [35,37,42], and are also lacking in information about *EC* of the processes investigated [35,37–39,42].

Considering the highly toxic potential of Pb(II) [1], and also the interest in its recovery for further industrial reuse, studies involving lead separation in order to obtain non-toxic diluate and concentrate solution with high lead content, and being also performed under conditions approaching those used in the pilot/industrial units can be of interest.

In this work, the feasibility of a batch ED process using Ralex CM-PES and Ralex AM-PES heterogeneous ion exchange membranes for the removal and concentration of lead ions from model wastewaters is thoroughly investigated. The influence of various process conditions (applied voltage, flow rate of the diluate and concentrate solutions, temperature and initial metal concentration in the feed) is studied by using an ED unit designed for simulating the industrial conditions. Besides the higher separation performance that can be achieved by using batch ED, the efficiency and therefore the applicability of the ED processes are evaluated by calculating key parameters, such as *CE* and *EC*; these reflect both the separation performance and also the degree of current utilization for the ED separation, which finally determine the cost of the ED process. Thus, as the bulk of the operating costs in ED is related to the energy consumption during the ED desalination [50], the aim of the present work is to optimize the batch ED process investigated from the point of view of *CE* and *EC*, concomitantly with achieving a very high separation of Pb(II) ions leading to the generation of a non-toxic diluate and a highly concentrated solution in the concentrate compartment suitable for further recovery of the metal.