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APPLICATIONS OF BIOPOLYMERS TO PROCESSES OF ENVIRONMENTAL CONTROL*

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ABSTRACT

Two new methods of insolubilizing in cellulose triacetate membranes, natural or synthetic polyelectrolytes, able to bind heavy metal ions, were experimented and discussed. The efficiency of the obtained membranes was tested by monitoring the cupric ion adsorption with a copper ion selective electrode (ISE).

INTRODUCTION

The researches about the procedures for the removal of heavy metals from aqueous media are very actual, as this problem applied to wastewaters is continuously more urgent (1). Traditional methods (precipitation, electrodeposition, etc.) can be used (2,3), but high costs, and other problems, e.g. secondary pollution, are still present. Some polyelectrolytes, both synthetic (e.g. copolymer of maleic anhydride with ethylvinylether) and natural (e.g. hexocellular polysaccharides from *Rhizobium trifolii*) were recently studied (4) for their high metal ions binding capacity (5), in order to point out practical applications of these compounds to environmental processes. In this procedure, the polyelectrolyte, generally watersoluble, is entrapped in polymeric matrices. In the research described here, a new entrapment procedure of the polyelectrolytes in cellulose triacetate membranes, derived from our long experience on this polymer as an entrapping medium of several enzymes (6,7), was investigated. This was realized by two methods: 1) by adding the polyelectrolyte to the cellulose triacetate viscose, before its coagulation; 2) by letting the polyelectrolyte diffuse into the cellulose triacetate, after its coagulation, but still in the gel state. The triacetate membranes, containing the polyelectrolyte, obtained by the two procedures, after drying, are dipped into an aqueous solution

containing cupric ions which are continuously analyzed by the copper ISE; the decrease in cupric ion concentration is due to the chelating action of the immobilized polyelectrolyte. When the process is completed, Cu^{++} concentration removed from the solution by chelation, was also spectrophotometrically determined (see experimental section). Finally, the chelation process of Cu^{++} by the polyelectrolyte, entrapped in cellulose triacetate, was also studied, by the chromatographic column technique.

EXPERIMENTAL

Samples and reagents

The copolymer of maleic acid with ethylvinylether (MAEVE) was synthesized in the laboratory of Prof. M. Aglietto of the University of Pisa, Italy. The hexocellular polysaccharide from Rhizobium trifolii strain, "TA-1" in the test, was kindly provided by Prof. L.P.T.M. Zevenhuizen of the University of Wageningen, The Netherlands. These polymers were purified by dialysis in aqueous concentrated NaCl solution (to remove possible traces of contaminating heavy metals), followed by extensive dialysis against distilled water and finally freeze-dried (8). Elemental analysis, sugar structural analysis and potentiometric titration data, of the two copolymers produced equivalent weights which are in good agreement with the theoretical values for the repeating unit structures depicted in figs.1 and 2 (9).

The average molecular weight of our TA-1 sample is 1.3×10^6 (light scattering data) and that of MAEVE is $\leq 30,000$ (viscosity measurements) (9,10). Cellulose triacetate (TAC) was supplied by Fluka, Buchs (Switzerland); cupric perchlorate, cupric nitrate and all other solvent and reagents were of analytical grade and supplied by Carlo-Erba, Milano, Italy.

Polyelectrolyte entrapment in polymeric membranes.

Using polymeric triacetate (TAC) matrix, two different procedures were applied:

a) To a (3-4% w/w) solution of cellulose triacetate polymer, in (98% w/w formic acid)/(water) 90:10 v/v, 1% by weight of polyelectrolyte was added; after homogenization of the viscose, this was stratified in a Petri dish (5cm diameter), allowing the solvent to evaporate for about 36 hours and the obtained membrane (5cm diameter and 2mm thickness) was washed with water and stored. This membrane was used, either in a 25ml glass cell under magnetic stirring or after cutting into small particles, as a stationary phase of a glass column, to check its binding ability to Cu^{++} ion.

b) Viscose as above, but without addition of polyelectrolyte, was slowly extruded in a specific thickness of gel film, which was coagulated by immersion in a water bath. The gel membranes, cut into 3cm diameter disks, were dipped into a 1% by weight polyelectrolyte solution. After about 48 hours in the polyelectrolyte solution, the membranes were extracted, vacuum dried, washed with water and stored.

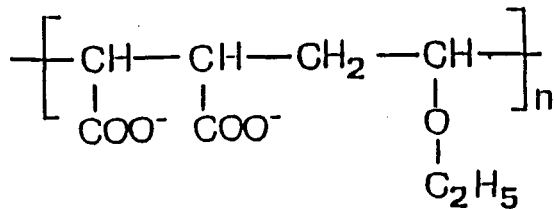


Fig. 1 - Monomeric unit of MAEVE synthetic polyelectrolyte.

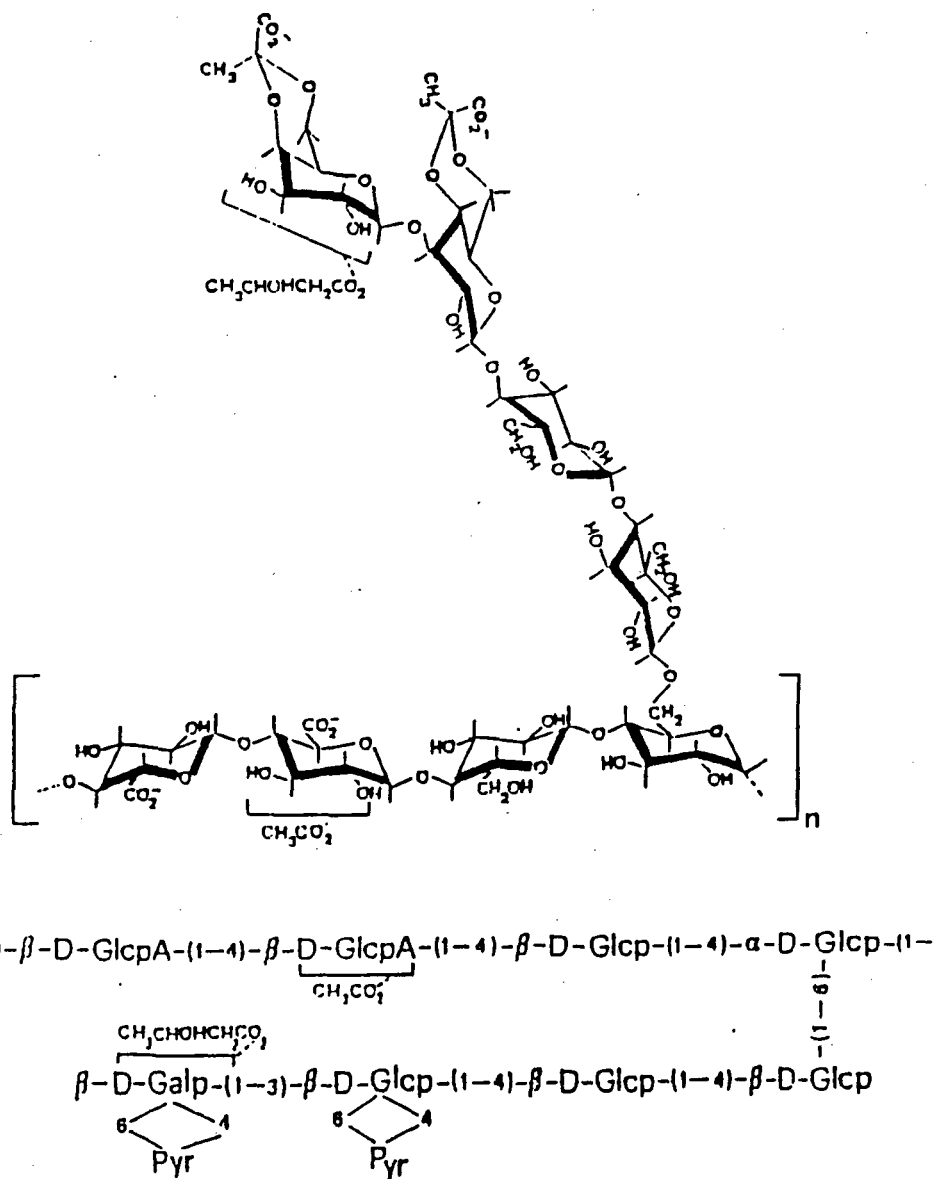


Fig. 2 - Monomeric unit of TA-1 natural polyelectrolyte.

Method and apparatus

Potentiometric data were collected using an Orion Model 901 Ionalyzer apparatus, equipped with an Orion electrode selective to Cu^{++} (cat. 0085044); this was used in combination with a reference calomel electrode. Both these electrodes were dipped into a thermostated cell (at 25 °C) containing an aqueous solution at a fixed concentration of $\text{Cu}(\text{ClO}_4)_2$, under magnetic stirring; the initial potential value was recorded. Then, the polymeric membrane containing polyelectrolyte was dipped into $\text{Cu}(\text{ClO}_4)_2$ solution, and potentiometric data were continuously recorded, until a constant value was reached. At the end of this process the polymeric membrane containing Cu^{++} , extracted from the solution, was first washed with water and then washed several times with $\text{EDTA } 10^{-2} \text{ mol l}^{-1}$ solution at pH 6. Preliminary tests (9) ensured that the relative strength values of the two cupric complexes, with the copolymer and with EDTA, were such as to make possible a full recovery of Cu^{++} . Solutions, containing CuEDTA complex, were collected and the absorbance values recorded, at $\lambda = 270 \text{ nm}$, against a blank of the above EDTA solution, in a 1cm pathlength quartz cell, using a Beckmann DU-40 spectrophotometer. Cu^{++} concentration was obtained by means of the calibration graph previously recorded. Other experiments were carried out (9,11), using a small glass chromatographic column (13.7mm diameter and 6cm height), filled to 4cm height with small particles of a cellulose triacetate membrane, containing polyelectrolyte and obtained using the procedure (a) described above. The column was eluted by a $\text{Cu}^{++} 1.5 \times 10^{-4} \text{ mol l}^{-1}$ solution and the concentration of Cu^{++} , in the eluate, continuously tested by means of the atomic absorption spectrophotometer (Thermo Jarrel Ash Smith-Hieftje 11, at $\lambda = 327.4 \text{ nm}$, using an acetylene-air flame.)

RESULTS

Previous papers (9,10) showed that the polycarboxylic compounds we used (synthetic polymer, as MAEVE, or biopolymers, as TA-1), had a sufficiently high charge to act as sequestering agents of polyvalent ions, particularly of cupric ions. Basic research previously performed (8-10), to investigate the interaction between these polyelectrolytes and cupric ions in aqueous solution, using equilibrium dialysis and calorimetric data, pointed out that the main driving force is entropic in nature in all the cases. In contrast, in this paper the practical application of these compounds, especially to environmental decontamination processes, are studied. The aim of the research was essentially to insolubilize the polyelectrolyte by entrapping it in a polymeric support without changing its chelating properties to metal ions. As described in the experimental part, two methods of entrapment in TAC were tested. The choice of polyelectrolyte entrapment in triacetate membranes is advantageous as a large surface area for exchange is present and, as we experimentally checked, no loss occurred either during or after the process to remove the metal present in the solution. Without any consideration of the experimental data, an advantage can be foreseen for procedure (a), based on the addition of the polyelectrolyte to the

polymeric viscose in that it is easy to determine the amount of polyelectrolyte added to TAC and this amount corresponds to the solubility in such a medium. The weak point of this procedure is the possibility that, in the formic acid and TAC viscose, the binding ability of the polymer to heavy metal ions could be modified. The second method (procedure (b)), based on the diffusion of the polyelectrolyte into the TAC gel, ensured that the compound remained unchanged during all the immobilization procedure, but it was hard to foresee how much polyelectrolyte could diffuse into the TAC membrane. The first control examined whether the concentration of the polyelectrolyte solution, into which the TAC-gelled membrane was dipped, affected the diffusion of the polyelectrolyte into the gel. Fig. 3 shows that, for concentrations of polyelectrolyte higher than 10 mg l^{-1} , the binding power of the so obtained membrane, to Cu^{++} ion, remains practically constant. Consequently all membranes obtained by the diffusion method, used in the following experiments, were treated with solutions containing 1% by weight of polyelectrolyte. Fig. 4 shows the potentiometric curve, relative to the absorption process of Cu^{++} ion from the TAC membranes containing MAEVE using procedure (a).

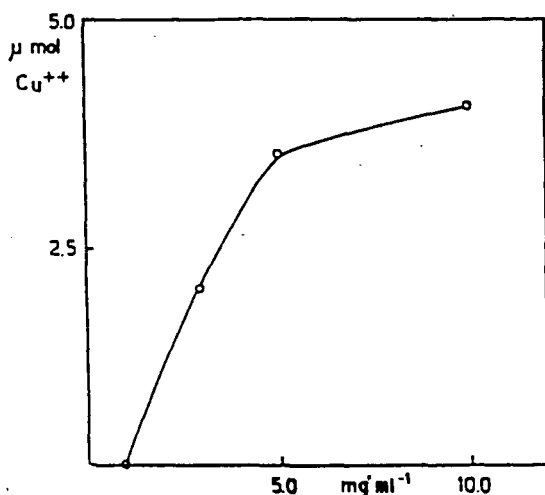


Fig. 3
 μmol of Cu^{++} bound by MAEVE, entrapped in cellulose triacetate membrane (method (b)), as function of MAEVE concentration in the aqueous solution, used for the diffusion process.

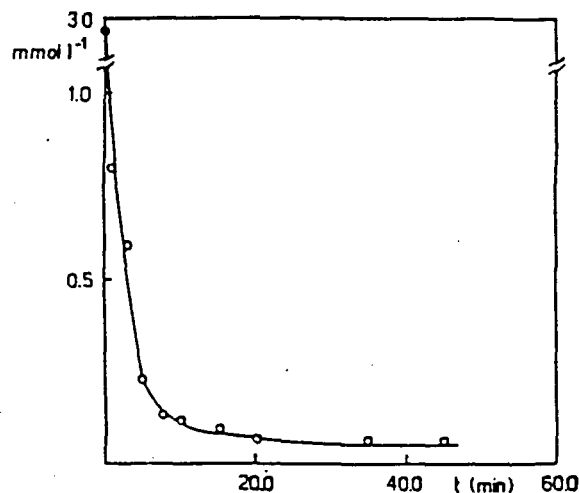


Fig. 4
Decrease of Cu^{++} concentration, due to the binding activity of MAEVE synthetic polymer, insolubilized in cellulose triacetate membrane by method (a). Concentration values of Cu^{++} , as a function of time, obtained by electrochemical measurements (using a copper ion-selective electrode).

It was not possible to obtain the analogous curve using polyelectrolyte TA-1, as this proved to be practically insoluble in the formic acid and TAC viscose. Fig. 5 shows the analogous potentiometric curves concerning the adsorption of Cu^{++} ion from the TAC membranes containing MAEVE, obtained through procedure (b). The curves refer to TAC membranes with varying thickness. In fig. 6 analogous curves are reported for membranes of TAC, containing the polyelectrolyte TA-1 adsorbed as in procedure (b).

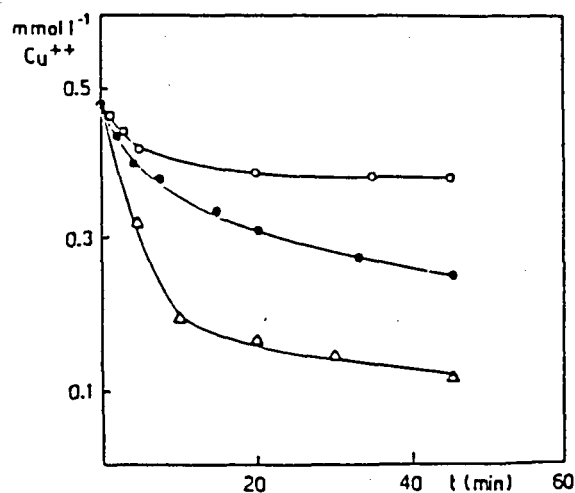


Fig. 5

Decrease of Cu^{++} concentration, due to the binding activity of MAEVE synthetic polymer, entrapped by method (b) in cellulose triacetate membrane by increasing their thickness. Concentration values of Cu^{++} , as a function of time, obtained by electrochemical measurements (using an ion-selective electrode). ($\circ = 0.3$ mm, $\bullet = 1.0$ mm, $\Delta = 1.5$ mm thickness)

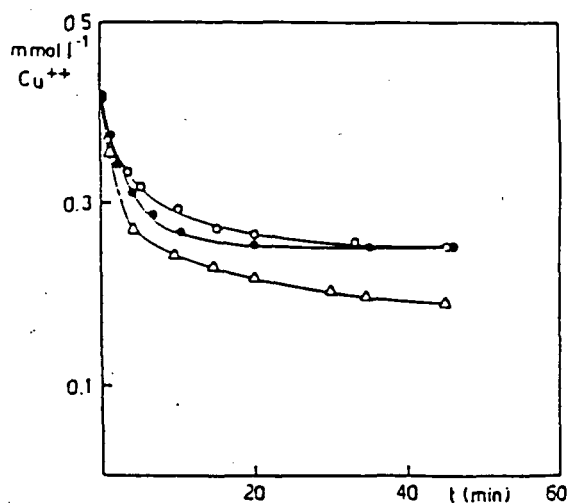


Fig. 6

Decrease of Cu^{++} concentration, due to the binding activity of TA-1 biopolymer, entrapped by method (b) in cellulose triacetate membrane by increasing their thickness. Concentration values of Cu^{++} , as a function of time, obtained by electrochemical measurements, (using an ion-selective electrode). ($\circ = 0.3$ mm, $\bullet = 1.0$ mm, $\Delta = 1.5$ mm thickness)

To ensure that all the copper was onto the polymer-membrane complex, we performed tests as above described, but using TAC membranes without polyelectrolyte and checked that, by this way, no copper bound was practically found in the membrane. Finally, in Table 1, we report the quantitative data referring to adsorption and release of cupric ion in the aqueous solution from different TAC membranes, containing the studied polyelectrolytes, obtained by means of copper ion-selective electrode and by absorption spectrophotometry.

Table 1 - Comparison of absorption and release of Cu^{++} from cellulose triacetate membranes containing two different polyelectrolytes.

thickness (mm)	MAEVE polyelectrolyte				TA-1 polyelectrolyte		
	membrane by method (a)	membrane by method (b)			membrane by method (b)		
	1	0.3	1	1.5	0.3	1	1.5
absorbed Cu^{++} ($\mu\text{mol cm}^{-2}$)	11	0.21	0.21	0.29	0.09	0.19	0.49
released Cu^{++} ($\mu\text{mol cm}^{-2}$)	7.8	0.15	0.15	0.11	0.09	0.15	0.11
% recovery of Cu^{++}	70.9	71.4	71.4	37.9	100	78.9	18.4

Figs. 7 and 8 show the adsorption process of Cu^{++} ion, on a TAC membrane containing the polyelectrolyte MAEVE, prepared by the method (a) and cut into little pieces, placed in a chromatographic column and the following elution process of Cu^{++} retained in column, by means of an EDTA solution.

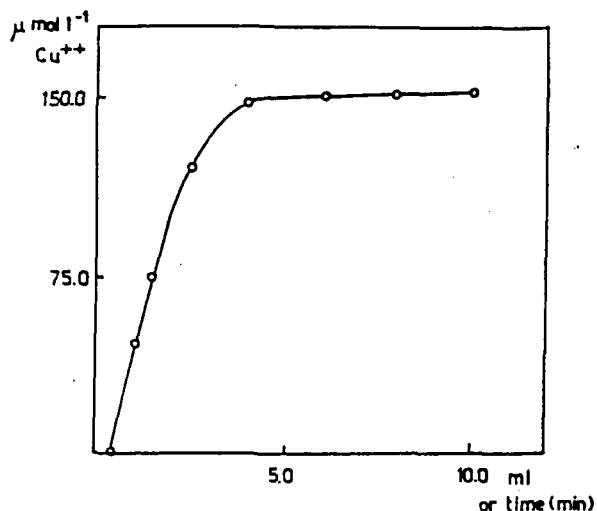


Fig. 7

Cu^{++} concentration trend, in the effluent solution of the chromatographic column, due to the binding activity of MAEVE synthetic polymer insolubilized in cellulose triacetate membrane by method (a). Concentration values of Cu^{++} , as a function of time, obtained by atomic absorption measurements. Experiments carried out using a glass column, filled with small particles of cellulose triacetate membrane. Flow conditions (1 ml min^{-1}).

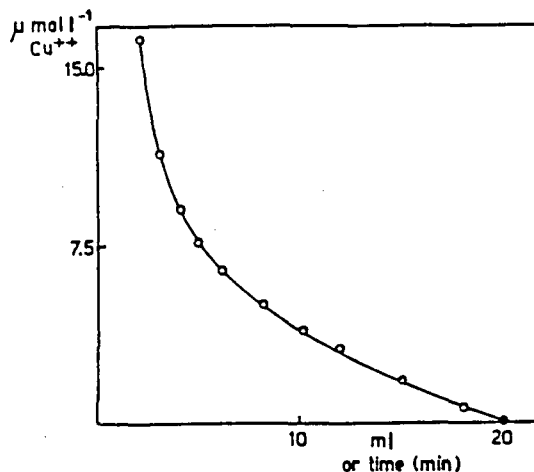


Fig. 8

Recovery, from chromatographic column of Cu^{++} , bound to MAEVE polymer, insolubilized in cellulose triacetate with method (a), by eluting the column with $10^{-2} \text{ mol l}^{-1}$ solution of EDTA. Flow conditions (1 ml min^{-1})

DISCUSSION

As it is possible to observe, both from the reported results of Table 1 and from the comparison of the curves reported in figs. 8 and 9, the efficiency of the adsorption process of Cu^{++} ions, on the TAC membranes containing the polyelectrolyte, introduced by its addition to the initial viscose (procedure (a)), is higher than the efficiency observed when the polyelectrolyte is let to diffuse into the TAC membrane (procedure (b)). This proves that the addition of the polymer to the initial viscose does not change markedly the chelating properties of the polymer. Obviously this conclusion applies only when the synthetic polyelectrolyte MAEVE is used. In contrast, when natural TA-1 polymer is used, the only method for its immobilization is by diffusion into the TAC membrane, due to the high insolubility of the polymer in the formic acid and TAC viscose. In addition, it can be observed from Table 1 and from the comparison of the curves of figs. 5 and 6, that, by means of the same immobilization method (i.e. diffusion), the membranes containing the synthetic polyelectrolyte are more efficient than those ones containing the natural one. Concerning the relationship between thickness and efficiency of the TAC membranes obtained by the diffusion method, the results presented in Table 1 and figs. 5 and 6, show that, on increasing the thickness, the efficiency also increases, especially if the polyelectrolyte MAEVE

is used. Nevertheless it can be observed also that, if the thickness of the membrane is increased (for instance up to 1.5mm), the recovery of cupric ions retained in membrane, by means of the EDTA solutions, becomes more problematic (for instance see the low percentages of the recoveries of Cu^{++} obtained with these membranes, in comparison with the membranes of lower thickness (0.3-1 mm). Finally the only advantage of TAC membranes being incorporated into a stationary phase of a chromatographic column, rather than as a heterogeneous phase in a cell under magnetic stirring, concerns the operating times of the cupric ion adsorption and elution processes. Indeed, by operating in the column, after 4 minutes, more than 90 % of the total cupric ion content is retained in column, against a value of 70 %, in the thermostated stirred cell. Also the elution process with EDTA of Cu^{++} ions retained on the membrane, is faster in column, than in batch conditions (about 0.5 hrs vs 48 hrs).

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