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Chromium separation from oxalic acid solution by dialysis

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ABSTRACT

Acid recovery from oxalic acid aqueous solutions containing trivalent chromium (Cr(III)) was investigated using dialysis in which a two-compartment dialyzer was prepared with a G-1201 or AMI membrane for carrying out batch-mode dialysis. To compare the performance of these anion exchange membranes, the overall mass coefficient was determined against volumetric flow rate, temperature and the initial concentrations of both oxalic acid and chromium. The results indicated that the overall mass transfer coefficient of the G-1201 membrane was twice that of the AMI membrane. Additionally, the G-1201 membrane exhibited an increase in overall mass transfer coefficient with increasing volumetric flow rate and temperature in the range of $2.29 \times 10^{-7} - 9.39 \times 10^{-7}$ m/s, as well as with reducing the initial concentration of oxalic acid and chromium in the range of $3.72 \times 10^{-7} - 1.52 \times 10^{-6}$ m/s. Furthermore, treatment of the oxalic acid leaching liquid with the G-1201 membrane was also investigated.

Keywords: Dialysis; Oxalic acid; Chromium; Membrane

1. Introduction

Leather is a material that has been widely used for manufacturing various items including bags, accessories and shoes. Leather-making using animal skins is one of man's oldest technologies which cause significant pollution. Currently, approximately 7 million tons of raw hides and skins are processed annually worldwide to yield greater than 0.55 million tons of heavy leather and around 1.3 trillion square meters of light leather [1].

Chromium is the most common element used in leather tanning which confers excellent mechanical resistance, hydrothermal resistance and softness. Globally, more than 80% of global leather production is still tanned with chromium salts although many potential hazards are associated with chromium pollution. For many years, leather industry has focused on finding alternatives for chromium tanning as it currently generates chromium-based solid wastes including chromium sludge and chrome-contaminated leather shavings and trimmings, which account for about 20%–40% of raw hide/skins, and even surpass the quantity of finished leather. Most of these wastes products are disposed through landfill or incineration processes which create serious environmental challenges. Oxidation of Cr(III) during landfill and combustion converts it to carcinogenic hexavalent chromium [2]. Increasing pressure from environmental authorities has led to urgency in developing cleaner technology to minimize wastes and to find more practical solutions for the disposal of potentially hazardous waste.

Different technological choices have been studied for the management of solid leather waste containing chromium [3]. Extraction of chromium with acidic solutions or organic chelates has shown some promise [4–6]. In terms of the order of stability of chromium complexes [7], the chromium–collagen complex lies approximately between (1) and (2) as shown in Fig. 1 in the range of stabilities. Therefore, oxalates, malonates and succinates behind (2) are able to remove chromium from the chrome-tanned leather. For the process to be viable, chromium has to be separated and recovered, and the leaching solution must be recycled. Many approaches have been tested to recover chromium from aqueous solutions including precipitation, filtration, extraction, adsorption and ion exchange. Acidic extraction of chromium can be performed with sulfuric,

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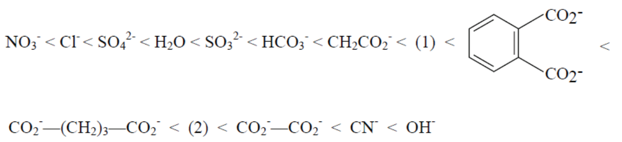

Fig. 1. Order of stability of chromium complexes.

oxalic, tartaric or citric acid, although the choice of acid is difficult and needs to be balanced against economic, technological and environmental considerations. However, the process is inefficient and generates environmental pollution and so there is an urgent need for developing alternative methods.

Diffusion dialysis is an ion exchange membrane separation process which has been applied for the separation and recovery of acids and alkalis from waste solutions [8]. To recover carboxylic acids, their diffusivity, permeability and selectivity in anion membranes for dialysis have been studied [9–12]. Similarly, recovery of inorganic acids from various effluents by membrane dialysis has also been investigated [13–17]. These experiences can be used to develop a separation and recirculation process of the leaching solutions containing chromium and acids of chrome in tanned leather. This study focusses on the dialysis separation of oxalic acid solutions containing Cr(III) produced during the leaching of chrome-tanned leather. The process is based on the ability of oxalate as an anion to permeate through an anion exchange membrane, but chromium is a cation and so will be rejected by the membrane.

2. Experimental details

A similar experimental setup was used as previously described [9]. Two compartments of the dialyzer were separated by an anion-exchange membrane. The dimensions of two compartments were 30 cm in length and 3 cm in width. The total depth of the compartments was 6 mm whilst the single depth and membrane areas could be changed by varying the size of the sealing plate on both sides of the membrane. The dialyzer was operated in either continuous or batch mode. The basic properties of the membranes are summarized in Table 1.

In batch mode (Fig. 2), the aqueous solution of oxalic acid and Cr(III) (feed), along with the stripping agent (deionized water) was first put into a retentate tank and a dialysate tank, respectively. They were then pumped through the compartments and entered into the tanks. Samples were taken at different time intervals. Acid concentration was determined by titration with a standard NaOH solution. Chromium content in the samples was determined using a spectrophotometer with 1,5-diphenylcarbazide after oxidation of Cr^{3+} to Cr^{6+}, with a mixture of concentrated acids and $KMnO_4$. The experimental conditions including temperature, volumetric flow rates, initial concentrations of oxalic acid and chromium in the feed are listed in Table 2.

3. Results and discussions

3.1. Performance comparison of the two membranes

To compare the performance of two membranes, a group of experiments in batch mode were conducted. The feed was prepared from water, oxalic acid dihydrate and chromic chloride hexahydrate. The content of oxalic acid and chromium was 0.102 and 0.019 mol/L, respectively. The volume of feed in the retentate tank was equal to that of deionized water in the dialysate tank at the start and was kept constant during the course of dialysis. Therefore, the oxalic acid concentration decreased until the retentate was equal to that rise of the dialysate. Temperature was kept at 25°C. The recorded concentration changes of oxalic acid in the dialysate is presented in Fig. 3, which shows that the oxalic acid concentration in the dialysate increases almost linearly with time for both membranes at a similar rate but with different magnitudes. Under the same conditions, more oxalic acid molecules passed through the AMI membrane than that of passed through the G-1201 membrane. After 10 h of dialysis, less than 10% of oxalic acid in the feed passed through the AMI membrane and entered into the dialysate tank,

Table 1
Properties of the membranes

Parameter value	AMI-7001	G-1201
Thickness, mm	0.52 ± 0.02	0.26 ± 0.02
Water content, g H_2O per g of dry membrane		0.45
Ion-exchange capacity, mole per kg of dry membrane	1.3 ± 0.1	1.9
Country of origin	Membranes International Inc. USA	Hangzhou Grion Environmental Technology Co., Ltd., China

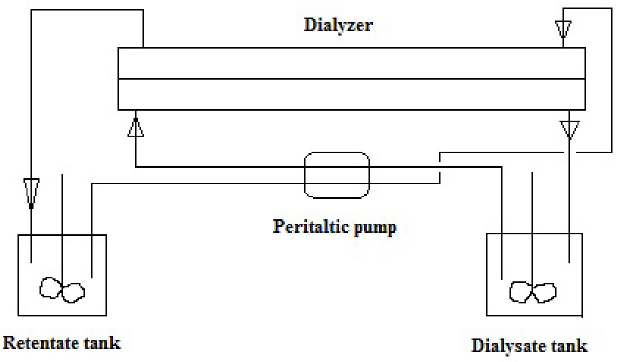

Fig. 2. Sketch of the experimental setup.

Table 2
Experimental conditions

Temperature, °C	25, 40
Volume flow rate × 10^4 m^3/h	1.20, 1.32, 1.50, 3.00
Initial concentration of oxalic acid, mol/L	0.102, 0.512, 0.817
Initial concentration of chromium, mol/L	0, 0.019, 0.038

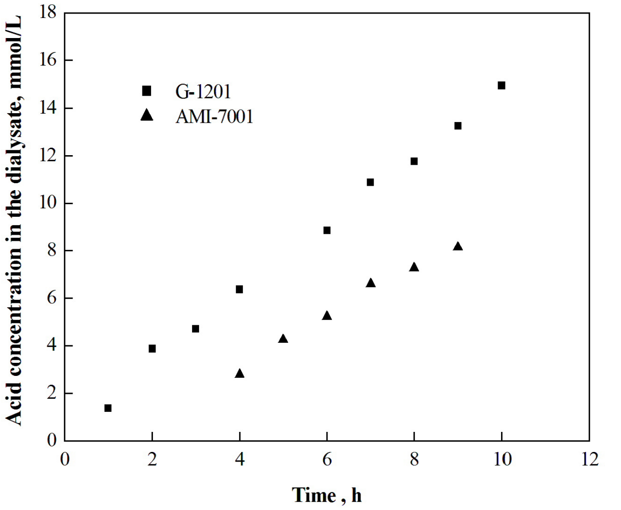

Fig. 3. Concentration change of oxalic acid in the dialysate with dialysis time (C_{F0} = 0.102 mol/L; flow rate = 1.2 × 10^{-4} m^3/h; 25°C).

whilst for the G-1201 membrane, the percentage was over 15%. The concentration change of oxalic acid for each pass through the dialyzer was small, at about 0.3% of the initial value. Therefore, the dialyzer can be considered the same as a two-compartment dialysis cell as used previously by Palatý and Bendová [18]. The overall mass transfer coefficient was calculated from Eq. (1):

$$C_d = C_{F0}\frac{k_V}{1+k_V}\left\{1-\exp\left[-\left(1+k_V\right)\frac{A}{V_1}Kt\right]\right\} \tag{1}$$

where C_d is the concentration of oxalic acid in the dialysate, mol/L; C_{F0} is the concentration of oxalic acid in the feed, mol/L; k_V represents the ratio of the residual volume V_1 (m^3) to the volume of the dialysate V_2 (m^3), A is the membrane area, m^2; K is the overall mass transfer coefficient, m/s; and t denotes the dialysis time, s. If V_1 is equal to V_2, Eq. (1) can be simplified to Eq. (2) or Eq. (3):

$$C_d = 0.5C_{F0}\left\{1-\exp\left[-\frac{2A}{V_1}Kt\right]\right\} \tag{2}$$

Or

$$\frac{V_1}{2A}\ln\frac{C_{F0}}{C_{F0}-2C_d} = Kt \tag{3}$$

$$\text{Let } Y = \frac{V_1}{2A}\ln\frac{C_{F0}}{C_{F0}-2C_d}, \text{ we have } Y = Kt \tag{4}$$

By plotting Y against t, a straight line is achieved and the slope is the overall mass transfer coefficient K. From the data shown in Fig. 3, the Y values were calculated and are given in Fig. 4. Fig. 4 shows a linear relationship between Y and t, and the fitting results are shown in Table 3. It is clear that the K value of G-1201 membrane is about two times that of the AMI membrane. Experimental results demonstrate that the rejection rates of Cr(III) in the two kinds of membrane are almost 100%. The color of the feed was dark green but the dialysate was almost colorless.

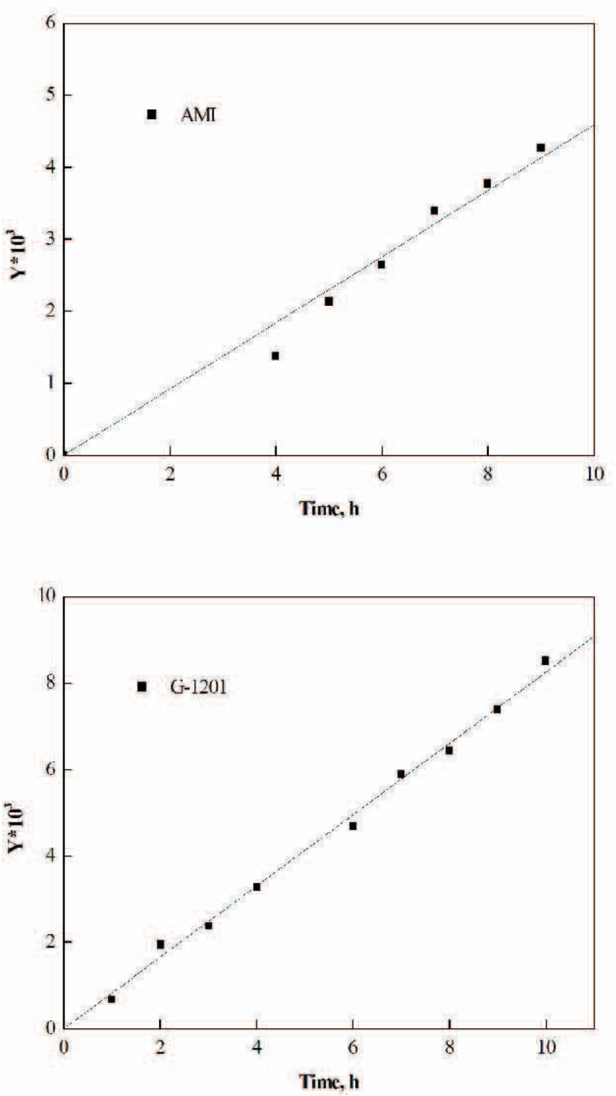

Fig. 4. Application of Eq. (3) for recorded C_d and t (C_{F0}=0.102 mol/L; flow rate = 1.2 × 10^{-4} m^3/h; 25°C).

Table 3
Fitted results from Fig. 4 (C_{F0} = 0.102 mol/L; flow rate = 1.2 × 10^{-4} m^3/h; 25°C)

Parameters	AMI-7001	Grion-1201
$K \times 10^7$, m/s	1.22	2.29
Correlation coefficient	0.988	0.997
Value – Probability	<0.0001	<0.0001

3.2. *Effect of flow rate*

In Fig. 5, the K values of the G-1201 membrane as a function of volumetric flow rates at 25°C and 40°C are presented, where for both temperatures K value of the G-1201

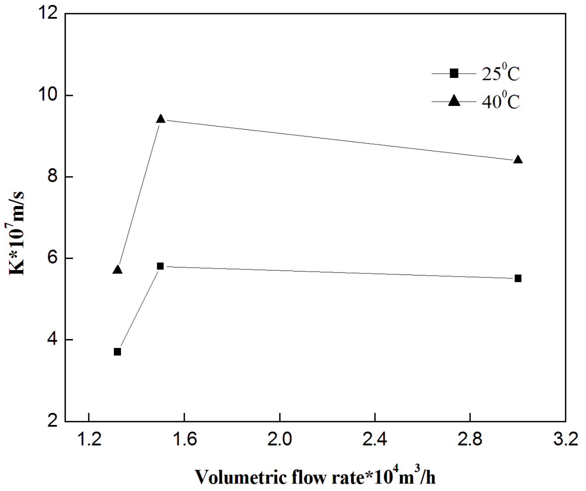

Fig. 5. Dependence of *K* value of the G-1201 membrane upon volumetric flow rate (C_{F0} = 0.102 mol/L).

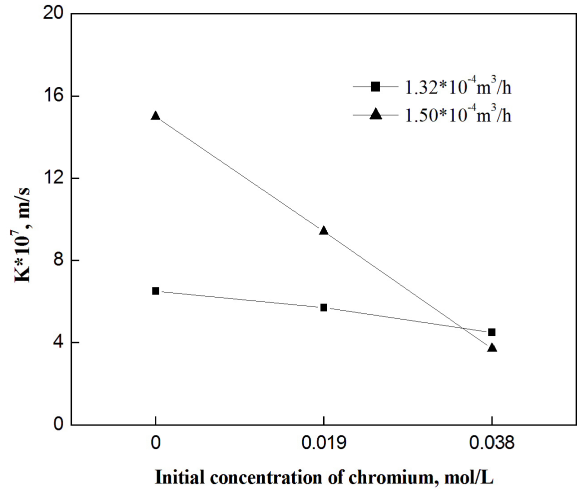

Fig. 6. Dependence of *K* value of the G-1201 membrane upon initial concentrations of chromium (40°C).

membrane increased with volumetric flow rate until it reached 1.5 × 10^{-4} m^3/h followed by a slight decrease. Additionally, it is observed that the *K* value was higher at 40°C. It is well known that the overall mass transfer coefficient *K* included three parts (shown in Eq. (5)): the mass transfer coefficients of the liquid films k_{L1}, k_{L2}, and the mass transfer coefficient of the membrane itself, km.

$$\frac{1}{K}=\frac{1}{k_{L1}}+\frac{1}{\mathrm{k_m}}+\frac{1}{k_{L2}} \tag{5}$$

The mass transfer coefficients of the liquid films k_{L1} and k_{L2}, increased monotonically with increasing flow rate in the laminar region [19,20]. Therefore, the oxalic acid can better permeate through the membrane. The *K* value of the G-1201 membrane is higher at 40°C which may be due to the fact that the diffusivity of the oxalic acid inside the membrane increases with temperature. Experiments also proved that the Cr(III) could be almost 100% rejected by the membrane.

3.3. Effect of Cr(III) concentration

Fig. 6 shows the relationship between the *K* value of the G-1201 membrane and initial concentrations of Cr(III) which indicates that the *K* value was affected more by Cr(III) at a higher flow rate than at a lower flow rate. Although Cr(III) exists as cations, quite a large number of Cr(III) complex cations [21,22] may gather at the membrane surface which blocks the exchangeable sites and hinders the passage of oxalic acid molecules through the membrane. At a lower flow rate, the effect of Cr(III) is weakened by liquid film resistance.

3.4. Effect of oxalic acid concentration

The effect of the initial concentration of oxalic acid on the *K* values of the G-1201 membrane was also studied and the results are shown in Fig. 7. The data show that the *K* value for the G-1201 membrane decreased with increasing the initial oxalic acid concentration. In addition, when the initial concentration of oxalic acid was increased to 0.5 mol/L, the rejection percentage for Cr(III) decreased to 80%. Therefore, when membrane dialysis was used for separating Cr(III) from oxalic acid solution, the initial concentration of oxalic acid should be limited to a low concentration range.

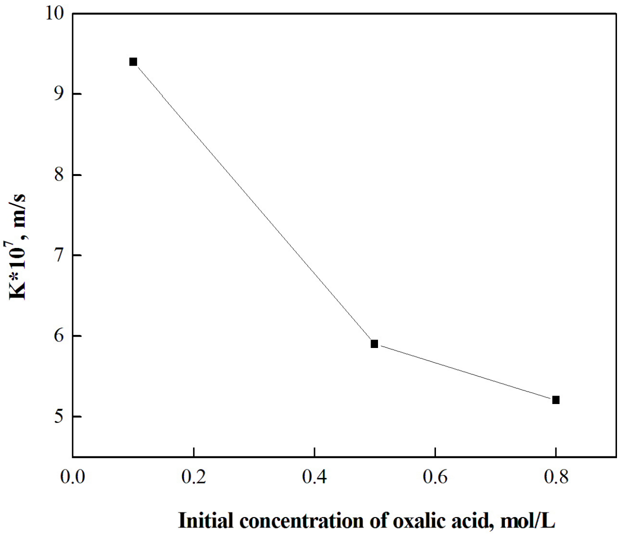

Fig. 7. Dependence of *K* value of the G-1201 membrane on initial concentration of oxalic acid (1.5 × 10^{-4} m^3/h, 40°C).

The *K* values of the G-1201 membrane for the different conditions are summarized in Table 4.

4. Dialysis experiments of oxalic acid leaching liquid

The leaching liquid preparation steps were as follows: first, leather slices and oxalic acid solution were mixed at a ratio of 1:10 (solid/liquid ratio, g/mL) in flasks. They were then oscillated at a fixed frequency and temperature for 12 h in a thermostat vibrator. Finally, the leaching liquids were collected by filtration. The results from the dialysis experiments are shown in Fig. 8.

Table 4
K value of G-1201 membrane

Temperature, °C	25	40
Volumetric flow rate × 10^4, m^3/h	1.32–3.00	1.32–3.00
Initial concentration of oxalic acid, mol/L	0.102	0.102–0.817
Initial concentration of chromium, mol/L	0.019	0–0.038
$K \times 10^7$, m/s	3.72–5.80	3.72–15.25

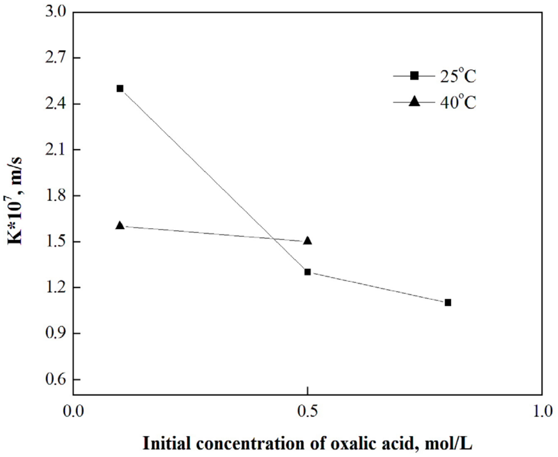

Fig. 8. Dependence of *K* value of the G-1201 membrane on initial concentration of oxalic acid on the leaching liquid (3×10^{-4} m^3/h).

Comparison of Figs. 7 and 8 shows that the *K* value of the G-1201 membrane in leaching liquids is smaller than that in the synthesized aqueous solutions. The reason is that leather collagen can be dissolved during the leaching process, and the dissolved collagen materials are adsorbed at the membrane which hinders oxalic acid dialysis. Measurements indicated that the concentration of Cr(III) in the leaching liquid is between 0.0096 and 0.023 mol/L, and the rejection percentage of Cr(III) drops from 90% to 70% continuously with increasing concentration of oxalic acid.

5. Conclusion

Batch mode dialysis experiments were carried out aiming to separate chromium ions from oxalic acid aqueous solutions. *K* values of two types of membranes were calculated. The *K* value of the G-1201 membrane was about two times than that of the AMI-7001 membrane due to the thickness of the former being half of the latter. It was found that the *K* value of the G-1201 membrane lies in the range of 2.29×10^{-7}–1.52×10^{-6} m/s which was affected by concentration, flow rate and temperature. Moreover, the dissolved collagen in the leather leaching process hinders dialysis of oxalic acid.

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