

USE OF ELECTRODIALYSIS AS A VFA RECOVERY PROCESS FROM ACIDOGENIC OF MSW SYNTHETIC LEACHATES

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ABSTRACT

An electrodialysis (ED) process was tested for volatile fatty acids (VFA) recovery from a simulated leachate of acidogenesis of municipal solid wastes (MSW). The effect of initial VFA concentration in leachate, applied voltage and flow rate on VFA removal efficiency were evaluated. Four different leachate compositions were examined at three different applied voltages and at three different flow rates. Higher removal levels were obtained at low VFA initial concentration, high voltages levels and high flow rates. ED process was showed higher removal efficiency with shorts chain acids, but VFA final concentration was directly related with initial concentration of each acid. After VFA recovery tests of chemical reaction with ethanol were carried out for ethyl esters production as gas oil additives. Results of these tests showed a transformation efficiency of 26%.

KEYWORDS

Anaerobic digestion, electrodialysis, VFA recovery

INTRODUCTION

Different membrane processes have been studied as a technologic alternative for the enhancement and improvement of conventional leachate treatments. Linde and Jönsson (1995) and Urase et al (1997) were studied the rejection efficiency of metal ions with a nanofiltration process applied on a leachate. Treatment by reverse osmosis has been reported (Linde et al, 1995; Peters, 1998 and Chianese et al, 1999) with high COD rejection and big reductions in concentrate volume. In the last years hybrid process has been used. Pirbazari et al (1996) were reported

95% TOC removal and absolutely removal of solids suspends and microorganisms when an ultrafiltration and biologically active carbon process was used in leachate treatment. Activated sludge-ultrafiltration-chemical oxidation and activated sludge-ultrafiltration-reverse osmosis were reported as alternatives for leachate treatment (Bohdziewicz et al, 2001), while Amokrane et al (1997) and Trebouet et al (2001) were worked coupling coagulation-flocculation with membrane process. However few authors report recovery of valuable substances from leachate as D'addario et al (1993) who report VFA recovery from acidogenic digestion of organic fraction of MSW.

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In landfills during anaerobic fermentation process, acetic, propionic, butyric and valeric acids are produced. These acids appear in the leachate and can affect the fermentation process when they are in high concentration, inhibiting the methanogenic process. In the biotechnology industry these VFA acids are recovered with several methods. Liquid-liquid extraction of acetic and propionic acids was reported by Solichien et al (1995) and Ozadali et al (1996), obtained in a fermentation process with *Propionibacterium Acidipropionici*, while Wodzki and Nowaczyk (1997) were studied the acetic and propionic separation by permeation in a hybrid system composed of liquid and anion membranes. Others authors evaluated the feasibility of ED for VFA recovery from fermentation broths and wastewaters. Weier et al (1992) studied the influence several operational parameters on propionic and acetic acid recovery from fermentation broth, while Chukwu and Cheryan (1999) was carried out experiments for acetate removal. Zhang and Toda (1994) found a kinetic relation for acetic acid recovery from synthetic solutions and Yu et al (2000) were applied an ED with bipolar membranes for acetic acid recovery from wastewater.

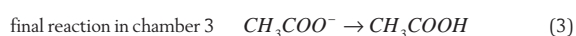
This study shows the results of an ED process applied on a simulated leachate for VFA recovery. Effect of initial leachate composition, applied voltage and flow rate on VFA recovery was evaluated. Final part of this work was carried out to evaluate the potential of ester production from VFA solutions recovered.

MATERIALS AND METHODS

Principle

The principle of VFA recovery from simulated leachate by ED is show in Figure 1. Leachate was pumping across of space 3 (dilute solution chamber), between anionic membranes A1 and A2. When the electric field is imposed only the negatives ions can cross the anionic membrane A1 and are transported to chamber 2

(concentrated solution), where are retained by the cationic membrane C and are evacuated by the distilled water. In this study the only anions in leachate were the acetate, propionate, butyrate and valerate. The anionic membrane A1 retains the positive ions from leachate. Similar ionization process it happens in the dilute solution chamber, in which water is separated and only hydroxyl groups can be transfer to concentrate chamber, where they react with ions H^+ to form water, as is showed in the next equations.



In this form the leachate is treated and VFA recovered. However is important to stand out that for real leachates not only VFA will be transported across of anionic membrane.

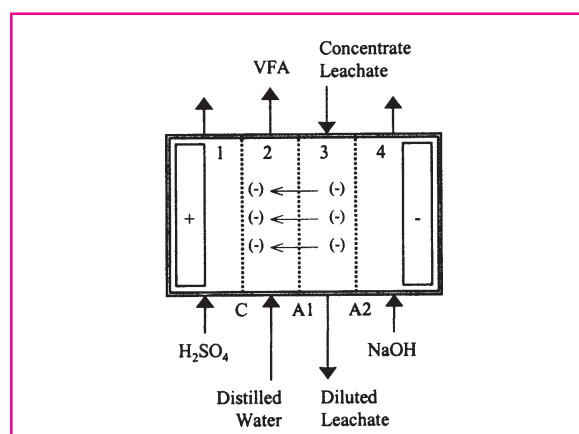


Figure 1 ED Principle

Experimental set-up

The experimental device used in this study is shown in Figure 2. An ED cell with four chambers was used. The technical specifications of ED cell are showed in Table 1. A variable-voltage power supply (0-20 V DC, 1200 mA) was used to create the electric field. In the first chamber a solution of sulfuric acid 0.1 N was used as electrolyte solution and recirculated permanently by a submerged

pump. Sodium hydroxide 0.1 N was pumped in the chamber 4 was electrolyte solution. Beginning the operation, distilled water was pumped to chamber 2 and recirculated. The synthetic leachate was pumped across chamber 3 in opposite sense at other flows.

Synthetic leachates were prepared based in previous works (Rios, 1999) and only acetic, propionic, butyric and valeric acids were used to simulate real concentrations of these substances. Table 2 shown typical leachate compositions used in this work. After preparation, the pH of solutions was adjusted between 6.4 and 7.2

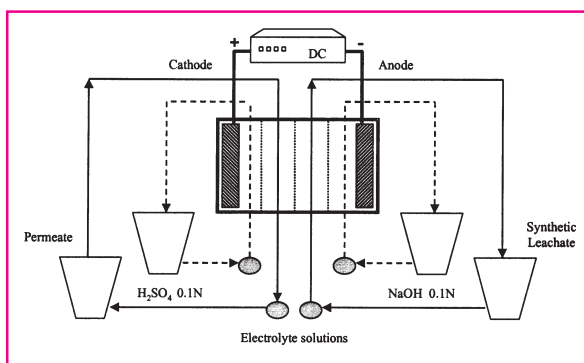


Figure 2 Experimental set-up

Table 1 Electrodialysis cell

Membranes	
Cation Membrane	Sybron Chemicals MC-3470
Anion Membrane	Sybron Chemicals MA-3475
Nominal distance between membranes	9 mm
Effective Membrane Area	0.015 m ²
Cathodes	
Cathode	Graphite
Area	0.008 m ²
Anode	Stainless Steel
Area	0.009 m ²
Nominal distance between cathodes	58 mm

Table 2 Compositions of synthetic leachates

Leachate	Sodium Acetate (mg/L)	Sodium Propionate (mg/L)	Butyric Acid (mg/L)	Valeric Acid (mg/L)
L1	15030	149	60	20
L2	4100	227	42	25
L3	1500	117	35	35
L4	685	61	77	90

Thirty- six different tests were made varying the applied voltages (7, 11 and 15 V DC), the flow rate in dilute and concentrate chambers (0.22, 0.54 and 0.86 m³/m².h) and the leachate

composition (L1, L2, L3 and L4). The during of each test was of 4 hours and each 30 minutes samples of the concentrate chamber were analyzed. After each test an inverse electrodedialysis process and water washing of membranes, were made for to clean the membranes.

After acids separation by ED, three test of ethyl-ester production with samples of VFA recovery were made. 100 ml of sample, 250 ml of ethanol and 0.8 ml of sulfuric acid concentrate were mixed and heated at 80 °C during three hours, to evaluate the transformation performance of VFA recovered in gas oil additives.

Analyses

VFA concentration in the samples was determined by gas chromatography with a FID detection system and the initial and final column temperature were of 40 and 120 °C. Before samples analysis, a derivatisation process was made on each sample with ethanol for to guarantee right results.

RESULTS AND DISCUSSION

Effect of initial VFA concentration

The effect of initial composition of VFA in the leachate on total VFA recovery was the first parameter evaluated. The figure 3 shows as higher VFA removals are obtained when the leachate used in the experience had the smaller initial concentration in VFA. Similar results were obtained when the flow rate in the chambers 2 and 3 were smaller (Figure 4 and 5), nevertheless the difference of performance between dilute and concentrate leachate was more small, with smaller flow rates. This difference can be explained by a hydrodynamic effect on the VFA removal, more high when the flow rate in the chambers was higher. As for the higher VFA removals obtained with dilute leachate one of principal causes it can be a more easy transports of ions across of the

membranes when the dilute leachate was feeding.

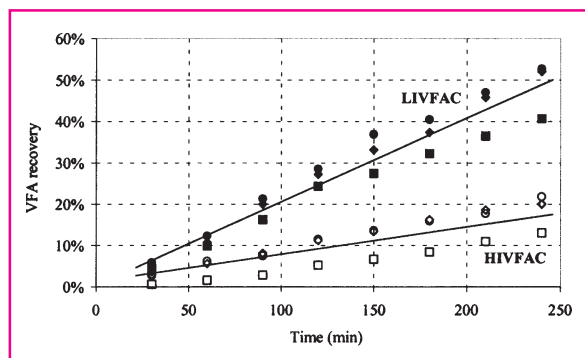


Figure 3 Effect of initial VFA concentration on final VFA removal. Flow rate of $0.86 \text{ m}^3/\text{m}^2.\text{h}$ in chambers 2 and 3. LIVFAC (low initial VFA concentration). HIVFAC (high initial VFA concentration)

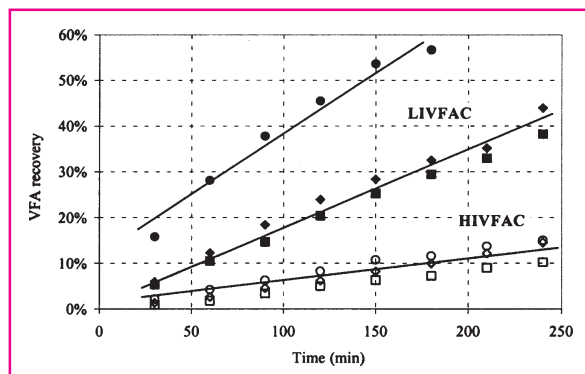


Figure 4 Effect of initial VFA concentration on final VFA removal. Flow rate of $0.54 \text{ m}^3/\text{m}^2.\text{h}$ in chambers 2 and 3

Effect of applied voltage

The second parameter evaluated in this work was the effect of applied voltage on VFA removal. For three different applied voltages, the removal of VFA of the leachate showed more high values when the applied voltage was more elevated, which was expected because the voltage is one of more important parameters in this type of process. Nevertheless the positive effect of applied voltage on VFA removal was different for process feeding with dilute leachate and with concentrate leachate. Figure 6 shows a minor slope for concentrate leachate.

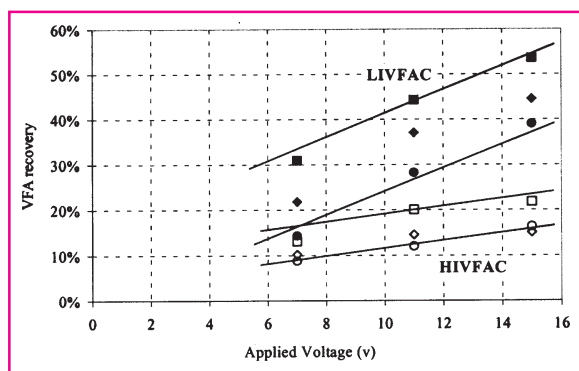


Figure 5 Effect of initial VFA concentration on final VFA removal. Flow rate of $0.22 \text{ m}^3/\text{m}^2.\text{h}$ in chambers 2 and 3

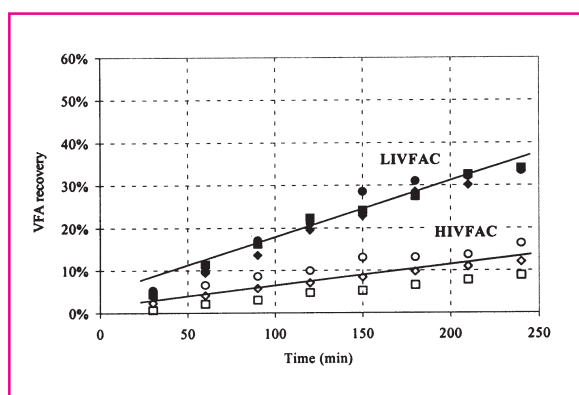


Figure 6 Effect of applied voltage on final VFA removal. $0.86 \text{ m}^3/\text{m}^2$, $0.54 \text{ m}^3/\text{m}^2$, $0.22 \text{ m}^3/\text{m}^2$

Effect of flow rate

The figure 7 shows the effect of flow rate in chambers 2 and 3, on total VFA removal. An important hydrodynamic effect on VFA transport across of the membranes is observed, then when more high velocities of flow (leachate and permeate) were applies, major levels of VFA removal were obtained, which shows that not only the applied voltage is the single driving force in ED process. Newly, the positive effect of this parameter is more important on VFA removal, when the leachate feeding to ED cell was the dilute leachate.

In summary, lower initial concentration of VFA in the leachate, higher applied voltages and higher flow rates in the actives chambers of the ED cell, were the better operational conditions for VFA removal of simulated

leachate, and, clearly, the combination of optimal values of each parameter, producing the higher removal efficiencies.

Effect of chain size of the acids

Once established the effect of some operational parameters on total VFA removal from a simulated leachate, the interest of the final part of this work was evaluated if each volatile fatty acid have a specific velocity of transport through membranes. For this purpose, a specific test was realized with leachate L3, in where the concentrations of butyric and valeric acid is the same. At three different times of operation, the concentration of each one of this acids was analyzed, for to compare its respective removals. Table 3 shows the results of this experience. For an operation time of 30 minutes, the removal of butyric acid from simulated leachate L3, was of 56%, while for the valeric acid was of 35%. At 2 hours of continuous operation the recovery of butyric acid and valeric acid were of 68 and 57%, respectively. At the end of the test, 90% of butyric acid was removed while for valeric acid the maximal removal was of 68%. This allows to observe as the acids with small chain size can be transported more easily across of the membranes in comparison with acid with molecular chains more longs.

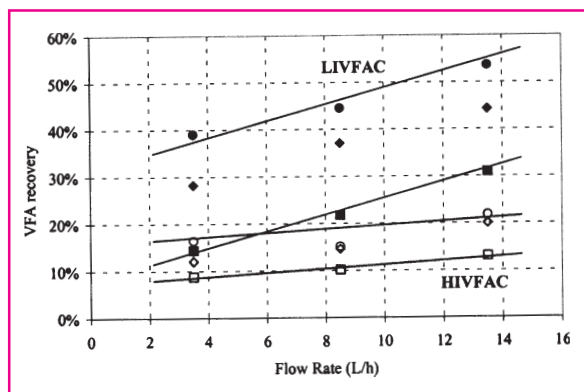


Figure 7 Effect of flow rates in chambers 2 and 3. \bullet 7 V DC. \square 11 V DC. \diamond 15 V DC

Table 3 Results in test of effect of chain size

Operation Time (min)	Butyric Acid (mg/L)	Valeric Acid (mg/L)
30	19.9	12.3
120	23.9	20
240	31.3	23.7

The final observation made in this work was a severe fouling on the membranes after each experimental test. Similar initial properties of the membranes were obtained after a process of reverse ED and a manual washing with distilled water made on each membrane, after the next test. But this is a very important disadvantages and one of more important problems to resolve for a possible full-scale application.

Esterification tests

After to evaluate the effect of principal variables in the recovery of VFA from a simulated leachate by ED, some test of esterification were carried out, for to observe the real possibility of ethyl-esters production from VFA recovered; the ethyl-esters can be used as gas oil additives for to improve the octane degree of the combustibles. For this purpose, some test were realized, used a reaction time of 3 hours, a operational temperature of 100 °C and an excess of ethanol of 50%. After each test, analyses of ethyl-esters were realized. The higher level of ethyl-esters production was of 26%, with a final concentration of 368 mg/L.

CONCLUSIONS

Recovery of VFA from leachate by electro dialysis is an alternative for to valorize the municipal solid wastes. Higher removal levels of VFA from leachate were obtained when a dilute leachate was feeding at ED cell, with high flow rates in actives chambers of ED cell and when high applied voltages were used. The transport of acids with small size of molecular chain is easier through the membrane. At full-scale applications the

fouling of the membrane by organic substances and inorganic precipitates can be the major problem of this process.

Although it is possible to obtain chemical substances used as gas oil additives from leachate with an electro dialysis process, the final concentrations of recovered substances is very low, and therefore is indispensable to find other complementary process for to obtain more high concentration of VFA.

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