

PURIFICATION OF POLLUTED WATERS BY FUNTIONALIZED MEMBRANES

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Abstract. Chromium VI was adsorbed by maleic acid-funtionalized cellulose membranes (MA-Cellulose) from an aqueous solution at a concentration of 200 ppm. Three different types of supports were used for the membranes: nylon mesh, polyester membrane (as primary support), and polyester fabric, which were coated by modifacated cellulose microparticles (with commercial fixer). The reaction between MA-Cellulose and Chromium VI was analyzed in aqueous solution and a first order type of reaction was obtained, with a value of κ' of 0.00869 with 0.99768 correlation factor. The polyester fabric membrane showed 40% higher flow rate than nylon mesh and polyester membranes, and a two-fold Cr VI adsorption capacity increase.

1. INTRODUCTION

Chromium is the 21st most abundant element in the Earth's crust. Although, it exists in several oxidation states. Cr (III) is a very stable oxidation state for chromium. In this state, the chromium is labile and kinetically very slow to react or form complexes. It is not a strong oxidizer and the human body acidity is enough for the chromium to keep to this Cr (III) state. Cr (VI) is not a very stable state when compared to Cr(III). The Cr (VI) is a very strong oxidizing agent (therefore very fast in reacting, unlike Cr (III) and likely to form complexes). Cr (VI), is extremely toxic for human and animals, even at concentrations of the order of only some parts per million. Indeed, continuous exposition to Cr (VI) by inhalation or skin contact causes severe effects, such as perforation of the nasal septum, asthma, dermatitis, dermal necrosis and may be fatal if swallowed, due to its strong oxidative potential [1,2]. In fact, chromium VI is a human carcinogen, as determined by the International Agency for Re-

search on Cancer and the U.S. Environmental Protection Agency [3,4]. This is a reason why World Health Organization recommends the toxic limits of chromium(VI) in waste water at the level of 0.005 ppm. [5] and according to the U.S. Environmental Protection Agency, the permissible limit of Cr(VI) in effluent is 0.1 ppm (or 0.05 mg/l). Many countries have regulations of the maximum permissible concentration. In Mexico, The Mexican Official Norm states $50 \mu\text{g}\cdot\text{l}^{-1}$ of total chromium as the maximum permitted level in drinking water, and the normal human serum concentration is about $0.2 \mu\text{g}\cdot\text{l}^{-1}$ [6]. Chromium-containing chemicals have been used in many industries including metal finishing and corrosion control, leather tanning, textile dyeing, wood preserving, drilling, as well as in the manufacturing of inks, pigments, glass, ceramics, and glues [7]. However, the most important source of the chromium present in natural waters is the wastewater discharged by the tanning and plating industries [8]. Thus, chromium has been released inadvertently and intentionally into the

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environment and has become one of the most frequently detected ground water and soil contaminants at hazardous waste sites [9].

Basic chromium (III) sulphate [$\text{Cr}(\text{H}_2\text{O})_5(\text{OH})\text{SO}_4$] (BCS) is widely used in the leather industry as the basic tanning agent. The minimum amount of chromium necessary to perform a good tanning is approximately 3 g of Cr_2O_3 for 100 g of leather [10]. The conventional tannery methods lead to discharge of solutions with chromium concentrations in the range of 1500–4000 mg/l to the sewage. For example, a recent estimate in India indicates that tanning salts equivalent to approximately 400 tons of chromium are being discharged in the water streams, with an annual consumption of about 40,000 tons of BCS salt [11]. It is reported that the Italian tannery industries located in Naples discharge 40 Mm³ of Cr(VI)-containing wastewater (500 mg of Cr/l) and 280,000 tons (1-5% Cr) of dry sludges per year [12].

In developing countries, urban clusters of dirty small- and medium-scale enterprises have severe environmental impacts. Since conventional public-sector regulation is generally ineffective in such situations, a promising second best approach is to promote the voluntary adoption of clean technologies. In Mexico, particularly, the historic colonial city of León in north-central Mexico produces about two thirds of the country's leather goods. Although exact numbers are not known, local regulators estimate that there are approximately 1,200 tanneries in León [13], with an estimated 10,000 tannery workers. An important risk factor for these persons is occupational exposure to chromium [10].

León's tanneries have dumped untreated effluents directly into municipal sewers, which deposit them directly into the Turbio River. León's water pollution problems attracted international attention in 1994 after a die-off of tens of thousands of aquatic birds wintering in a local reservoir fed by the Turbio River [13].

A wide range of technologies is available for the removal of hexavalent chromium from wastewaters, some of which are well-established methods that have been in practice for decades such as precipitation and coprecipitation. These processes simply remove chromium from wastewaters by reduction, coagulation, and filtration. Although these technologies are quite satisfactory in terms of purging chromium and other heavy metals from water, they produce solid residues (sludge) containing toxic compounds whose final disposal is generally by landfilling with related high costs

and still a possibility of groundwater contamination. From the environmental point of view, removing pollutants from liquid wastewater does not solve the problem but transfers it from one phase (usually liquid) to another phase (usually solid) [14,15]. Emphasis in recent years has been on methods for recovery and reuse of metals rather than disposal. These include activated carbon adsorption [14,15] and liquid membrane separation [5,16-18].

In fact, important efforts have been made by scientific and industrial organizations to reinforce stringent environmental regulations towards the prevention and remediation of Cr VI-polluted reservoirs.

Accordingly, in the present work, nylon mesh (NM), polyester fabric (PF), and polyester membrane (PM) were used as templates for producing membranes of cellulose modified with malic acid, which constitutes not only a novel approach to the problem, but it also represents a feasible, technologically and economically speaking, alternative.

2. EXPERIMENTAL

Micro granular cellulose, L(-) malic acid, hydrochloric acid, and acetone were purchased from Sigma as high purity grade reagents. Seven grams of cellulose were treated with an aqueous diluted solution 1:1 of hydrochloric acid for thirty minutes under stirring, filtered, washed with deionized water (until the eluted stream pH was nearly seven) and dried at 38 °C. In a 500 ml flask, activated cellulose was reacted with 1 g of L(-) malic acid in an organic medium (acetone) for 210 minutes at 58 °C with reflux of 30 ml/min. Solvent was separated and esterified cellulose was stored for its fixation on the three different matrixes.

Fourier transform-infrared (FT-IR) spectra were obtained of cellulose and MA-Cellulose with an FT-IR spectrometer, Nicolet 510.

NM, PF and PM were used to support the cellulose compound. The three were commercial grade. Also commercial fixer was applied on every support to fix micro granules of modified cellulose.

A solution of 200 ppm Cr VI was prepared by dissolving potassium dichromate reagent grade in distilled water. 210 ml of 200 ppm Cr VI solution were passed across each of the membranes. Seven eluted portions (30 ml each one) were collected for further spectrophotometric analysis (Spectrophotometer Spectronic 20 Bausch & Lomb). The Cr(VI) concentration in solutions ([Cr(VI)]_{aq}) was determined using the diphenyl carbazide colorimetric method [19] in which sto-

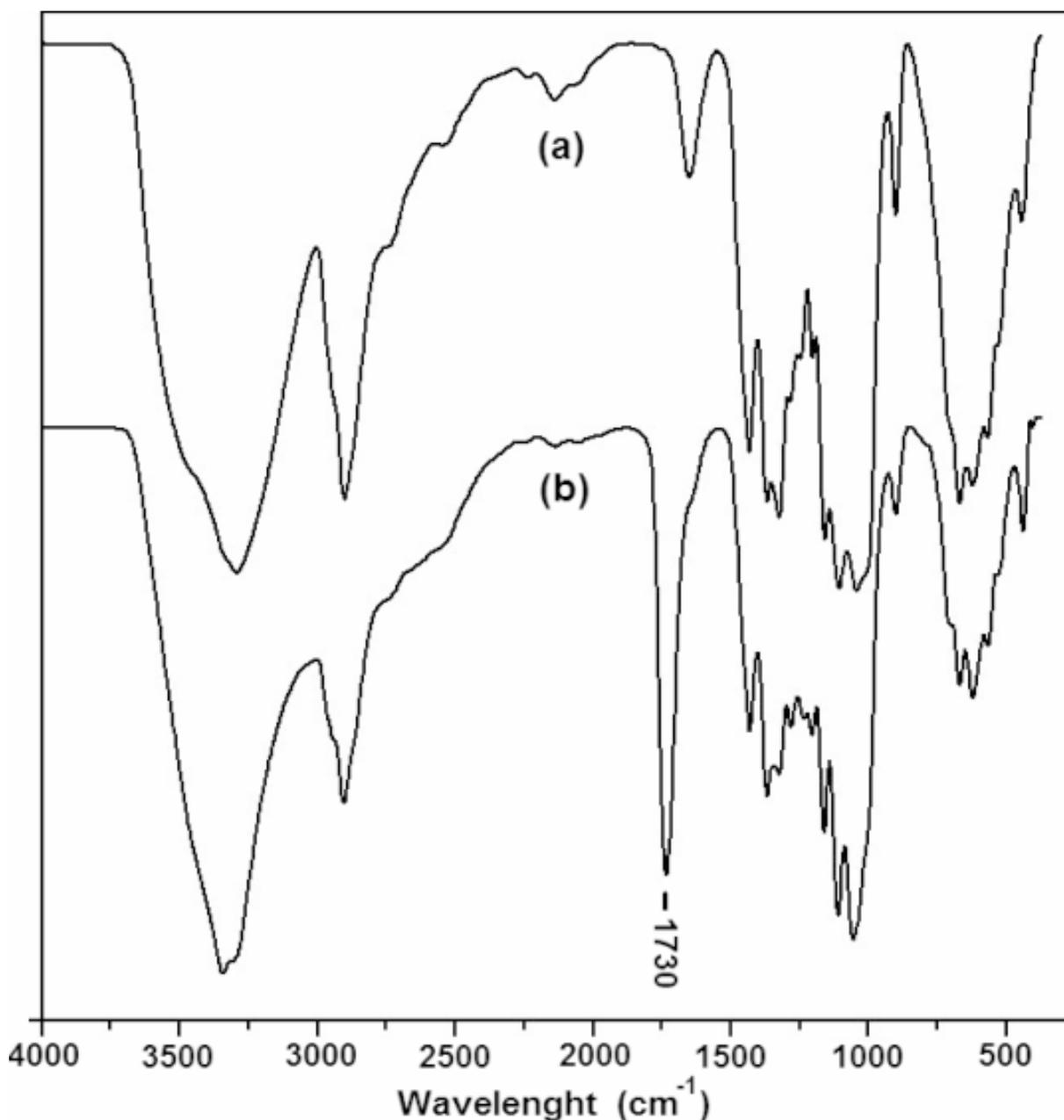


Fig. 1. IR spectrum (a) of pure cellulose and the IR spectra (b) for the functionalized cellulose sample (malic acid).

ichiometric oxidation of the diphenyl carbazide reagent yielded a product with an absorption peak at 540 nm.

3. RESULTS AND DISCUSSION

The typical peaks (FT-IR spectra) of cellulose are shown in Fig. 1a and the FT-IR spectra of MA-Cellulose are shown in Fig. 1b, the spectrum exhibits a strong absorption band at 1730 cm^{-1} corresponding

to the C=O stretching vibration of malic acid molecules.

NM had a regular distribution and shape of its hollows (Fig. 2). PM structure had narrow and wide hollows in an intricate distribution. Finally, PF showed the narrowest hollows, well distributed along the surface of this support. After the fixer was air-sprayed over each of the materials, cellulose compound was applied and fixed by gently spreading on both sides of the primary base.

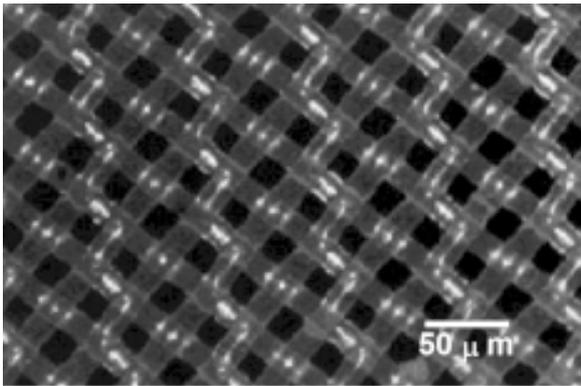


Fig. 2.- Polyester fabric hollow structure.

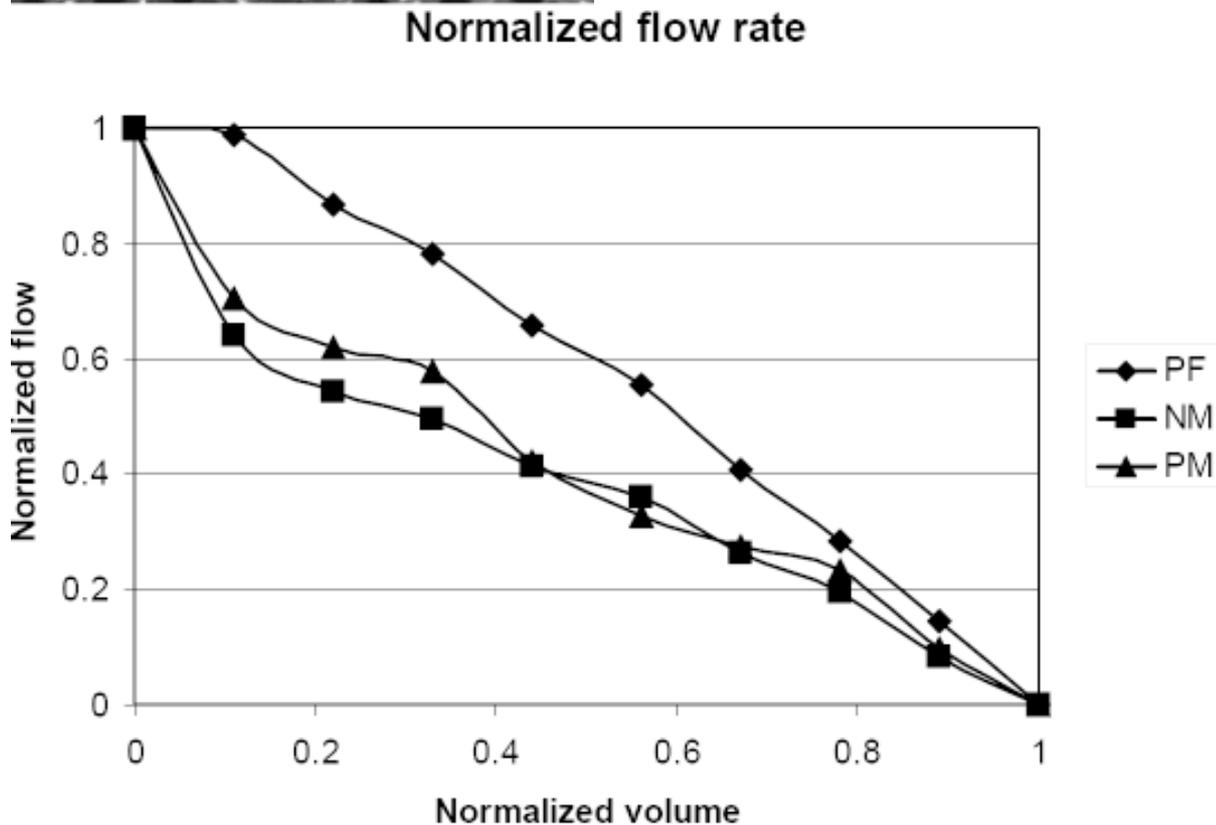


Fig. 4. Normalized flow vs normalized time for the three types of membranes.

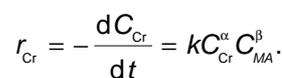
Filtration rate was calculated for each type of membrane. Portions of 210 ml were passed through the different membranes and time was measured for every 10 ml gathered. Flow rate and volume rate were normalized according to the following expression:

$$\Psi^* = \frac{\Psi - \Psi_{\min}}{\Psi_{\max} - \Psi_{\min}}$$

where Ψ^* = normalized variable value; Ψ = variable value obtained for each 10 ml collected; Ψ_{\min} = minimum variable value of all collected data; Ψ_{\max} = maximum variable value of all collected data.

Thus, the normalized value of Ψ_i , is Ψ_i^* and their ranges are: $\Psi_{\min} \leq \Psi_i \leq \Psi_{\max}$ and $0 \leq \Psi_i^* \leq 1$. The respective curves of all normalized data are shown in Figs. 3 and 4. For the Cr(VI) separated from solution, Fig. 5 shows the three different membranes and the proportion of Cr(VI) separated.

The liquid phase rate reaction between malic acid (MA) and Chromium VI (Cr) obeys the mass action law:



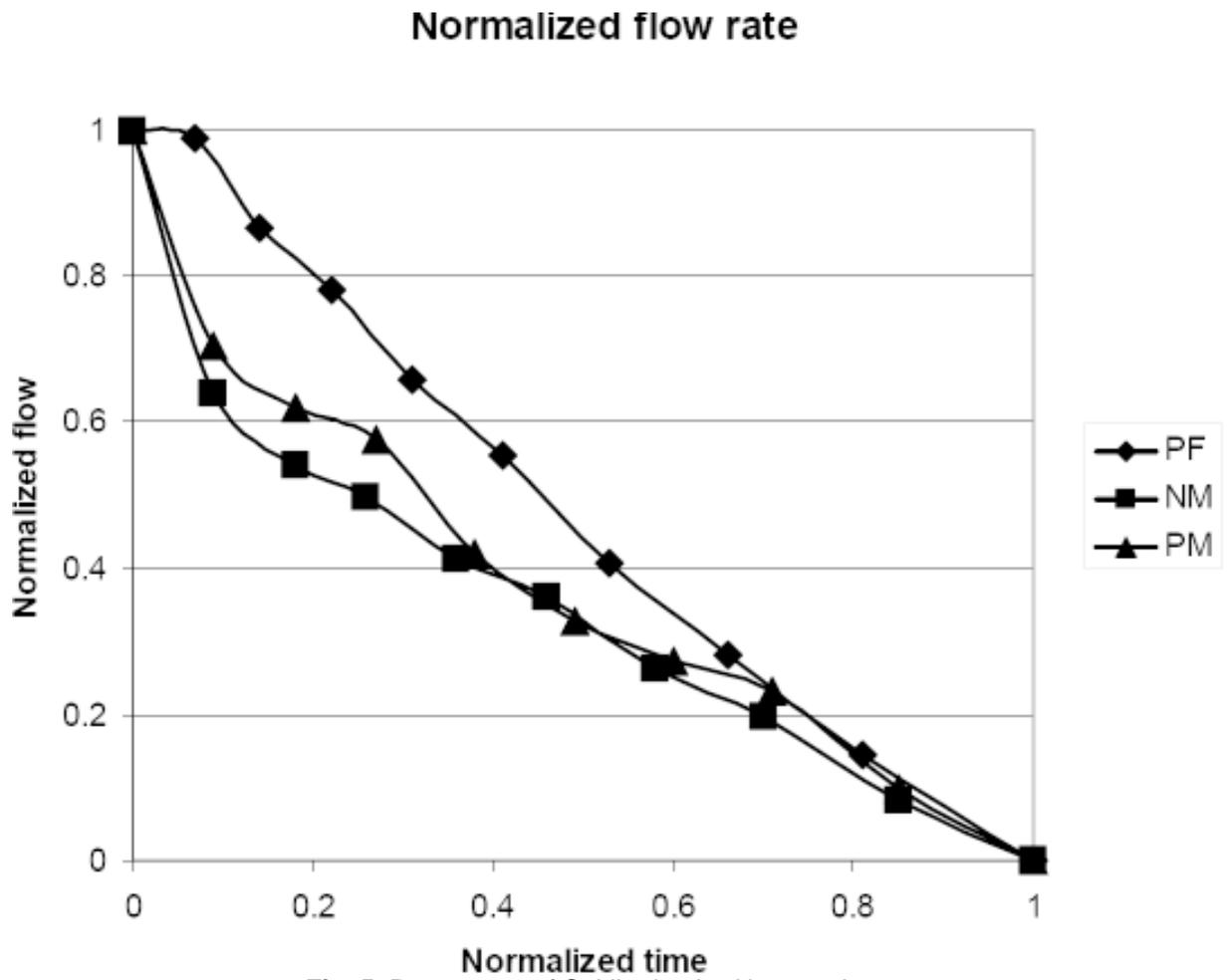


Fig. 5. Percentage of Cr VI adsorbed by membranes.

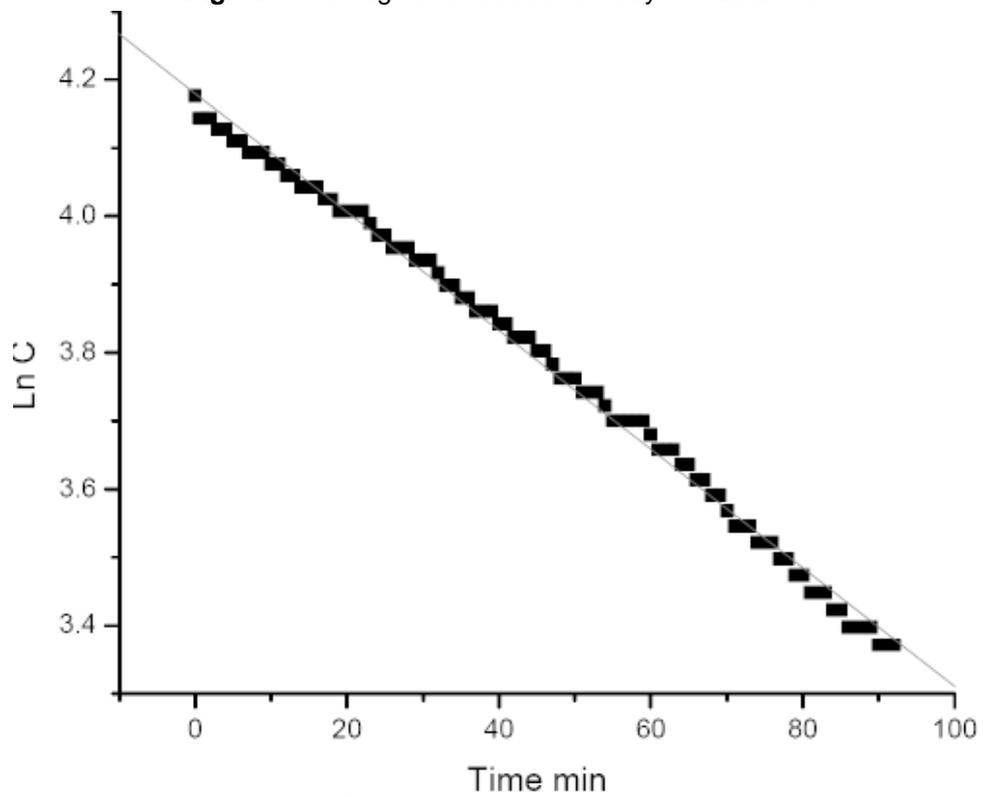


Fig. 6. First order reaction kinetics for Cr VI-Malic acid. $A=1$, $\kappa = 0.00869$, $r= 0.99768$.

Concentration of MA used was much more higher than Cr concentration for the determination of a constant value. Thus, new constant k' was calculated:

$$-\frac{dC_{Cr}}{dt} = k' C_{Cr}^{\alpha}, \quad k' = k C_{MA}^{\beta},$$

furthermore, the integrals $\int -dC_{Cr} / C_{Cr}^{\alpha} = \int k' dt$, for $\alpha = 1$ are shown in Fig. 6.

4. CONCLUSIONS

A difference near 40% was observed between PF and two others (NM, PM) membranes for flow rate; substantially NM and PM flow rate obtained were similar. Although PF hollows were narrower than NM and PM ones, flow rate obtained for the former was higher in almost 40 percent. This was possible because cellulose was fixed over the horizontal surface plane of PF instead of fixation of micro particles of cellulose "within" macro pores (as succeeded in NM and PM supports).

Reaction MA-Cr in liquid phase was first order for Cr VI concentration. Some differences in type of fixation of particles of cellulose "over" and "inner" matrixes and loss of activated sites were due to the relative sizes or hollows and the type of fixer used. PF Showed the highest separation of Cr because there were more free endings in malic acid structure attached.

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