Removal of phosphate by Donnan dialysis coupled with adsorption onto calcium alginate beads

Ikhlass Marzouk Trifi, Beyram Trifi, Sirine Ben Ayed and Béchir Hamrouni

ABSTRACT

In this study the removal of phosphates from solution by Donnan dialysis and by adsorption onto calcium alginate beads were studied separately and then together. This hybrid process was conducted in order to benefit from each process, and it is an original and new combination. First, the Donnan dialysis process was performed with different parameters: the type of counter-ion, the concentration of the counter-ion, the initial phosphate concentration, the pH of the solution and the choice of anion-exchange membranes. Donnan dialysis achieved 68% and 12.5% phosphorus removal with AMX and AFN membranes respectively. Then a preliminary study into the adsorption of phosphate onto calcium alginate beads was carried out. A full factor design was applied in order to determine the effect of the main parameters and their mutual interactions for the adsorption process. The removal of phosphate onto calcium alginate beads reached 82.5%. Finally, coupling Donnan dialysis with adsorption onto calcium alginate beads for the removal of phosphate reached 89.5% with the AMX membrane. This hybrid process can be considered to be a solution for improving the contact time and for enhancing the removal of phosphate by 10% compared to adsorption onto calcium alginate.

Key words | adsorption, alginate, anion-exchange membrane, Donnan dialysis, phosphate

INTRODUCTION

Tunisia has significant deposits of phosphate and produces about 8 million tonnes annually, making Tunisia the fifth largest phosphate products exporter in the world (OECD et al. 2006). Phosphate manufacturers in particular cause considerable amounts of water pollution. Phosphates are frequently present in groundwater and urban/industrial wastewater. Phosphorus is a significant element for agricultural and industrial products. It is an essential nutrient in the aquatic environment, but excessive phosphate concentrations in surface water may lead to eutrophication (De-Bashan & Bashan 2004; Ma & Zhu 2006). Consequently, phosphate removal from wastewater can be an effective method for controlling eutrophication (Bhargava & Sheldarkar 1993; Ozacar 2006). Municipal sewage and urban wastewater contain from 1 to 5 mg/L phosphorus as P. Industrial wastewater from detergent manufacturing and metal coating processes, for example, may contain 10 mg/L of phosphate and more (Mezenner & Bensmaili 2009).

Removal of phosphates has been investigated using electrocoagulation (Bektaş et al. 2004), microfiltration (Yıldız 2004), membrane bioreactors (Kim et al. 2010), membrane processes such as reverse osmosis (Van Voorthuizen et al. 2005), nanofiltration (Lv et al. 2008; Hong et al. 2009) and Donnan dialysis (Chen et al. 2014). Donnan dialysis is a useful membrane process used to recover valuable ions and remove undesirable ones from some waste effluents (DiNunzio & Jibara 1983; Dieye et al. 1998; Hichour et al. 1999, 2000; Seneviratne et al. 2000; Cengeloglu et al. 2003; Marzouk et al. 2013a, 2013b). Among those methods, adsorption onto activated carbon is commonly used owing to its high efficiency, ability to separate a wide range of chemical compounds, simplicity of design and economic feasibility (Boki & Tanada 1987). In last few decades, biosorption (Divya et al. 2012) and biopolymers (Leduc et al. 2014; Wang et al. 2018; Husein et al. 2017) have received a great deal of attention due to the fact that they are more environmentally friendly than commercially available materials. Special attention has been given to calcium alginate (Sujitha & Ravindhranath 2017). The aim of this work is the removal of phosphate by Donnan dialysis coupled
with adsorption onto calcium alginate beads. This combination has never been done before and it is a new and original method for improving the removal of phosphate.

MATERIAL AND METHODS

Membranes

For the Donnan dialysis process three anion-exchange membranes (AEMs) were used: Neosepta® ACS, Neosepta® AMX and Neosepta® AFN. Details of their chemical structure are not disclosed but they do contain quaternary amine functional groups, and their properties are listed in Table 1.

In order to stabilize their physical-chemical properties and remove any impurities that may have come from the manufacturing process, it was necessary to condition the samples. The treatment was done according to the French standard NF X 45–200 (AFNOR 1995). It consists of immersing the 10 cm² samples in different solutions. We started by immersing a sample in HNO₃ 0.1 mol/L. It was rinsed with water and dried with filter paper, then immersed for 1 hour in HCl 0.1 mol/L and rinsed by immersing it in NaCl 0.1 mol/L. The procedure was repeated twice and finally, the membrane was kept in HCl 0.1 mol/L for 24 hours.

Donnan dialysis

Donnan dialysis is an ion-exchange membrane separation process in which ions of the same electrical charge are exchanged between two solutions through an ion-exchange membrane (Strathmann 2004). The driving force in Donnan dialysis is the chemical potential gradient; there is a stoichiometric exchange of co-ions through an ion-exchange membrane, and the process ends only when the Donnan equilibrium is reached. In this process the electroneutrality of the solutions is upheld, so stoichiometrically equal amounts of co-ions should flow from the feed solution to the receiver solution (Strathmann 2004).

Donnan dialysis is a continuous, low energy process, requiring only a few, simple chemicals and a workforce that can be unskilled. This means that the process is very economical and can be implemented quickly even at remote locations. We prepared one-component solutions, named the receiver solution, which 0.1 mol/L of NaCl. In the feed compartment we used a phosphate solution at a concentration of 10 mg/L. The process was conducted in the laboratory set-up for dialysis, which comprised two compartments separated by an AEM. The phosphate concentration in the aqueous solution was determined by the UV-spectrophotometry method (Rodier 2009).

The removal rate of phosphate was calculated by Equation (1):

\[ \% Y = \frac{C_0 - C_e}{C_0} \times 100 \]

where \( C_0 \) and \( C_e \) are the initial and equilibrium phosphate concentrations respectively (mg/L).

The device used to study phosphate removal by Donnan dialysis was presented in a previous study (Marzouk et al. 2013a, 2013b). It is composed of a thermoregulated water bath containing a cell with feed and receiver compartments separated by an anion-exchange membrane. The solutions are pumped through the cell with a peristaltic pump fitted with a pair of identical heads and a speed variator to allow for variable flow rates. The hydrodynamic conditions on both sides of the membrane can be adjusted by two variable-speed stirring rods. The dialysis cell consists of two detachable compartments made of polymethylmethacrylate (Plexiglass). It is composed of four parts joined by three stainless steel threaded rods. The junction of the central compartments (receiver and feed) was secured by bolsters. The two central compartments, consisting of two

Table 1 | Properties of three anion-exchange membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Neosepta® AFN</th>
<th>Neosepta® AMX</th>
<th>Neosepta® ACS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Homogeneous</td>
<td>Homogeneous</td>
<td>Homogeneous</td>
</tr>
<tr>
<td>Composition</td>
<td>polystyrene/divinylbenzene</td>
<td>polystyrene/divinylbenzene</td>
<td>polystyrene/divinylbenzene</td>
</tr>
<tr>
<td>Fixed ionic group</td>
<td>( \text{NR}_3 )</td>
<td>( \text{NR}_3 )</td>
<td>( \text{NR}_3 )</td>
</tr>
<tr>
<td>Ion-exchange capacity</td>
<td>3.00</td>
<td>1.30</td>
<td>1.85</td>
</tr>
<tr>
<td>Water content %</td>
<td>47.8</td>
<td>26.0</td>
<td>18.9</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>0.12</td>
<td>0.13</td>
<td>0.15</td>
</tr>
</tbody>
</table>
tubes, are symmetrical. Two threaded holes penetrate each compartment and are for introducing and circulating the solution in the compartment. The membrane is sandwiched between these two compartments, making a seal at the same time (Dammak et al. 1997).

**Preparation of calcium alginate beads**

A solution of 2% sodium alginate and calcium chloride (0.1 mol/L) were prepared separately in deionized water. For the preparation of calcium alginate beads, 2% sodium alginate solution was added drop wise to the calcium chloride solution. The water-soluble sodium alginate was converted to water-insoluble calcium alginate beads, which were then washed with deionized water several times to remove the excess unbonded calcium chloride from the bead surfaces. The washed beads were then dried at 60 °C for 24 hours and stored in a clean, dry glass bottle.

**RESULTS AND DISCUSSION**

**Donnan dialysis**

**Choice of counter-ion**

The main characteristics, for the choice of the counter-ion, are high mobility and non-toxicity. Two counter-ions, Cl⁻ and OH⁻, were chosen for the differences in their diffusion coefficient values and chemical behaviour. These two counter-ions are commonly used in Donnan dialysis and remain inexpensive for industrial applications (Marzouk et al. 2013a, 2013b). The counter-ion was added to the receiver compartment (at a concentration of 0.1 mol/L) and in the feed compartment there was a solution of phosphate at 10 mg/L. The stirring speed was 500 r/min and a phase temperature of 298 K were used. In this part, the two compartments were separated by the AFN membrane and dialysis lasted 7 hours. Each hour a sample was taken from the receiver to measure the concentration of phosphate. The results obtained indicate a progressive and continuous increase in phosphate in the receiver compartment using both counter-ions.

From Figure 1(a), it is clear that the Cl⁻ counter-ion provides better phosphate transport through the AFN membrane, with 12.5% of phosphate removed, compared to the OH⁻ counter-ion, for which the percentage of phosphate removal did not exceed 5%. This is due to the effect of the pH variation in the feed compartment leading to a change in the nature of the ions present. Therefore it was better to use Cl⁻ as a counter-ion because it is a strong electrolyte, not toxic for the environment, it has a high mobility and does not react with the other components of the solution to be treated.

**Effect of counter-ion concentration**

The effect of the counter-ion (Cl⁻) concentration in the receiver solution on the removal of phosphate from the feed solution is shown in Figure 1(b). The receiver compartment contained the counter-ion at a concentration of 0.01-0.1 mol/L and the feed compartment contained a solution of phosphate at 10 mg/L. The stirring speed was 500 r/min and the phase temperature was 298 K. The two compartments were separated by an AFN membrane. It can be clearly seen that the phosphate concentration at the outlet of the feed solution decreased progressively and then reached a steady state when the concentration of the Cl⁻ in the receiver solution was in the range of 0.01–0.1 mol/L. When the Cl⁻ concentration was 0.01 mol/L, the phosphate concentration in the receiver solution was very low. The phosphate concentration in the feed solution had a removal efficiency of about 12.5% when the Cl⁻ concentration was 0.1 mol/L. Generally, with a higher counter-ion concentration in the receiver solution, ion exchange is faster, and the concentration of the ion being removed from the feed solution is lower owing to the higher concentration difference (i.e., difference in electrochemical potential) between the counter-ion and the ion to be removed from the feed solution (Wisniewski et al. 2005).

When the Cl⁻ concentration was increased from 0.01 to 0.1 mol/L, the phosphate concentration in the receiver solution increased significantly for the same experimental time. With the higher Cl⁻ concentration (0.1 mol/L) in the receiver solution, the ions or ionisable groups for phosphate exchange to the receiver solution increased, resulting in the phosphate concentration in receiver solution being much higher compared with the Cl⁻ concentration of 0.01 mol/L. A similar result was also reported by Tor et al. (2004) and by Chen et al. (2014).

**Effect of initial phosphate concentration**

The initial phosphate concentration has an important effect on the transport of phosphate through the anion-exchange membrane. With a stirring speed of 500 r/min and phase temperature of 298 K, the phosphate concentration was increased from 1 mg/L to 50 mg/L with a Cl⁻ concentration of 0.1 M in the receiver compartment. The two compartments were separated by an AFN membrane. The effect of the initial
phosphate concentration on the removal of phosphate from the feed solution is shown in Figure 1(c). The results show that increasing the initial concentration of phosphate to 10 mg/L improved the removal rate from 1.3% to 12.5%, but the rate decreased significantly to 3.8% when the initial concentration reached 50 mg/L. This can be explained by the saturation of the pores of the membranes for the highest concentration. In fact the transport of phosphate involves three steps: the phosphate in the feed solution is exchanged with the ions or ionisable groups in anion-exchange membrane; the phosphate in the membrane is transported to the side of receiver solution; the phosphate is transferred to the receiver solution with counter-ions. (Hichour et al. 2000; Sato 2002).

**Effect of pH on feed compartment**

The transport of phosphate through the anion-exchange membrane was evaluated at different initial pH values of feed solution ranging from 2 to 12. The counter-ion concentration was 0.1 mol/L, the initial phosphate concentration was 10 mg/L, the stirring speed was 500 r/min and the phase temperature was 298 K. The variation of the phosphate concentrations at the outlet of the receiver solution under different initial pH values is shown in Figure 1(d). The analysis of the curves leads to the conclusion that the phosphate concentration at the outlet was much higher with an initial pH of 12 than 5 to 9. This was attributed to existing forms of phosphate in aqueous solution under
different pH values (Oneil et al. 2003). The HPO$_4^{2-}$ and PO$_4^{3-}$ ions are dominant species in aqueous solutions when the initial pH of the feed solution is 12.

**Choice of membranes**

AFN, AMX and ACS membranes have proved their worth during deflourination (Hichour et al. 2000) and denitrification (Ben Hamouda et al. 2017) of surface waters by Donnan dialysis, so the removal of phosphate was performed with these anion-exchange membranes, with a stirring speed of 500 r/min, phase temperature of 298 K, pH of the feed compartment of 12 and phosphate concentration at 10 mg/L, with a Cl$^-$ concentration of 0.1 M in the receiver compartment. Each hour, a sample was taken from the receiver compartment to measure the concentration of phosphate. The two compartments were separated by a membrane (AFN, AMX and ACS in turn) and the dialysis lasted 7 hours. It was observed that the rate and efficiency of the ion removal in Donnan dialysis depended significantly on the properties of the AEM.

Figure 1(e) shows the transport of phosphate through three membranes. AMX seems to be the best, with 68% of the phosphate removed in 6 hours, compared to 12% with AFN. The most effective membrane should indeed be AFN as it has a macro-porous structure that contains a low amount of cross-linked agents and a large concentration of inorganic groups; this membrane has a relatively high ion-exchange capacity and the highest water content. But the AMX membrane was better at allowing the transport of phosphate than AFN. This can be explained by the fact that the diffusion boundary layer’s thickness decreases significantly from 0 to 200 r/min but the thickness remains almost constant from 200 to 900 r/min (Danmak et al. 1999). The AMX membrane leads to a significant concentration of phosphate in the receiver compartment. This is due to the difference in the surface state of both anion-exchange membranes used. Indeed, the AFN membrane is reinforced with a PVC frame, which gives it a significant surface roughness. This roughness creates turbulence, which increases sharply with stirring and probably creates a layer of negative charges on one side of the membrane (Akretche & Kerdjoudj 2000). This layer can induce a stronger electrostatic repulsion to multivalent than to monovalent ions. The ACS membrane is the worst performer, with a very low phosphate removal percentage: less than 1.2% in 6 hours. The ACS is the membrane that has the lowest permeability because of its high thickness and low water content.

**Adsorption of phosphate onto calcium alginate**

Adsorption is a highly effective process for a variety of applications, including the removal of phosphate from wastewaters, and it is considered one of the most efficient methods for removing impurities.

In order to determine the most significant parameters affecting adsorption of phosphate onto calcium alginate beads, a full factorial design was applied. It is a very effective and time saving model for studying the influence of experimental parameters on the response, significantly reducing the number of experiments and facilitating the optimum conditions by considering interactions between experimental parameters.

**Effect of pH**

Adsorption is strongly governed by the pH of the solution and by the surface chemistry of the solids. The effect of pH on the removal of phosphate, through adsorption onto calcium alginate beads, was examined at pH values between 4 and 13. The tests were carried out at constant experimental conditions with an initial solution concentration of 10 mg/L of phosphate, 1.5 g of adsorbent and a temperature of 25 °C. The effect of pH is illustrated in Figure 2(a). All the tests were carried out at a constant retention time, 180 min. The results show that pH is an important factor regarding phosphate adsorption onto calcium alginate. The removal of phosphates was comparatively lower at the slightly basic pH values due to H$_2$PO$_4^-$ and HPO$_4^{2-}$ being present at pH values between 4 and 10 (Karageorgiou et al. 2007). For pH values around 12, the concentration of PO$_4^{3-}$ species became significant and the maximum rate was 81.1%. But removal decreased to 28.8%, and this was due to competition with OH$^-$. It has been concluded that phosphorus removal is better under alkaline conditions, i.e. at higher pH values (Karageorgiou et al. 2007).

**Effect of adsorbent dose**

It is well known that the amount of adsorbent added to a solution determines the number of binding sites available for adsorption. So to investigate the effect of adsorbent dose on phosphate adsorption, experiments were carried out with an initial phosphate concentration of 10 mg/L and varying adsorbent doses at room temperature and at pH 12. The results are
shown in Figure 2(b). The results show that the percentage removal increased with increasing adsorbent dose due to the increase in the total available surface area of the adsorbent particles. The increase in solid-liquid ratio develops an additional number of sites, thus making the adsorption process more efficient. Figure 2(b) indicates that a 2 g adsorbent dose was sufficient to remove a maximum number of adsorbed ions. The same results were found by Mahmoud et al. (2015).

Effect of initial phosphate concentration

To investigate the effect of initial concentration on phosphate adsorption onto calcium alginate, experiments were carried out with an initial phosphate concentration of 1 to 10 mg/L and 1.5 g of adsorbent dose, at 25 °C and at pH 12. The results are shown in Figure 2(c). The results show that the percentage removal increased with increasing initial concentration, which indicates that phosphate adsorption onto the calcium alginate had not reached saturation due to the low contact opportunities at low phosphate concentrations.

Full factorial design for adsorption

In order to evaluate the influence of operating parameters on the removal of phosphate by adsorption, three main parameters were chosen. A two level full factorial design $2^k$ was carried out to determine the influence of these factors and their interaction on the removal of dyes by adsorption onto calcium alginate. In these types of designs, variables (k) are set at two levels (minimum) and (maximum) normalised as (−1) and (1). The experimental response associated to a $2^k$ factorial design (for three variables) is represented by a linear polynomial model with interaction:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3 \quad (2)$$

where $Y$ is the experimental response, $X_i$ is the coded variable (1 or −1), $b_i$ is the estimation of the principal effect of the factor $i$ for the response $Y$, $b_{ij}$ is the estimation of the interaction effect between factors $i$ and $j$ for the response $Y$. The coefficients of the equation model Equation (2) were calculated under the experimental field listed in Table 2.

### Table 2 | Experimental region investigated for the removal of phosphate

<table>
<thead>
<tr>
<th>Variables</th>
<th>Symbol</th>
<th>−1</th>
<th>+1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose of calcium alginate (g)</td>
<td>$X_1$</td>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>pH of solution</td>
<td>$X_2$</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Initial concentration of phosphate (mg/L)</td>
<td>$X_3$</td>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>
The choice of the limits of the experimental field was investigated in the previous study. The experimental design and results are represented in Table 3.

According to the results obtained, the coefficients of the polynomial model were calculated using the NEMROWD Software.

\[
Y(\%) = 48.61 + 20.89X_1 + 6.91X_2 + 2.04X_3 + 2.19X_1X_2 + 0.56X_1X_3 + 0.89X_2X_3 + 0.41X_1X_2X_3 \tag{3}
\]

The different coefficients of the polynomial model Equation (3) calculated using software that represented the effects and interactions of the various investigated factors shown in Figure 3.

The three parameters studied had a positive effect on the response, in other words, increasing the parameters led to increases in the removal of phosphate onto calcium alginate. Their contributions on the response were only 0.8% for pH and 9.7% for calcium alginate versus 88.5% for initial phosphate concentration. Thus, removal can be considered to be influenced by only one parameter: the initial phosphate concentration.

**Donnan dialysis coupled with adsorption onto calcium alginate beads**

The removal of phosphates by Donnan dialysis was studied, and shown to be efficient when using the AMX and AFN membranes: the removal rates were 68% and 12.5% respectively. In order to improve this result, we opted for coupling Donnan dialysis to a physical process, adsorption onto calcium alginate. Adsorption is one of the most important separation techniques for improving the kinetics of Donnan dialysis and the removal of phosphates. Indeed, this process has proven its great performance in the phosphate removal rate of 82.5%. Thus, these two processes are complementary, so coupling them draws on the benefits of each one. An innovative and original process has been developed and named DD-AA.

Figure 4 shows a schematic flow diagram of Donnan dialysis system coupled with calcium alginate beads is shown. The experiments were carried out with the optimal conditions established in the Donnan dialysis study using the following: 10 mg/L of phosphate in the feed compartment, in which the pH was 12. The receiver compartment contained 0.1 mol/L of Cl⁻, and a membrane separated the compartments. Two membranes, AFN and AMX, were used, with the addition of the calcium alginate at the rate of 15 g per 500 mL in the receiver compartment. The dose of calcium alginate was added to the receiver compartment, as shown by the schematic flow in Figure 5(a). Figure 5(b) shows the amount of phosphate removed in the feed compartment in 6 hours, without (●) and with DD-AA coupling (♦).
Figure 5(a) and 5(b) show the amount of phosphate in the receiver compartment after it had passed through the anion exchange membrane. It should be noted that the removal of phosphate is improved by Donnan dialysis coupled with calcium alginate adsorption (37.6%), compared to Donnan dialysis only (12.5%) for the AFN membrane.

The AMX membrane shows a great improvement, with 89.5% of phosphate removed by Donnan dialysis coupled with calcium alginate adsorption. It is worth noting that there was an increase of 24% for AFN and 22% for AMX of phosphate removed when the calcium alginate was added, which can be explained by the fact that phosphate was adsorbed onto calcium alginate in the receiver compartment so the Donnan dialysis kinetics increased. This contributes to keeping the concentration gradient of phosphate high, therefore improving the kinetics of the process.

CONCLUSION

The removal of phosphates by Donnan dialysis reached 68% and 12.5%, using AMX and AFN membranes respectively, from a solution of phosphate with an initial concentration of 10 mg/L in the feed compartment and 0.1 mol/L of Cl⁻ as the counter-ion in the receiver compartment. According to a full factor design, the initial phosphate concentration was the most significant parameter affecting the removal of phosphate by adsorption onto calcium alginate beads. There was a very high phosphate-removal performance of 82.5%.

The combination of Donnan dialysis and adsorption onto calcium alginate beads allows the efficiency to be improved to 89.5% for AMX and 37.6% for AFN. This hybrid process can be considered a successful and original coupling, especially using the AMX membrane, which enhanced the removal of phosphate by 10% compared to adsorption with calcium alginate alone.

ACKNOWLEDGEMENTS

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REFERENCES


