

Application of Donnan Dialysis for Cyanide Removal from Aqueous Solutions

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ABSTRACT: Cyanide ion, is an environmentally significant pollutant in many industrial wastewaters. Therefore, a considerable number of methods have been studied for the wastewater treatment containing cyanide. The goal of our work consists in applying a simple and economic process for solving this problem of pollution. The removal of cyanide ions by using three anion exchange membranes has been studied under Donnan dialysis conditions as a function of initial concentration of cyanide, receiver phase composition and co-existence anions in the feed phase. The feasibility of the system was examined and the highest cyanide removal was obtained when the initial concentration of cyanide on the feed phase was 10-2 M. In addition, the accompanying counter-anions were also influenced in the cyanide transport in the order chloride > hydrogenocarbonate > sulphate. It was also observed that the cyanide transport efficiency of the Neosepta AFN was higher than that of the Neosepta AM3 and IONAC MA3475XL membranes. The better result for AFN membrane was obtained with chloride ion as a counter-anion in the receiver phase.

Key words: Cyanide, Aqueous solutions, Donnan dialysis, AFN, Anion exchange membrane

INTRODUCTION

Wastewater discharged by industrial activities is often contaminated by a variety of toxic or otherwise harmful substances which have a negative effect on the water environment. For example, the industry of metal finishing and electroplating units are one of the major sources of heavy metals and cyanide pollutants. These pollutants, which are non-biodegradable and highly toxic contribute greatly to the pollution load of the receiving water bodies and therefore increase the environmental risks (Monser & Adhoum, 2002).

Cyanide is wide spread used in gold and silver extraction, electroplating, synthetic fiber production, coal cooking and coal conversion effluents, organic chemical and other industries. Cyanide is highly toxic to humans and aquatic organisms. This is why strict environmental regulations are applied to waters which contain free cyanide ions and other cyanide compounds. In general, these waters can be released to the environment only after detoxification (Aydiner *et al.*, 2005). However, for economical and ecological considerations, the reduction and the recovery of these substances from waste water are the best ways to reduce this pollution before its discharge in the environment (Marder *et al.*, 2003). Several cyanide removal processes have been described in the literature

(Monser & Adhoum, 2002; Adhoum & Monser, 2002; Shen *et al.*, 2004). In a recent publication, (Han *et al.*, 2005) describe a number of processes such as alkaline chlorination, sulfur oxidation, hydrogen peroxide oxidation, acidification–volatilization–recovery (AVR), activated carbon adsorption, ion exchange, ozonation, photochemical destruction and microbiological degradation. However all of these methods have their drawbacks. For example, alkaline chlorination which is one of the more commonly used processes. However, this process suffers from several problems such as less effective removal of iron cyanides. Thus cyanide cannot be recovered and reused, and more severely, chloramines and free chlorine remain in solution leading to the production of secondary contaminants. While microbiological degradation avoids using toxic or hazardous chemicals and can be used to treat iron cyanides, it may not be possible to treat waste waters containing high concentrations of cyanide. Further, this process may be adversely affected by cold temperatures.

The use of membrane processes in wastewater treatment is another process of decyanidation, which is now commonly used because it presents many advantages (Aydiner *et al.*, 2005). Cyanide removal from wastewaters using nanofiltration and reverse

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osmosis has also been described (Santoyo *et al.*, 2003; Minhalma & Norberta de Pinho, 2004; Goel *et al.*, 1998). However the rejection by these membranes is often not high enough to meet the U.S. Environmental Protection Agency (US EPA) requirements. Further, since the membrane will reject other solute species as well, the purity of the concentrated cyanide in the retentate is usually not sufficiently high to make recovery of the cyanide commercially viable. Other membrane processes have been applied for the removal of cyanide from waste waters such as liquid membranes, electrodialysis and electro- electrodialysis coupled to chemical oxidation (Aydiner *et al.*, 2005; Marder *et al.*, 2003; Gherrou & Kerdjoudj, 2002; Christophe, 1994).

As another example of membrane processes is the Donnan dialysis (DD), which 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 (Marzouk *et al.*, 2013). and the process ends when Donnan equilibrium is reached (Wisniewski *et al.*, 2005). Moreover, Donnan dialysis is both an economical, simple technological and energy saving process, however this technique is not applied in industry mainly because of its slow kinetic (Akretche & Kerdjoudj, 2000).

Nevertheless some potential applications have been studied at laboratory scale. Concerning the cyanide medium, few studies were carried out. Thus, (Law, 1982) has examined the recycling of gold cyanide baths using a neutralization of the excess of KOH by acid produced by Donnan dialysis. (Hamil, 1982) has studied the recovery of some heavy metals, as their complex cyanide anions, from cyanide process electroplating wash waters by a Donnan dialysis process using anion exchange membranes. (Akretche & Kerdjoudj, 2000) has examined the behaviour of gold silver and copper in cyanide medium by the same process. Studies using the Donnan dialysis as a process for removal of free cyanide ions are rare. they are not much studied as other system for exemple removing nitrate and fluoride. Therefore, the objective of this work is to eliminate cyanide ions of a synthetic solution using anion exchange membranes. To achieve this aim, DD method was investigated to extract cyanide from diluted solution with quasi-stationary

circulating mode of the receiver and feed solution continuously. Three commercial anion exchange membranes; AFN, AM3 and IONAC were tested. The effect of concentration, the accompanying of the general common anions as Cl^- , HCO_3^- and SO_4^{2-} on the feed or receiver phase were investigated in detail. This study will enable us to find the best conditions for the removal of cyanide by Donnan dialysis. These conditions will be used for future application of this process to extract cyanide from a real rinsing water of a bath silver plating.

MATERIALS & METHODS

Ultrapure milliQ water with a resistivity of 18 M Ω cm was used for all the experiments.

All chemicals were purchased from Sigma Aldrich which are reagent grade. The Three commercial anion exchange membranes (Neosepta- AFN, AM3, and IONAC MA3475XL) were produced by the Japanese firm Tokuyama Soda Co. Ltd. All these membranes were strongly basic anion exchangers that contain quaternary ammonium bases $-\text{N}(\text{CH}_3)_3^+$ as ionic groups and the polymer base of these membranes is the divinylbenzene. These membranes differ in the structure, the degree of cross-linking, ion-exchange capacity, and water content. The membrane characteristics which are presented in Table 1, were determined in our laboratory by measuring the water content, the ion exchange capacity and the thickness. Cyanide concentration was determined by polarography 746 VA Trace Analyzer (Metrohm) equipped with a 747 VA Stand, with dropping mercury electrode (HMDE). The polarographic method for determining cyanide is quicker, sometimes more sensitive, and, above all, simpler than comparable methods. For these reasons we have chosen this method to analyze the samples. Before the experiments, all membranes were first immersed in deionized water for 12 h to remove impurities, then acid-conditioned with 0.1 M HCl for 24 h, followed by washing with deionized water, and 0.1 M HNO₃ for 24 h several times to convert the exchange sites to the desired ionic form.

Donnan dialysis experiments were carried out using a laboratory cell consisting in two detachable compartments made of Plexiglas, the volume of each compartment is 25 cm³. Between these compartments,

Table 1. Characteristics of the anion exchange membranes

Membrane	Exchange capacity (meq/g)	Water content (%)	Thickness (mm)	Nature of structure
AFN	2.33	32.00	0.145	homogeneous
AM3	1.13	22.00	0.170	homogeneous
IONAC MA3475XL	0.65	15.09	0.400	heterogeneous

an anion exchange membrane was inserted. Its working area is 4.52 cm² and all experiments were carried out at 25°C. Both the feed and the stripping solutions with the same volume of 1 liter, were circulated by means of peristaltic pump through the respectively compartments. Dialysis was carried in quasi-stationary regime with a low flow (200 mL h⁻¹) in both compartments. During the process we measured the concentration of cyanide in the feed and in the receiver phase.

RESULTS & DISCUSSION

In order to discuss the effect of the concentration of the feed solution, the experiments were performed using a KCN solution, having different concentrations, as the feed solution and the strip solution is NaHCO₃ 0.1 M by using the AFN membrane. KCN solutions of 10⁻² M, 5.10⁻³ M and 10⁻³ M were used for each experiment, and the results obtained are shown in Fig. 1. We observed that the transport of cyanide increases with the initial concentration of cyanide. During the DD process, an ion exchange took place between ions presented in both phases resulting from a difference in the chemical potentials under the driving force of hydrogenocarbonate ions, which increases in the feed phase while cyanide ion decreases with time. Thus, the feed phase was enriched by hydrogenocarbonate ions. For this reason, when the concentration of feed solution is 10⁻² M, the maximum amount of cyanide is transported to the next phase. The results found in the present study are in agreement with that have been reported by (Durmaz *et al.*, 2005; Ruiz *et al.*, 2003), concerning the removal of fluoride from water by using anion exchange membrane under Donnan dialysis conditions. It was reported that the flux of fluoride increases with increasing its concentration in the feed phase. For the rest of this study, we chose the analytical cyanide concentration 10⁻² M in feed phase.

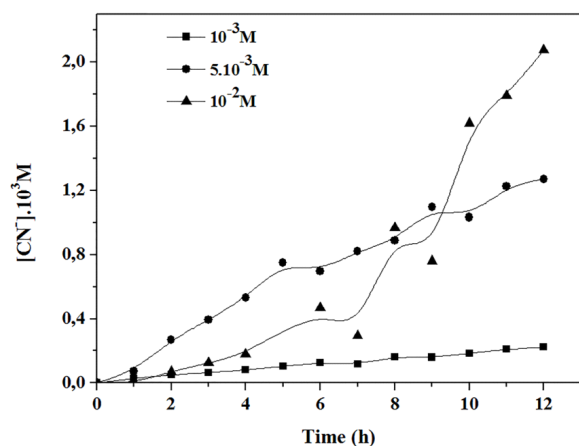


Fig. 1. Time course of cyanide transport through AFN membrane at different initial concentration.

The influence of the feed phase composition on the cyanide transfer was studied under various feed composition: chloride, sulfate and hydrogenocarbonate ions were progressively added to the feed solution at the same concentration of cyanide (10⁻² M) in order to better analyze the effect of each one. The receiver phase was taken as the same solution (0.1 M HCO₃⁻) and dialysis was performed in quasi-stationary regime with a low flow (200 mL h⁻¹) in both compartments. The main purpose of this part of our study is to be close to the real composition of cyanide waste water, which contains chloride, hydrogenocarbonate and sulphate ions in presence of cyanide. By the addition of counter ions to the feed phase, the order of cyanide transport through the AFN anion exchange membrane is Cl⁻ > HCO₃⁻ > SO₄²⁻ as shown in Fig. 2.

As seen in Fig. 2, it is clear that the addition of the anions in the feed phase promotes the transport of cyanide. In fact, the diffusion of cyanide only (shown in Fig. 1) is lower than in the case of mixture, this behavior was perceived by (Ben Hammouda *et al.*, 2012), who studied the effect of accompanying ions in the feed phase on the transport of nitrates, he noted that this behavior is probably due to the structure of the membrane and the mobility of the ions through the membrane.

Indeed, this phenomenon can be explained by the increase of the membrane conductivity in a mixed form as a function of the ionic fraction of the more mobile species. This phenomenon can also be interpreted by the increase in ionic strength of the feed solution that is confirmed by the study of the effect of concentration in the first part of this work. When the rate of cyanide in the presence of the three anions were compared, it have been noticed that the rate in the presence of Cl⁻ ion was the faster. This can be explained based on the

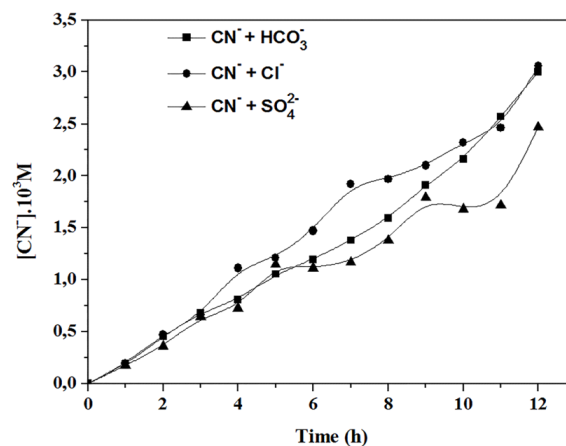


Fig. 2. Effect of counter ions present in the feed phase for cyanide removal. The NaHCO₃ concentration in the receiver phase is 0.1 M.

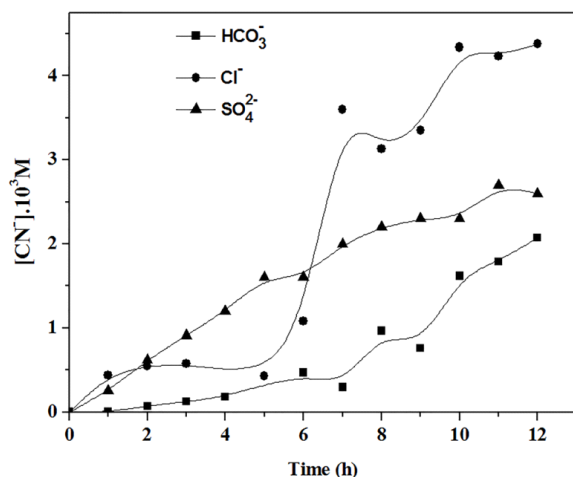


Fig. 3. Effect of counter ions present in the receiver phase for cyanide removal. The KCN concentration in the feed phase is 10^{-2} M.

hydratized radius in the order $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^-$. In addition, the transport of SO_4^{2-} ion is expected to be lower than HCO_3^- and Cl^- ion as its ion charge is higher than the others. The sulphate ions plug the pores of the membrane and did not allow easy the transport of cyanide. This result, based on the hydratized radius, is consistent with that of (Ayyildiz & Kara, 2005; Kir *et al.*, 2011), which detail the boron removal by anion exchange membranes.

It was reported that the transport of boron through membrane became more difficult with increasing hydratized radius of ions. This result can be also explained by the mobility of the mono and bivalent ions in an ion exchange membrane as was investigated by (Miyoshi, 1998), who reported that in the structure of the ions through membranes. A monovalent ion makes a pair ion with a fixed site in the membrane and it is transferred step by step between neighboring fixed ions. In the case of bivalent ions, two fixed ions were used by bivalent ions for transport. Thus, monovalent ion needs only one fixed charged ion that is corresponding of a half-set of a bivalent ion. The results obtained from the present study were in agreement with this explanation. Under these conditions, the transport of cyanide was decreased by increasing valence of accompanying anions.

To study the effect of the nature of driving ion, DD operations were performed with different receiver phase composition through AFN anion exchange membrane when concentration of feed phase is 10^{-2} M KCN and concentration of receiver phase is 0.1 M. As presented in Fig. 3, the order of cyanide transport is $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$. In the case of HCO_3^- , we

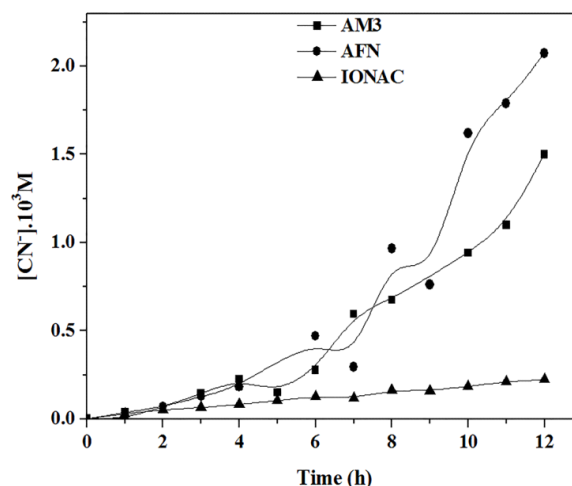


Fig. 4. Time course of cyanide transport across different anion exchange membranes. The initial concentration of cyanide is 10^{-2} M.

observe that the transport of cyanide is low compared with other anions, this is probably due to the presence of carbonate ions in the receiving phase from the chemicals reactions between the different anions.

The CO_3^{2-} and HCO_3^- ions compete between them and with other anions passing through the membrane. The presence of carbonate ions has been verified by the precipitation test. Compared to other anions, carbonate is more voluminous and has the largest hydratized radius, for this reason, these anions move more difficult through the membrane sites. In order to select the most effective anionic exchange membrane for DD, the experiment for cyanide transport was performed using only a 10^{-2} M KCN feed solution and NaHCO_3 0.1 M in the receiver phase. During the experiments three commercial membranes (Neosepta-AFN, AM3 and IONAC) were used for cyanide transport.

It was observed that the rate and the efficiency of the ion removal in the Donnan dialysis depend significantly on the properties of an AEM. The variation of cyanide concentration in the receiver phase with time was plotted in Fig. 4. It is clear that the IONAC is the membrane that has the lowest permeability because of its high thickness and low water content. Moreover, its low exchange capacity does not allow attaining a good selectivity in the transfer of the cyanide. In addition, its heterogeneous structure is unfavorable to the diffusion of cyanide compared to the homogeneous structure of other studied membranes (Prakash *et al.*, 2004). As can be seen from the Fig. 4, the most effective membrane is the Neosepta AFN which have a macro-porous structure that contains a low amount of a cross-linked agent and a large concentration of ionogenic groups. This

Table 2. Cyanide removal percent under the optimum conditions during 12 hours of Donnan dialysis

[CN ⁻] _i (mol / L)	Membrane	Driving ion	Percent decyanidation (%)
0.01	AFN	Cl ⁻	38
		SO ₄ ²⁻	22
		HCO ₃ ⁻	18

membrane have relatively high ion-exchange capacity and the highest water content (Durmaz *et al.*, 2005). In the case of AM3 membrane, its water content was lower, so transport efficiencies are less than the AFN membrane. The ion exchange capacity of the membrane is another important factor for the ion transport. This feature was emphasized by (Altintasa *et al.*, 2009), who reported that transport of nitrate increased with an increase in membrane ion exchange capacity.

To estimate the removal of total cyanide from solutions by means of Donnan dialysis, the following relation was used:

$$P_{CN^-} = \frac{C_i - C_f}{C_i} \times 100$$

Where C_i is the initial concentration of cyanide and C_f is the final concentration of cyanide from the feed compartment. The results from Table 2, suggest that the most decyanidation percent can reach 38% using the AFN membrane and chloride ion.

After all these dialysis, we concluded that the equilibrium time can't be reached. It seems that the kinetics of cyanide removal is slow and the decyanidation percent depends on the dialysis time. For this reason, we determined the percent of cyanide removal after 30 hours of dialysis, we obtained 64% using the same system: CN⁻(10⁻²M) |AFN| Cl⁻ (0.1 M).

CONCLUSIONS

Several experiments were performed under various conditions to determine the most suitable situations. The results showed that transport of cyanide through anion exchange membranes by Donnan dialysis is viable. Cyanide transport depends on membrane structure, the concentration of the feed phase as well as the co-existence anions in the feed phase and the nature of the receiver ion. From these experiments we can conclude that the highest cyanide transport was achieved at cyanide 10⁻²M, using AFN membrane and chloride as the receiver ion. Investigation of the experiments illustrates that bivalence of the co-existence anions in the feed phase has a greater decreasing effect on the cyanide transport than monovalent co-anions. The kinetics of cyanide removal is slow and the decyanidation percent depends on the dialysis time.

After 12 hours of dialysis, the percent of cyanide removal of the order of 38%. This percent can be improved to 64% after 30 hours of dialysis. We can consider that this process is a promising technology for cyanide concentration and removal from wastewater.

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