Characterization of Micellar Systems for Removal by MEUF of Refractory Organic from Contaminated Groundwater

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Introduction

One of the severe problems challenging management of aquifers, is their contamination by small molecular weight organic compounds. Rehabilitation of or recovery from such aquifers requires developing techniques for removing the contaminants either in-situ or by pump and treat schemes. One of the methods that has been extensively studied is micellar enhanced ultrafiltration (MEUF) [1-2]. There are a number of aquifers in Israel that are challenged by this problem and may be amenable to treatment by MEUF. Tribromo-neopentyl alcohol (TBNPA), a biorefractory compound, was found at relatively high levels in groundwater samples in a number of test wells in the Negev. The present study examined the feasibility of removing it by MEUF, based on an evaluation of its distribution coefficient between the micellar and aqueous phases:

\[ K = \frac{O_w}{S_m O_w}, \text{ in units of M}^{-1} \]

where O refers to organic solubilizate and S refers to surfactant molar concentrations relative to the aqueous solution volume. The subscripts m and w refer to the micellar and aqueous phases respectively.

Experimental

The distribution coefficients were determined by micellar enhanced ultrafiltration using centrifuge tubes [3] equipped with regenerated cellulose membrane of 10 kDa MWCO (Amicon Centriprep YM membranes in 10 ml centrifuge tubes) and operating the centrifuge at 2500 rpm at 15 minutes. In the MEUF experiments, the permeate will contain only monomeric surfactant at a concentration \( S_w \) and non-solubilized organic in the aqueous phase at a concentration \( O_w \). The concentration of the monomeric surfactant \( S_w \) should be that of the critical micelle concentration (cmc). If the surfactant has a low cmc which is the case for the nonionic surfactants used in this work, then \( S_m \sim S_{tot} \). Preliminary concentration experiments in a stirred cell (Amicon 8200) equipped with regenerated cellulose (Hoechst C-10) showed that permeate composition was constant in going from VCF=1 to VCF=8. This supported the use of the UF in centrifugation to determine the distribution coefficient. Solid phase matrix extraction of the TBNPA from a micellar solution was used as an alternative method to determine the distribution coefficient, since only free TBNPA can absorb in the solid phase matrix.

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Analyses of the organic solubilizate in the permeate were determined by GC. Sample preparation was carried out by solid phase matrix extraction (SPME) and electron capture was used as the detection method.

Samples of 10 g/L of Brij 58 (C16EO20) and 1 g/L of Brij 58 in presence of 100 mg/L of TBNPA concentrated 10 fold by centrifugal UF were studied by Cryo-TEM to determine effect of high solubilizate loading on micelle size and shape.

Results

The distribution coefficient for the most effective surfactant (Brij 58) was ~500 M\(^{-1}\) and was fairly constant over a wide range of loadings (mole fraction of TBNPA in micelle from 0.07-0.45). It was also found that the distribution coefficient was not significantly affected by the presence of 1% NaCl. The distribution coefficient was somewhat higher in the presence of toluene leading to speculation that toluene loading causes expansion of the micelle.

Distribution coefficients determined by SPME were significantly lower (~380 M\(^{-1}\)) than when centrifugal UF was used. The difference is ascribed to concentration polarization of the micelles in the centrifugal UF experiments. Therefore the SPME–based distribution coefficient is the correct one and centrifugal UF-based distribution coefficient is an apparent value.

Cryo-TEM shows that the Brij 58 micelle size (5-7 nm in absence of TBNPA) became less uniform with the appearance of some micelles with much larger diameters (>15 nm) upon loading with TBNPA, possibly due to mechanical action in the centrifugal UF process.

References