São Paulo - Brazil - May - 24th to 26th - 2017

INTERNATIONAL WORKSHOP
ADVANCES IN CLEANER PRODUCTION

Years
2007 - 2017

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Evaluation of the Electrodialysis Process in the Treatment of Phosphate Containing Solution

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Abstract

Phosphorus (P) is inherent to all life forms. The increasing in crop production requires an increase in the use of P as fertilizer, usually produced from phosphate rocks, a non-renewable source that are being depleted. On the other side, high levels of P on surface water from wastewater and agricultural may lead to environmental problems, such as eutrophication. Therefore, the present work evaluated the technical feasibility of a 5-compartment electrodialysis (ED) cell in the treatment of phosphate containing solution, prepared using $Na_2HPO_4.7H_2O$ and $NaH_2PO_4.H_2O$ salts, aiming the recovery of P from municipal wastewater. Heterogeneous cation- (HDX100) and anion- (HDX200) ion-exchange membranes were used. Current-voltage curves (CVCs) showed that the current density to be used in electrodialysis tests was limited by the HDX200 anion-exchange membrane. The average percent extraction (pe%) of sodium was 92%, while for phosphate-containing species was 61%. The phosphate-containing species removal may be restricted by the formation of a non-chargeable specie, H_3PO_4, resulted from changes on the pH conditions in the diluted compartment.

Keywords: phosphorus, sewage, membrane process, P-recovery.

1. Introduction

Phosphorus (P) is an essential nutrient for all life forms. P can be considered a limiting nutrient to the growth and production of marine, freshwater and terrestrial ecosystems as it is a crucial component in structuring any molecule (Childers et al., 2011; Desmidt et al., 2015). To meet the demand of food and commodities industry, phosphorus is produced from phosphate rocks, a limited and non-renewable source, considered by the European Commission one of the 20 critical raw materials (Koppelaar and Weikard, 2013; European Commission, 2014). In contrast, excessive P loads inserted on natural water bodies from wastewater and agricultural may cause serious eutrophication (Shepherd et al., 2016). Thus, the concern with the scarcity of this nutrient and with the environmental problems caused by its excessive discharge have lead to researches on technologies to phosphorus recovery from wastewater.

In last years, different processes were proposed to the recovery and concentration of P, such as crystallization (Le Corre et al., 2009), precipitation (Qiu and Ting, 2014), biochar adsorption (Shepherd et al., 2016) and membrane-based process, e.g. electrodialysis (Xie et al., 2016). Electrodialysis (ED) is a membrane separation process in which ionic species are transported through ion-exchange membranes by the application of an electric field between two electrodes. Cation- and anion-exchange membranes are alternately arranged in a filter press-like system, called stack, where negative charged

ions are able to permeate only the anion-exchange membrane and the positive ones only the cation-exchange membrane (Marder et al., 2003; Bernardes et al., 2014). Therefore, ED can be used to directly recover and concentrate soluble phosphorus in the form of ortho-phosphate ($H_2PO_4^-$ and HPO_4^{2-}), leaving it in a crop-available form (Ebbers et al., 2015). Several studies reports the viability to recover phosphorus from sewage sludge ash (SSA), the by-product of dewatered sewage sludge combustion in an incinerator (Guedes et al., 2014; Ottosen et al., 2016; Parés Viader et al., 2016), method that is not commonly used in Brazil.

Therefore, the objective of this work was to test the technical feasibility of a 5-compartment ED cell in the treatment of a phosphate containing solution aiming the recovery of P from municipal wastewater. The limiting current density was determined, as well as the ionic transport and the recovery efficiency in terms of percent extraction of Na^+ and PO_4^{3-} ions.

2. Materials and Methods

2.1. Solutions

For the tests, a phosphate containing solution with conductivity and pH similar to a real municipal wastewater treated by macrophytes was used. This solution was prepared by the addition of 0.65 g L^{-1} of $Na_2HPO_4.7H_2O$ and 0.33 g L^{-1} of $NaH_2PO_4.H_2O$. To ensure system conductivity, an electrolytic solution containing 4 g L^{-1} of Na_2SO_4 was used. All reagents were of analytical grade purity.

2.2. Electrodialysis cell

The experiments were carried out in a laboratory-scale electrodialysis cell. The cell was made of transparent acrylic with five compartments containing two pairs of membrane, alternately arranged, and one pair of electrodes (Fig. 1). Heterogeneous cation- (HDX100) and anion- (HDX200) exchange membranes, supplied by Hidrodex®, with 16 cm² of effective area were used (Buzzi et al., 2013; Martí-Calatayud et al., 2014; Marder et al., 2016). Commercial titanium electrodes coated with titanium and ruthenium oxides ($70TiO_2/30RuO_2$) with 16 cm² of effective area were used as anode and cathode at the both sides of the stack (Benvenuti et al., 2014). The cell was fed by a centrifugal pump with flow rate of 80 L h^{-1}, also ensuring the circulation of the solutions in the four reservoirs.
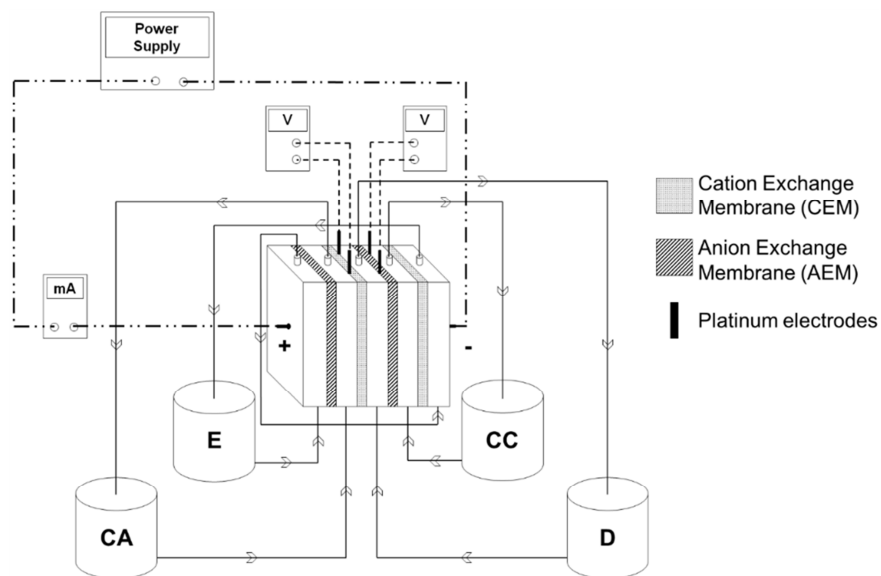

Fig. 1. Schematic representation of the electrodialysis system used in the experiments. (CA) refers to the reservoir of the concentrated anode compartment; (CC) refers to the reservoir of the concentrated cathode compartment; (E) to the reservoir of the electrodes compartments and; (D) to the diluted central compartment.

2.3. Determination of the limiting current density

It is desirable to operate an electrodialysis system with the highest possible current density, maximizing the ion flux throughout the effective area of the membrane. However, when the transport of the ions through the membrane is greater than from the bulk solution to the membrane, a phenomenon called concentration polarization occurs. The current density which this phenomenon begins to be perceptible is called limiting current density, i_{lim}, and if exceeded can cause several problems to the ED process. To determine this parameter, a well know method called current-voltage curve (CVC) can be used, relating the applied current density, i, with the potential of the membrane, U_m (Bernardes et al., 2014).

The limiting current density (i_{lim}) adopted in the electrodialysis tests was determined by the current-voltage curves (CVCs) method. In the reservoirs of the laboratory-scale cell (item 2.2), 1 L of the electrolytic solution was circulated in the electrode compartment (E), while the central compartment (D) and the concentrated ones (CA and CC) were filled with 2 L and 1 L of the P-containing solution, respectively.

Platinum (Pt) wires were arranged at the interfaces of the cationic and anionic membrane of the central (diluted) compartment. The difference in the potential of each membrane was determined by two digital multimeters (SKMD-100, Skill-Tec) installed in parallel. The amount of the current was gradually increased at a rate of 2 mA each 30 seconds using a power supply (ICEL Manaus, PS-7000). To ensure greater accuracy in current application, it was installed a third multimeter (same model) connected in series to the current source and the cell anode. The values reported by the multimeters were recorded and current-voltage curves were plotted. This assay was performed in duplicate.

2.4. Electrodialysis experiments

Once the optimum operating current density (item 2.3) was established, electrodialysis (ED) tests were carried out in triplicate. Using the cell described in item 2.2, all the reservoirs received 0.5 L of the P-containing solution, except the E reservoir, filled with 1 L of the electrolytic solution. Prior to conducting the ED experiments, the membranes were equilibrated in the solutions to be used subsequently during periods between 18 and 24 hours.

Throughout each hour of the ED test, conductivity (conductivity meter AZ8361, AZ Instruments) and pH (PHS-3B, PHTEK) values of all working solutions were monitored, as well as the applied current and the cell potential. In addition, aliquots of approximately 5 mL were collected from the reservoirs at 3-hour intervals and submitted to ion chromatography analysis (ICS 3000, Dionex). The results enabled the study of the ions transfer and an evaluation of the efficiency of the ED process to remove and recover phosphate, calculated as a function of the percent extraction (pe%, Eq. 1) of Na^+ and PO_4^{3-} ions (Bernardes et al., 2014).

$$pe\% = \frac{(C_i - C_t)}{C_i} \times 100 \qquad (1)$$

where: C_i is the initial ion concentration and C_t is the ion concentration at time t of ED treatment.

3. Results and Discussions

3.1. Limiting current density

The CVCs obtained in this study are presented in Fig. 2. As it can be observed in Fig. 2a, the cation-exchange membrane HDX100 presents a typical behavior (Scarazzato *et al.*, 2015), with three regions and one limiting current density, $i_{lim,CEM}$ (point 1). For the anion-exchange membrane HDX200 (Fig. 2b) the CVC differs from the conventional one by presenting two plateaus (between points 1-1' and 2-2') and, consequently, two limiting current densities: $i_{lim,AEM1}$ in point 1 and $i_{lim,AEM2}$ in point 2.
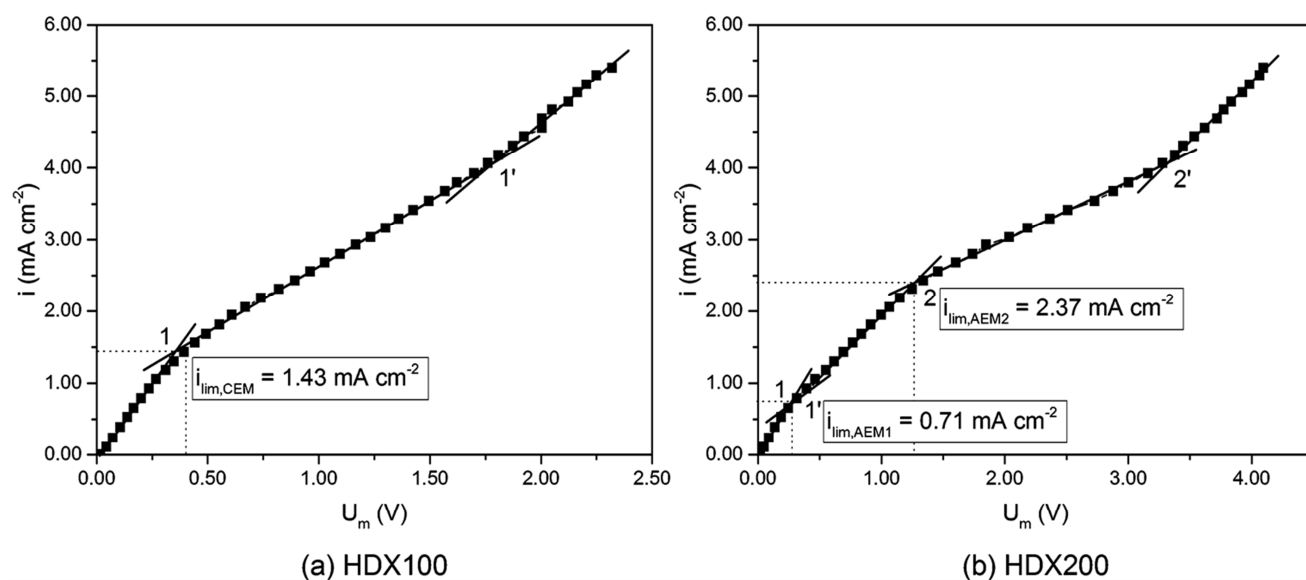
Fig. 2. Current-voltage curves of the HDX100 cation-exchange membrane (a) and HDX200 anion-exchange membrane (b) in contact with the P-containing solution.

The presence of two plateaus in CVCs of phosphorus containing solutions as also reported by Pismenskaya *et al.* (2001). This behavior may be related to different phosphorus-containing species that can be formed in the solution and in the membrane/solution interface according to the pH conditions, as it can be observed in the speciation diagram (Fig. 3) calculated and plotted using the Hydra-Medusa® software (Puigdomenech, 2004).
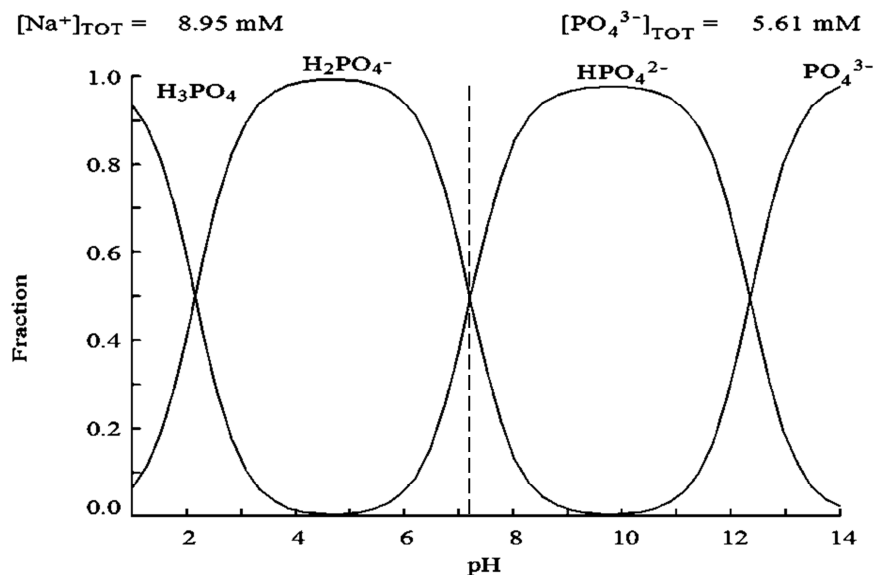

Fig. 3. Diagram of distribution of phosphorous-containing species in the P-containing solution calculated and plotted using the Hydra-Medusa program. (Vertical dashed line represents the initial equilibrium conditions).

3.2. Evaluation of Electrodialysis

The ED experiments were run in galvanostatic mode for 15 hours at room temperature. The current density used was based on the results of the CVCs (item 3.1). According to Buzzi *et al.* (2013), the maximum current density that should be applied to an ED system may be 70% to 80% of the value of the limiting current density obtained from the CVC method. Thus, considering the point 1 from the

anion-exchange membrane as the limiting current density of the system, it was applied 0.53 mA cm^{-2}, approximately 8.50 mA.

Conductivity, pH and cell potential were monitored along the ED experiment. The determined pH value represents the bulk solution pH and not necessarily the pH in the membrane/solution interface (Marder et al., 2003). The behavior of the monitored parameters can be observed in Fig. 4, 5 and 6.
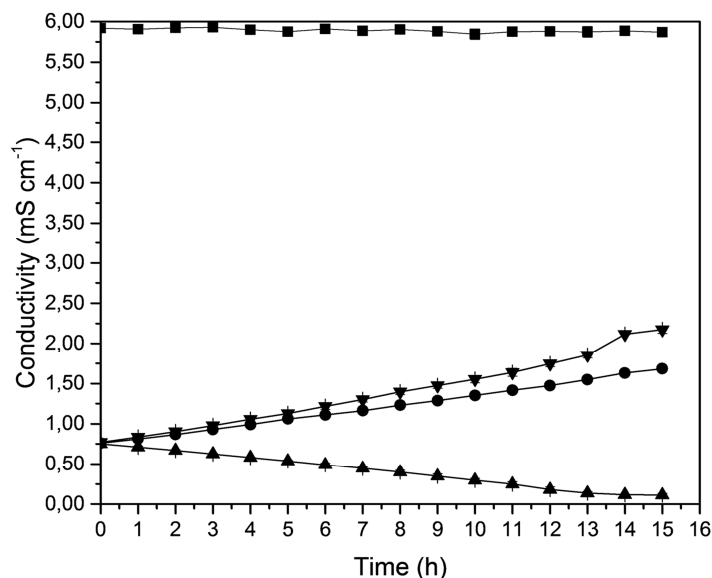

Fig. 4. Average values of solution conductivity in the electrodialysis cell compartments. (■) Electrodes; (●) concentrated anode; (▲) diluted and; (▼) concentrated cathode.
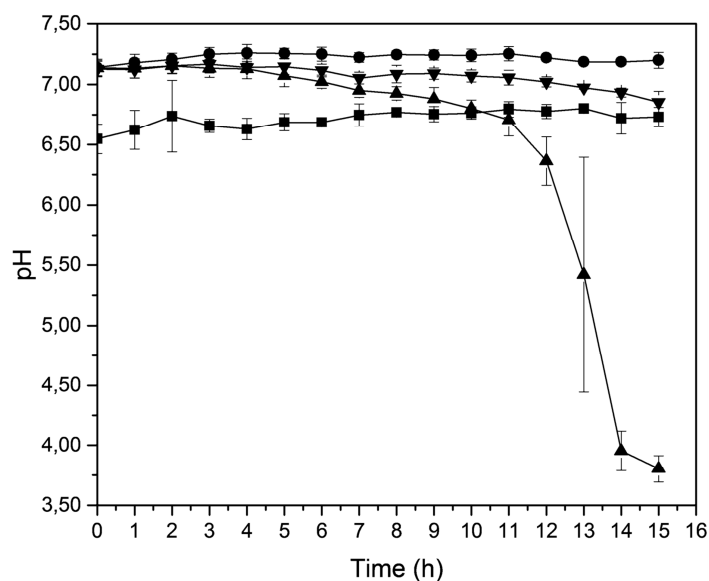

Fig. 5. Average values of solution pH in the electrodialysis cell compartments. (■) Electrodes; (●) concentrated anode; (▲) diluted and; (▼) concentrated cathode.
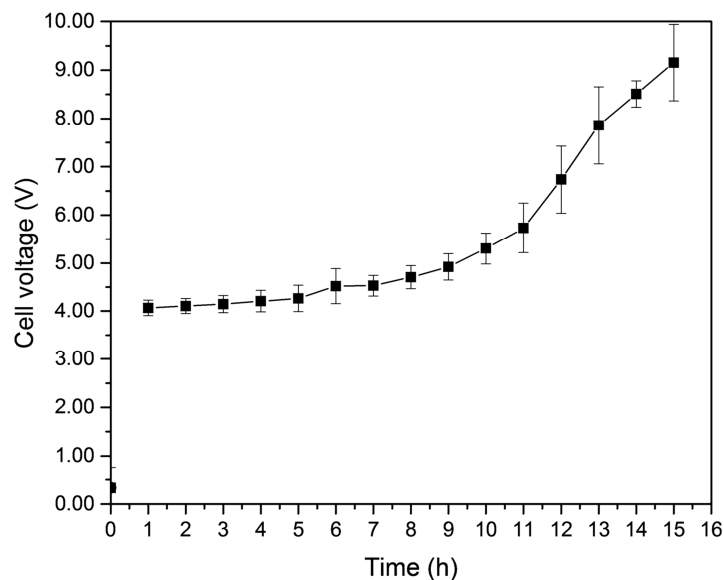
Fig. 6. Average values of the cell potential along the experiment.

During the ED, the conductivity in the diluted compartment (D) decrease, while it increase in the concentrated compartments (Fig. 4). Conductivity decreasing in the central compartment (D) indicates the removal of phosphate species (HPO_4^{2-} and $H_2PO_4^-$) and Na^+ from the P-containing solution. For the anodic concentrate compartment (AC), the increasing in conductivity may be associated to the transport of the phosphate species from D compartment and Na^+ from the electrodes compartment (E). Regarding the cathodic compartment (CC), this behavior may be attributed to SO_4^{2-} from E compartment and to the Na^+ transport from D compartment.

Fig. 5 shows that the bulk solution pH in the diluted compartment decreased. It may be related to the current density applied on the cell. Since in this work 0.53 mA cm^{-2} was applied during 15 hour, and considering the depletion of phosphate ions in the diluted compartment, the system could have reached or exceed the limiting current densities, leading to the formation of H^+ and OH^- ions due to water dissociation. The OH^- ions may pass through the anion-exchange membrane, while H^+ shifts the equilibrium to the formation of H_3PO_4.

Cell voltage increased along the ED experiments (Fig. 6). It may be referring to the removal of the number of ions available in the central compartment, intensifying the solution electrical resistance. Furthermore, when Fig. 5 and Fig. 6 are compared, it can be observed that the increase of the resistance of the cell accompanies the decrease of the pH of the central compartment. It may be related to an anion-exchange membrane concentration polarization in addition to the formation of H_3PO_4, a non-chargeable phosphorous-containing specie (Fig. 3).

The changes on the pH conditions in the D compartment may also affects the average percent extraction (pe%) of phosphate (Table 1). While the pe% for Na^+ is over than 92%, phosphate-containing species reported a lower value, around 61%, possibly due to H_3PO_4 availability.

Table 1. Percent extraction from the diluted compartment for phosphate and sodium.

Ionic specie	Percent Extraction (pe%)*
Phosphate-containing species ($H_xPO_4^{x-3}$)	(60.82 ± 6.48) %
Sodium (Na^+)	(92.21 ± 1.21) %

4. Conclusions

It was evaluated the application of electrodialysis (ED) in the treatment of a phosphate containing solution aiming the recovery of phosphorus from municipal wastewater. Current-voltage curves (CVCs) were conducted, showing an unusual behavior for the anionic-exchange membrane (HDX200) presenting two plateaus and two limiting current densities, probably due to the availability of different phosphorus-containing species in the solution and membrane/solution interface. The CVCs indicated that the current density to be applied in ED experiments was limited by the HDX200 anion-exchange membrane. The ED promoted a percent extraction of sodium greater than 92%, while for phosphate-containing species around 61%. The phosphate-containing species percent extraction was restricted possibly due to the formation of the non-chargeable specie H_3PO_4 resulted from changes on the pH conditions in the diluted compartment. Further experiments should be done to try to achieve higher phosphate species recovery. Controlling the solution pH, operating in a continuous way or changing successively the solution in the diluted compartment may be appropriate.

Acknowledgements

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