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## Journal of Membrane Science

journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)

# A step forward to a more efficient wastewater treatment by membrane surface modification via polymerizable bicontinuous microemulsion



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## ARTICLE INFO

## Article history:

Received 26 November 2014

Received in revised form

10 February 2015

Accepted 14 February 2015

Available online 4 March 2015

## Keywords:

Polymerizable surfactants  
 Polymerizable bicontinuous  
 microemulsions  
 Surface modification  
 Water treatment  
 Membranes

## ABSTRACT

An innovative hydrophilic and anti-fouling coating material for application in membrane technology for wastewater treatment has been developed by polymerization of a polymerizable bicontinuous microemulsion (PBM) and used for surface modification of a commercial flat polyethersulfone (PES) membrane. The novel nanostructured coating has been produced using acryloyloxyundecyltriethylammonium bromide (AUTEAB) as a co-polymerizable surfactant, obtained through a synthetic method characterized by a lower cost and a higher reproducibility compared to other known polymerizable surfactants. The novel composite membranes have been characterized and compared with the uncoated PES membranes. Coated membranes resulted in a smoother surface and a higher hydrophilicity with respect to the uncoated ones, and showed a particular nano-size channel-like morphology making them highly resistant to the fouling phenomenon. The covalent anchorage of the surfactant on the membrane surface ensured the embedment of the molecule in the polymeric matrix avoiding its leaching and also leading the coated membranes to have significant antimicrobial activity, which is very important for reducing the biofouling phenomenon.

All these aspects make the tailored coating material an ideal and efficient coating for modifications of commercial membrane surfaces, to be used in membrane processes in wastewater treatment.

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## 1. Introduction

Water is essential for the life of all living organisms and its preservation and responsible use is one of the global challenges that humanity will face in the next future. The United Nations estimated that by 2025 two-thirds of humanity will have to cope with the problem of water scarcity turning this precious resource into the blue gold of the third millennium.

The question of water scarcity is directly linked to the evidence that the world's water resources are not unlimited and the increasing demand of water due to urbanization and population growth together with global climate changes have a very strong effect on water availability [1].

The increasing worldwide demand for clean water is pushing more and more the market to find new strategies and innovative alternatives that can be applied for water reuse. The development of efficient wastewater treatment technologies can, thus, give complete answers to many of the problems related to water purification. In particular, membrane processes devoted to wastewater treatment are gaining more and more attention thanks to their high efficiency, energy saving systems, easy scale-up and flexibility.

In this study, a novel surface modification method based on polymerizable bicontinuous microemulsions (PBMs) was developed and proposed for a potential application in wastewater treatment.

A particularly interesting feature of microemulsions lies in the possibility to polymerize these bi-phasic systems by employing, between the components of the microemulsion, suitable monomers, usually dispersed in the oil channels. The surfactant used to stabilize the microemulsion may be either non-polymerizable or

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polymerizable; clearly, in the latter case, the polymerizable surfactant also acts as a co-monomer in the polymerization process. The thus obtained microemulsions are called polymerizable bicontinuous microemulsions (PBMs). Their polymerization produces transparent porous polymeric micro- and nanostructured solid materials [2–4], which have gained increasing attention during the last years due to their possible application in catalysis, as drug delivery systems and, last but not least, as coating materials in separation processes through membrane functionalization [5]. In fact, the polymerization of the monomers present in the oil channels leads to the formation of a solid polymer matrix, which can be used as coating for surface modification of known and, possibly, even of commercial membranes, with the aim of improving their performances without the need for developing new performing materials. PBMs have been widely investigated and employed, for instance, as coating material for hollow fiber membranes [6]. On the other hand, Gan et al. studied the polymerization of methyl methacrylate (MMA) using different types of polymerizable and non-polymerizable surfactants [2,3,7,8]. In 1996 Chieng et al. [9], produced porous polymeric membranes using the anionic surfactant sodium dodecyl sulfate (SDS) and the cationic surfactant dodecyltrimethylammonium bromide (DTAB). In another approach, a double-chained surfactant, didodecyl dimethylammonium bromide (DDAB) was used for the polymerization of MMA and silica gels [10,11]. In these works, the optimal polymerization conditions (i.e. temperature and microemulsion composition) have been identified and discussed for tailoring the pore size of the PBM membrane produced. However, the above-mentioned PBMs have not been ever applied for the surface modification of flat sheet membranes, and not designed for a possible application in the field of wastewater treatment.

Surface modification techniques are, in particular, aimed at reducing membrane fouling (caused by the accumulation of organic substances on membrane surface) or biofouling (caused by accumulation of biomolecules or even microorganisms on membrane surface) by acting on parameters strongly related to this phenomena, such as membrane roughness, hydrophilicity, and membrane charge [12,13].

Fouling and biofouling are, in fact, major drawbacks in membrane operations, which cause a rapid decline in membrane performances and in membrane durability [14–16]. Many strategies have been applied so far in order to control the fouling, such as: reducing the flux, increasing the aeration rate, back-flushing the membrane, using physical or chemical cleanings [17]. However, the possibility to reduce fouling and/or biofouling by preparing membranes with intrinsic anti-fouling properties via surface membrane modification, remains the most attractive, but still challenging, approach. Improvements of the antifouling properties were obtained by Shao et al. [18] by the surface modification of polyvinylidene fluoride (PVDF) membranes by means of the self-polymerization of polydopamine acting as “bio-glu” for the entrapment of hydrophilic TiO<sub>2</sub> nanoparticles. The hydrophilicity and the water flux of the modified membranes were increased. The anti-fouling properties of modified membranes were proved by using bovine serum albumin (BSA) protein and attributed to the increased hydrophilicity of the membrane surface. A flux recovery of more than 90% after BSA filtration was obtained.

Cheng et al. [19] worked on the surface modification of PES membranes by interfacial polymerization of amino-functional polyethylene glycol (PEG) and trimesoyl chloride. The higher hydrophilic moiety, the positive surface charge and larger pore size were the main responsible of the improved performances in terms of salt rejection and water permeability. Furthermore, the properties exhibited by the modified membranes, may also contribute to an important anti-fouling activity.

In the present work, a novel PBM has been prepared, polymerized, and used as a coating material for surface modification of commercially available PES membranes. The coating obtained here, in particular, has been realized by employing the polymerizable surfactant acryloyloxyundecyltriethylammonium bromide (AUTEAB), obtained by a simple and particularly efficient synthetic strategy. AUTEAB has been used as an expedient alternative to the similar surfactant acryloyloxyundecyltrimethylammonium bromide (AUTMAB), which has already been used in the literature for other applications [2,4,20]. As a matter of fact, the synthesis of AUTEAB, reported in the present work, allows for a much higher yield and reproducibility (and therefore to significantly lower production costs making it possible to scale-up) when compared to those already known such as AUTMAB or other polymerizable surfactants. In addition, the novel formulation of the PBM developed in this work, which employs AUTEAB in conjunction with the other components of the microemulsion, has led to a coating with significant anti-fouling and anti-biofouling properties, connected with its hydrophilic character and to the antimicrobial activity of the covalently bonded cationic surfactant [21]. These properties have been verified by the considerably improved performances of commercial PES membranes after their surface modification with this newly developed nanostructured interconnected channels coating.

Improved hydrophilicity, smoother surface, channel-like structure and antimicrobial activity are the main benefits exhibited by PBM membranes making them ideal candidates to be applied in wastewater treatment processes, such as membrane bioreactors (MBRs), where membranes with anti-fouling and anti-biofouling properties are highly desired.

## 2. Experimental

### 2.1. General

The organic compounds synthesized in this work were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and FT-IR spectroscopies. IR data were taken with Perkin Elmer Paragon 1000 PC FT-IR spectrometer. NMR spectra were performed at room temperature in *d*<sub>6</sub>-DMSO solutions with TMS as the internal standard, using a Bruker DPX Avance 500 spectrometer. Chemical shifts ( $\delta$ ) and coupling constants (*J*) are given in ppm and MHz, respectively.

### 2.2. Synthesis of the surfactant acryloyloxyundecyltriethylammonium bromide (AUTEAB)

The synthesis of a pure polymerizable surfactant is a key step in the formation of microporous materials from PBMs. All the chemicals used for the AUTEAB synthesis were purchased from Sigma-Aldrich with purity higher than 98% (analytical grade) and were used as such without further purification. AUTEAB has been synthesized in 59% overall yield starting from commercially available 11-bromoundecanol by a two-step procedure involving esterification of 11-bromoundecanol with acryloyl chloride to give 11-bromoundecyl acrylate followed by the reaction of the latter with Et<sub>3</sub>N (Scheme 1), as detailed below.

#### 2.2.1. 1st step: esterification of 11-bromoundecanol with acryloyl chloride to give 11-bromoundecyl acrylate

To a stirred solution of 11-bromoundecanol (5.0 g, 20 mmol) in anhydrous MeCN (110 mL), maintained at room temperature in a Schlenk flask, was added 2,6-di-*tert*-butyl-4-methylphenol (30 mg, 0.14 mmol; used as radical inhibitor), followed by acryloyl chloride (dropwise; 2.26 g, 25 mmol), and activated molecular sieves 3 Å (4.3 g). The flask was sealed, and the mixture allowed to stir at 90 °C for 24 h. After cooling, the mixture was filtered in

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