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Ancillary effects of surfactants on filtration of low molecular weight contaminants through cellulose nitrate membrane filters

Aybike N. Olcay [a], Mehmet Polat [a], Hurriyet Polat [b],∗

[a] Izmir Institute of Technology, Department of Chemical Engineering, Izmir, Turkey
[b] Izmir Institute of Technology, Department of Chemistry, Izmir, Turkey

HIGHLIGHTS

- Membrane filtration is commonly employed for removal of LMWCs.
- Surfactant molecules are invariably present in such waste waters.
- MB removal with a cellulosic membrane was tested in the presence of surfactants.
- Membrane interactions with contaminant and surfactant influence removal strongly.

GRAPHICAL ABSTRACT
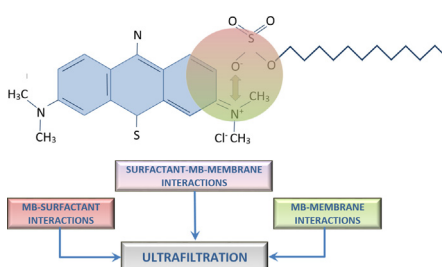
ARTICLE INFO

ABSTRACT

Removal of contaminants with low molecular weight (<800 Dalton) requires the use of advanced separation techniques such as ultrafiltration (UF) or micellar enhanced ultrafiltration (MEUF). However, surface active agents invariably co-exist in waste waters along with these contaminants or they may be added intentionally as part of the separation process as in the case of MEUF. Though it is quite likely that both the filter medium and the contaminants would interact with the surfactant molecules or their micelles, there is not sufficient emphasis in the literature on the concomitant aspects of such interactions.

The ancillary effects created by anionic (sodium dodecyl sulfate, SDS), cationic (hexadecyltrimethyl ammonium bromide, CTAB) and non-ionic (ethoxylated octylphenol, TX-100) surfactants on the mechanism and efficiency of the filtration process were investigated in this study. Methylene blue (MB) and cellulose nitrate membrane (CNM) filters were employed as model retentate and the separation medium. A combination of surface tension, contact angle and charge measurements demonstrated that the addition of surfactants had a remarkable effect on the filtration outcome. The effect depended on both the type and concentration of the surfactant and was manifested mainly through the creation of MB-surfactant entities which acted differently than the MB alone; but more importantly, through the interactions of the surfactant molecules/micelles and the MB-surfactant pairs with the separation membrane.

1. Introduction

Low molecular weight contaminants (LMWCs) with molecular weights less than 800 Dalton originate from metal-plating, textile, circuit-board manufacturing, photo-processing, petroleum and mining industries and pose a serious environmental concern (Table 1) [1–7].

The problems with LMWCs are compounded due to removal problems with classical techniques such as chemical oxidation, coagulation, biodegradation, adsorption and extraction owing to smaller molecular size, high solubility and higher dilution rates. The membrane separation is one of the effective methods for removal

∗ Corresponding author. Fax: +90 232 7507509.
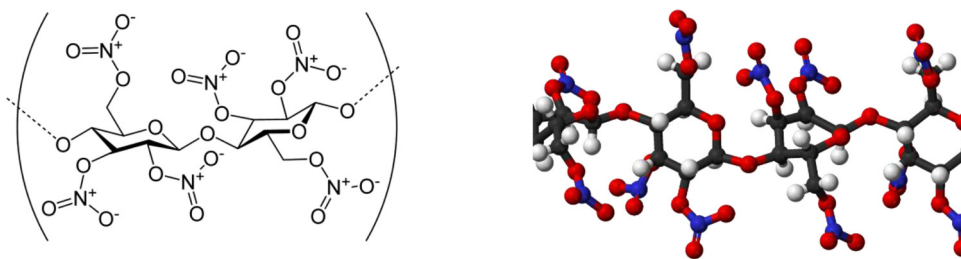E-mail address: hurriyetpolat@iyte.edu.tr (H. Polat).

Fig. 1. The cellulose nitrate membrane (CNM) structure.

Table 1
Examples of LMWCs.

LMWCs	Molecular weight (D)
Polycyclic (2 or 3 fused rings) aromatic hydrocarbons (PAHs)	152–178
Acid anhydrides	100–218
Methylene blue (MB)	374
Cyclonite	222
Atrazine	216
2,4-Dichlorophenol	163
Eosin dye	692

of such contaminants from the wastewater. Ultrafiltration (UF) and micellar enhanced ultrafiltration (MEUF) which fall in this category have been studied extensively to improve both the selectivity and the flux in the removal of these substances [7–17].

Surface active agents which are invariably co-present with the LMWCs in contaminated waters, or added intentionally as part of the ultrafiltration process, may interfere with separation. Though surfactant-contaminant interactions have been addressed to a degree in the literature [7–9], there is not sufficient emphasis on the interaction of the surfactant entities with the membrane material. Moreover, the possible interaction of the membrane with the contaminant itself and with the contaminant-surfactant complexes further compounds the problem. Therefore, a systematic characterization of the system with respect to the magnitude and effect of these interactions is extremely important for properly interpreting both the mechanism and success of separation in such advanced removal technologies.

This work quantitatively demonstrates that interactions of various anionic, cationic and non-ionic surface active agents with a model contaminant, Methylene blue (MB), and with the separation medium, cellulose nitrate membrane, (CNM).

2. Experimental

2.1. Materials

Selected anionic (sodium dodecyl sulfate, SDS), cationic (hexadecyl trimethylammonium bromide, CTAB) and non-ionic (ethoxyleted octylphenol, TX-100) surface active agents and a model contaminant (methylene blue, MB) were employed in the experimental studies (Table 2). All chemicals were reagent grade and obtained from Sigma–Aldrich, United States.

The choice of the separation medium was negatively charged cellulose nitrate membrane (CNM) filters. They were used in two distinct pore sizes of 0.2 and 0.45 μm and were supplied by Sartorius Stedim Biotech, Germany. Cellulose nitrate (nitrocellulose) is produced by treating cellulose with nitric acid. Each glucose unit in the cellulose polymer is esterified with three nitrate groups, and these nitrate groups are responsible for both the negative charge of nitrocellulose at neutral pH and the unusual flammability of dry nitrocellulose (Fig. 1). The negative charge on the membrane sug-
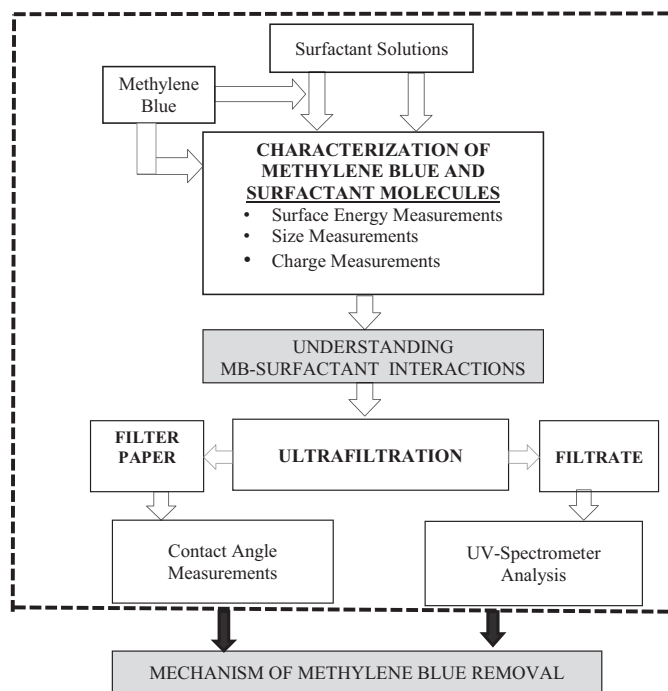

Fig. 2. The methodology employed in this study.

gests that electrostatic interaction may play a significant role in the capture of the contaminants, though it has been stated that hydrophobic interactions also play a role in the capture of proteins of these membranes [18].

2.2. Methods

The general methodology followed in this work is presented schematically in (Fig. 2). Surface energy measurements were conducted with a Digital Tensiometer (Kruss K10ST) employing the Du-Noüy Ring method using solutions of SDS, TX-100 and CTAB at concentrations from 10^{-2} to 10^{-6} M. Zeta potential measurements were carried out with SDS, CTAB and TX-100 solutions in the presence of 10^{-5} M ($\sim$2 ppm) MB by Laser Doppler Velocimetry (LDV) (Malvern Zeta Sizer Nano ZS). Particle size distribution (PSD) measurements were carried out with the solutions of the same surfactants using Dynamic Light Scattering (DLS) mode of the Zeta Sizer; however, only TX-100 solutions at 10^{-2} M resulted in meaningful PSDs. UV/Vis spectroscopy (PerkinElmer Lambda 45) was used to determine MB concentrations in solutions without and with surfactants of varying strength. Ultrafiltration experiments with the MB-surfactant solutions were carried out at surfactant concentrations from 10^{-2} to 10^{-6} M employing the CNM filters with pore sizes of 0.2 and 0.45 μm.