



Improvement of the adsorption of quaternary ammonium on polypropylene affinity membrane through the control of its surface properties



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ABSTRACT

Polypropylene fiber meshes were plasma-treated in order to attach new chemical functions corresponding to acidic or basic groups without altering the roughness of such thin material. An almost complete wettability of these plasma-treated materials is obtained. Because of the plasma-grafting of acid or amino moieties, such surface treatment allows increasing the adsorption rate of quaternary ammonium molecule like Aliquat 336. This increase was explained by specific interactions of ammonium head of the Aliquat 336 and hydrophilic group of plasma-treated PP, followed by the adsorption of a further layer of Aliquat 336 through hydrophobic interactions of its hydrocarbon chain. These interactions between the carrier and the polymeric surface were characterized leading to physisorption mechanism. Such new material could be applied to the extraction process since no evidence of aging was given.

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1. Introduction

The occurrence of drug residues in the aquatic environment emerged as a matter of public concern since conventional sewage treatment plants do not fully degrade residues of pharmaceuticals. Thus, developing sensitive methods for extracting of bioactive molecules has reached significant proportions. With such goal, affinity membranes have been developed as potentially valuable technology for the separation and the concentration of charged or neutral species. Among several membranes types, the solid membranes such as the polymer inclusion membranes (PIM) [1,2] were shown to be efficient because of their higher stability in separation processes. Such affinity membranes involve the complexing agents, referenced as ion carriers able to quench species onto the membrane phase. However, this separation route needs to prepare a specific membrane, to control its thickness and to incorporate a large amount of the targeting molecules [3]. However, Fontas et al. [4] show a progressive reorganization of the polymeric material because of the enhancement of the preferential solvent interactions between the carrier and the plasticizer.

Therefore, studies on other membrane configurations have received more attention. Due to their high packing density and their high surface area per unit module volume, the hollow fibers have found application in various membrane based extraction processes, such as supported

liquid membrane, emulsion liquid membrane,[5]. The nature of the microporous membrane can be hydrophobic or hydrophilic, which means that the pores of the membrane are organic or aqueous-filled, respectively. Most of hydrophobic membranes are composed of polymeric materials thermally stable and resistant to a wide range of organic or inorganic agents, such as polyethylene (PET), polypropylene (PP) and polyvinylidene fluoride (PVDF). Since the specific surface area of the membrane is one of the most important factors for its efficiency, materials composed of meshes should have same separation behavior and will be prospected here.

Complexing agents such as aliphatic amines have been widely employed as carriers. In general, the efficiency of the amine decreases in the order quaternary > tertiary > secondary > primary under the same experimental conditions. Aliquat 336, a water insoluble quaternary ammonium salt composed of a large organic cation associated with a chloride, acts as an anionic (basic) liquid exchanger that has been used for the recovery of metal ions [1,6–8], amino acids [9,10], enzymes [10,11], peptides [12], drugs [13–15]. The results obtained in those experiments fully demonstrated the usefulness of the supported liquid membrane extraction. However, the efficiency of such extraction is highly dependent on the filling and emptying kinetics of carrier solutions in or from the membrane cavities.

The objective of this work is to develop PP fiber meshes as membrane and to study the impregnation Aliquat, the Aliquat-coated PP meshes then allowing the penicillin extraction. Such material is a bulky one, without any porosity but present a high specific surface

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area. Since PP is hydrophobic polymer and Aliquat a more polar molecule, PP fibers were plasma-treated in order to enhance the interfacial affinity and consequently, to attach polar chemical groups without any PP physical alteration.

2. Experimental

2.1. Materials

2.1.1. Polypropylene plates and fibers

Before plasma-treatment, the polypropylene plates (Exxon-Mobil) or fibers (so-called Aquatextil, Cailleton) were cleaned in a solution of ethanol stirred under ultrasound for 15 min. Then, samples were then dried in a laminar flow hood. Plates were only plasma-treated in order to improve the wettability measurement.

Triocetyltrimethylammonium chloride, so-called Aliquat 336 (Aldrich ref 205 6130) and other reagents were used without purification.

2.2. Cold plasma modification

Experiments were performed in a RF plasma reactor. The system is pumped with a turbomolecular pump with the nominal pumping speed of 900 m³/h backed with a two-stage oil rotary pump with a pumping speed of 25 m³/h. The discharge chamber is made of aluminum and has a volume of approximately 9 L. Commercially available, highly purified CO₂ (purity > 99.995 %, Air liquide), N₂ and H₂ (purity - 99.999 %, Air liquide) or CF₄ gas (purity > 99.999 %, Messer) is leaked into the discharge chamber through a precise flow controller at variable flows. The powered electrode is connected to a matching network that is in turn connected to a 13.56 MHz RF generator. The output power of the RF generator is adjustable up to 120 W. Samples (plates or fibers) are mounted on the bottom of the discharge chamber. With such apparatus, the pressure and flow parameters are bound together. With used flow, the total pressure is comprised between 1.5 and 3.0 10⁻⁴ mbar.

2.3. Adsorption protocol

The adsorption kinetics was studied with specific conditions. 50 mg of Aliquat 336 (m_{aliquat} , $M_{\text{aliquat}} = 404.16$ g/mol) were dissolved in 25 mL of chloroform (V , $[C_i] = 0.01$ mol/L), under stirring and controlled temperature (24 ± 1 °C). Then, 50 mg of virgin or plasma treated PP fibers (m_s) were added and then titrated as follows.

After a certain duration (t), the modified fibers are dipped into 10 mL of glacial acetic acid solution then 10 mL of mercury acetate (Aldrich ref 83352) were added. The solution was stirred during 10 min and titrated with perchloric acid solution (0.1 N in glacial acetic acid) in the presence of few added droplets of hexamethylpararosaniline chloride, so-called crystal violet (Aldrich ref C3886). The adsorbed quantity of Aliquat (Q , mmol/g) was then calculated as:

$$Q = \frac{(C_i - C_f)V}{m_s * M_{\text{aliquat}}}$$

with C_f , the remained concentration of Aliquat in the solution and the fiber mass.

When varying one of the adsorption studies, the others are kept constant as follows:

- $0.01 \leq [C_i] \leq 0.8$ mol/L; $m_{\text{aliquat}} = 50$ mg, $V = 25$ mL, $T = 24 \pm 1$ °C, $m_s = 50$ mg, $t = 60$ min.
- $5^\circ \leq T \leq 45^\circ$; $[C_i] = 0.01$ mol/L, $V = 25$ mL, $m_{\text{aliquat}} = 50$ mg, $m_s = 50$ mg, $t = 60$ min.

At least, three experiments were onto PP or modified-PP fibers.

2.4. Specific surface measurement of PP fibers

The specific surface measure of PP fibers was run thanks to the study of dye adsorption. The used dye, hexamethylpararosaniline chloride, so-called crystal violet (Aldrich ref C3886) was dissolved in water. The specific surface is calculated from:

$$S = Y * N * A$$

with S , the specific area (m²/g); Y the concentration of adsorbed dye (mol/g); N , Avogadro number ($6.023 * 10^{23}$ molecules/mol) and A , the surface layered by one dye molecule (50 \AA^2). More informations were given in supplementary data files.

2.5. Wettability measurement

The contact angle was measured with ultra pure milliQ water, diiodomethane and formamide drops (3 μ L). Several drops were put on a sample and the contact angle was measured with a goniometer (Ramé Hart Inc). The resolution of the device is around 1°. The surface energy of the samples was calculated from the contact angle measurements of the three different liquids using the Fowkes and Owens–Wendt method:

$$\begin{aligned} \gamma_l(1 + \cos \theta) &= 2(\gamma_s^d \gamma_l^d)^{1/2} \quad \text{and} \quad \gamma_l(1 + \cos \theta) \\ &= 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^{nd} \gamma_l^{nd})^{1/2} \end{aligned}$$

where γ stands for surface energy, θ for contact angle and the indexes s and l indicate the solid and liquid respectively. The exponents d and nd present dispersive and polar components of the surface energy. The surface energies of different liquids are gathered as followed:

Water :	$\gamma_l = 72.8$ mJ/m ²	$\gamma_l^d = 21.8$ mJ/m ²	$\gamma_l^{nd} = 51.0$ mJ/m ²
Diiodomethane :	$\gamma_l = 50.8$ mJ/m ²	$\gamma_l^d = 49.5$ mJ/m ²	$\gamma_l^{nd} = 26.4$ mJ/m ²
Glycerol :	$\gamma_l = 63.4$ mJ/m ²	$\gamma_l^d = 37.0$ mJ/m ²	$\gamma_l^{nd} = 26.4$ mJ/m ²

2.6. Scanning Electronic Microscopy (SEM)

The SEM images were obtained after gold metallization thanks to the scanning electron microscope (Hitachi type 2300).

3. Results and discussion

The purpose of this work is the study of the enhancement of adsorption onto polyolefin meshes. In order to achieve such a goal, polypropylene fibers were plasma-treated for increasing their affinity towards ammonium derivative compound dissolved in organic medium (chloroform). Such molecule, here the Aliquat 336 is mainly polar, even if substituted with long aliphatic chains.

3.1. Characterization of the plasma-treated polypropylene

Selected plasma treatments only modify the surface of material without altering its bulk properties, this feature is of course important when the material is formed of fibers. Such treatments also allow the attachment of new hydrophilic chemical groups, therefore having a greater affinity towards ammonium such as Aliquat molecule. CO₂, N₂ or N₂/H₂ plasmas respectively lead to the formation of oxidized groups (hydroxyl, carbonyl, acid...), amines in proportions dependent on the operating parameters [16]. Since, this type of treatment is fully described in the literature [17], the hydrophilic character of plasma-treated polypropylene is here only described as the dependence of water contact angle on energy dissipated by the phase plasma, as defined by Yasuda [18] (Fig. 1). Thus, when the W/FM increases beyond 0.3 W.sccm⁻¹.g⁻¹, the water contact angle decreases to an almost

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