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Application of Donnan Dialysis Coupled to Adsorption onto Activated Alumina for Chromium (VI) Removal

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ABSTRACT

The aim of this paper is the assessment of Donnan dialysis coupled to adsorption process for the removal of chromium from aqueous solutions. This study was conducted in order to benefit from each process, and it was an original and new combination. The coupling was a solution to improve the contact time and the amount of chromium (VI) removed. The coupling was successfully performed with 90% of chromium (VI) removed after 6 hours.

Keywords: Donnan Dialysis; Chromium (VI); Anion-Exchange Membrane; Adsorption; Activated Alumina

1. Introduction

One of the heavy metals that have been of major concerns in water and wastewater treatment is chromium. Its hexavalent form has been considered to be more hazardous due to its carcinogenic properties [1]. The chromium (Cr) is widely used in various industrial applications leading to an increase in Cr concentration in water (industrial discharges), air (coal combustion), and soils (waste disposal). Chemical, leather and textile manufacturing, electropainting and chromium plating are the main human activities leading to an increase in Cr (VI) concentrations in the environment. Chromium has been considered as one of the top 16th toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern [2]. Therefore, it is necessary to eliminate Cr (VI) from the environment in order to prevent the deleterious impact on ecosystem and public health. Because of the stricter environmental regulations, a cost effective alternate technology for the treatment of Cr (VI) contaminating wastewater is highly desired in the industrie. There are several treatment technologies available to remove Cr (VI) from wastewater such as chemical precipitation [3], ion-exchange [4-9], membrane process, as reverse osmosis and ultrafiltration [10-13], flotation [14], electrocoagulation [15], solvent extraction [16], reduction [17], dialysis or electrodialysis [18] and adsorption [19-24]. The adsorption of chromium (VI) onto different types of adsorbents, such as activated carbon, activated alumina, peat, leaf mould and wheat bran, has been studied and showed a good affinity with chromium and high amount of removal [19-23]. The Donnan dialysis is a useful membrane process used to recover valuable ions and remove undesirable ones from some waste effluents [24-32]. The theory and principles behind the Donnan dialysis process are recently reviewed by Luo *et al*. [33]. A number of fundamental and experimental studies have been conducted including treatment of alkali, alkali earths, transition and rare metals [34-39].

The idea of chromium (VI) removal by Donnan dialysis application coupled to adsorption onto activated alumina was performed in order to benefit from each one. This jointed process has never been done before. Accordingly, the present study deals with a new and original application of Donnan dialysis coupled to adsorption onto activated alumina in order to improve the removal of chromium (VI).

2. Experimental

2.1. Material and Methods

2.1.1. Membranes

For the Donnan dialysis process two AEMs have been used: Selemion® AMV and Neosepta® AFN. The AFN

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membrane was generously provided by Eurodia Industries S.A. and the AMV one was purchased from ASAHI GLASS. Details of their chemical structure are not disclosed, however, they do contain quaternary amine functional groups and their properties are listed in **Table 1**.

Prior to any measurement, it was necessary to condition the samples in order to stabilize their physical-chemical properties and remove any impurities that may come from their manufacturing process. The French standard NF X 45 - 200 was followed to achieve this treatment [40]. It consists in immersing the samples of 10 cm^2 in solutions of different natures. We started immersing the sample in 0.1 M HNO_3. It was rinsed with water and dried with filter paper, then immersed for one hour in HCl 0.1 M and rinsed by immersing in NaCl 0.1 M. The procedure was repeated twice and finally, the membrane was conserved in HCl 0.1 M for 24 H.

2.1.2. Activated Alumina

The granular activated alumina used was supplied by Sigma-Aldrich (particle size spherical 150 mesh, pH (in the water) 4.5, melting point 2040˚C, molecular weight 101.96 $g \cdot mol^{-1}$, pore diameter 58 Å and surface area 155 $m^2 \cdot g^{-1}$). It was dried at 110˚C for 24 h in order to eliminate the impurities and to prepare the activated alumina.

2.1.3. Reagents

The stock solutions of chromium (VI) were prepared by dissolving sodium chromate salt ($Na_2Cr_2O_7$) in 1 liter of distilled water to have an initial concentration of Cr (VI) 1.00 $g \cdot L^{-1}$. All other reagents used were analytical reagent grade.

2.1.4. Donnan Dialysis

The 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 [41]. The Donnan dialysis is a continuous low energy process, requiring only few and simple chemicals and a workforce that can be unskilled.

Table 1. Properties of the two anion-exchange membranes used in this study.

Parameter	Selemion® AMV	Neosepta® AFN
Type	Homogeneous	Homogeneous
Structure property	PS/butadiene	PS/DVB
Fixed ionic group	$-NR_3^+$	$-NR_3^+$
Ion-exchange capacity ($mmol \cdot g^{-1}$)	1.85	3.15
Water content (%)	19.9	40.5
Thickness (mm)	0.11	0.12

All meant that this process is very economical, can be implemented quickly even at remote locations.

We prepared one-component solutions containing NaCl the concentration of 0.1 M (the receiver). As the feed compartment we used the Cr (VI) solution with the concentration of 100 $mg \cdot L^{-1}$. The process was conducted in the laboratory set-up for dialysis, which comprised 2 compartments separated by AEM.

The samples were analyzed for residual Cr (VI) concentration by reaction with 1.5-diphenylcarbazide followed by absorbance measurements at 540 nm using a UV-visible spectrophotometer. This method was validated in a previous study [43].

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

$$Y_{Cr}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium Cr (VI) concentrations ($mg \cdot L^{-1}$).

Figure 1 shows the device used to study the chromium (VI) removal by Donnan Dialysis. It is composed of a thermoregulated water bath (25.0˚C ± 0.1˚C), 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 allowing 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 in two detachable compartments made with polymethylmetacrylate (plexiglass). It is composed of four parts joined by three stainless steel treaded rods. The centring is assured by bolsters.

The two central compartments, consisting of two tubes are symmetrical. Two threaded holes penetrate each compartment and serve as supports for introducing and circulating solution in the compartment. The membrane is sandwiched between these two compartments, making a seal at the same time [42].

To supply the receiver compartment a NaCl solution is used at the concentration of 0.01 M or 0.1 M. The feed compartment is filled with Chromium (VI) solution at the concentration of 100 or 300 $mg \cdot L^{-1}$.

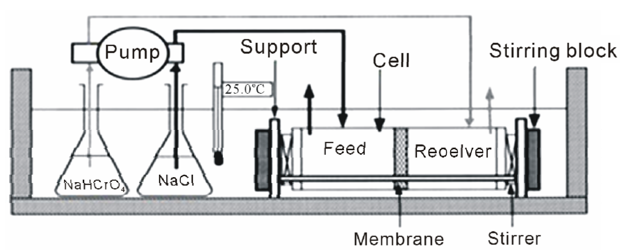

Figure 1. The experimental device of the Donnan dialysis process.

3. Results and Discussion

3.1. Donnan Dialysis

Figure 2 shows the amount of chromium (VI) removed in the receiver compartment, for AFN membrane during 24 hours. In these conditions, only 10 % of the chromium was removed, then after 24 hours the concentration grew-up to 20 mg·L^{-1}. Concerning the AMV membrane, the concentration of chromium remained constant during the 24 hours up to 7 mg·L^{-1}.The differences between the concentrations of chromium (VI) obtained can be explained by the difference in the ion-exchange capacity and the water content as shown in **Table 1**. So we can conclude that AFN membrane is more suitable than AMV membrane for the Donnan dialysis process.

The amount of chromium (VI) removed by the Donnan dialysis was determined on the basis of the following parameters: initial chromium concentration, type the anion-exchange membranes, Cl^- concentration and magnetic stirring. The experiments have been carried out using a 2^4 full factorial design to study the effect of the main and interaction parameters. The study allowed us to find the best conditions to remove the chromium (VI) by Donnan dialysis. These conditions were obtained in previous study ([Cr (VI) = 100 mg·L^{-1}; [Cl^-] = 0.1 mol·L^{-1}; AFN and high speed of magnetic stirring) and will be used for this study in order to improve the efficiency of this process for the removal of chromium [44].

3.2. Adsorption onto Activated Alumina

Adsorption is a highly effective process for a variety of applications such as removal of metal ions from wastewaters and it is considered one of the most efficient and fast methods to remove impurities. However, the elevated cost of activated alumina and the regeneration are its disadvantages. Adsorption experiments were carried out in mechanically agitated in a thermostatically bath, the beakers containing 100 mL of chromium with initial concentration 100 mg·L^{-1} and with different amount of activated alumina from 1 to 10 g, for 90 min and at 25˚C [43]. The content was agitated with a constant stirring rate at 140 rpm. Samples were withdrawn after a definite time interval and filtered through Whatman N˚ 1 filter paper (0.45 µm). In **Figure 3**, results show that the optimal dose of activated alumina was 4 g (4 g of AA/100 mg·L^{-1} of initial concentration of Cr (IV)). The fastness and the efficiency of this process were the advantages of activated alumina, but its major inconvenient was the cost.

3.3. Donnan Dialysis Coupled to Adsorption onto Activated Alumina

In order to improve the amount of chromium (VI) removed by Donnan dialysis and reduce the experimental time, we have tested for the first time the Donnan dialysis process coupled to the adsorption onto activated alumina. First, experiments were performed with 0.1 mol·L^{-1} of NaCl solution only in the receiver compartment, and 100 mg·L^{-1} of initial chromium concentration. Then the dose of activated alumina 1 g was added, even the optimal dose was 4 g, we choose to reduce the amount of activated alumina, as shown by the schematic flow of in **Figure 4**.

Figure 5 shows the amount of chromium (VI) removed in the feed compartment during 6 hours in two cases: without (■) and with DD-AAA coupling (◆). It is noteworthy, an imminent increase of 86% of chromium (VI) removed when the activated alumina was added, this can be explain by the fact that chromium (VI) was adsorbed onto activated alumina in the receiver compartment so the Donnan dialysis kinetics increased.

Figure 6 shows the amount of chromium (VI) remained free in the receiver compartment after passage through the anion exchange membrane. It should be noted that despite the large amount of chromium (VI) that happens in the case of a coupling DD-AAA (90%

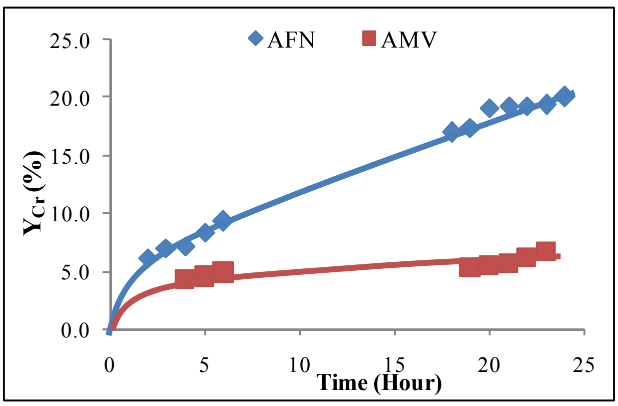

Figure 2. The amount of chromium (VI) removed by Donnan dialysis using AFN and AMV membranes.

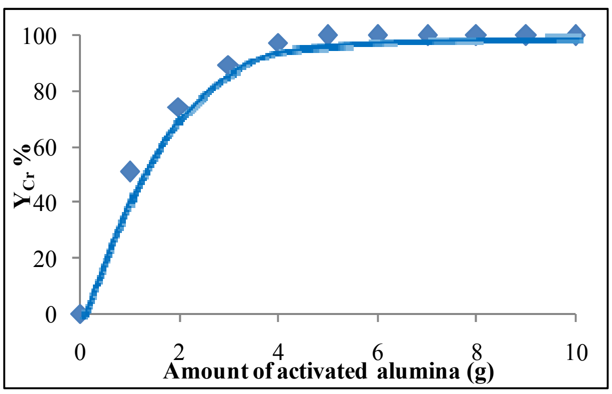

Figure 3. Effect of adsorbent dose on chromium (VI) removal.

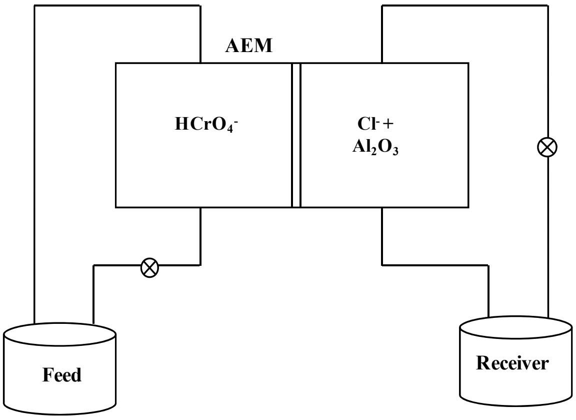

Figure 4. Schematic flow diagram of Donnan dialysis system coupled with activated alumina.

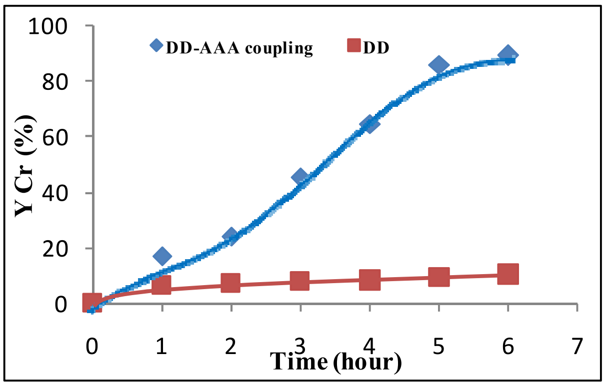

Figure 5. Amount of the chromium (VI) removed in the feed compartment with and without DD-AAA coupling.

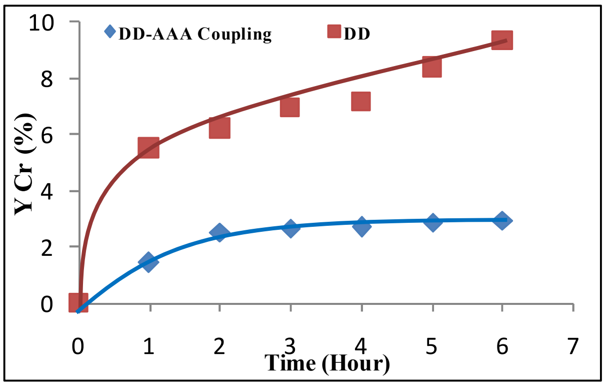

Figure 6. Amount of the chromium (VI) in the receiver compartment with and without DD-AAA coupling.

after 6 hours), there is a small amount of free chromium (VI) (2% after 6 hours) compared to the case of not coupling. This contributes to maintain the concentration gradient of Cr (VI) high, therefore improving the kinetics of the process.

4. Conclusion

This study shows that the application of Donnan dialysis coupled to adsorption onto activated alumina is a successful and original coupling. This combination allows to improve the efficiency, the kinetics of transmembrane transfer and to reduce the amount of activated alumina to regenerate. The amount of chromium removed is obtained about 90% in six hours.

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