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Characterization of ultrafiltration membranes fouled by quantum dots by confocal laser scanning microscopy

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ABSTRACT

The extensive applications of engineered nanomaterials (ENMs) can result in their release into waters. Membrane processes have great potential in reducing ENMs release. In that case, the issues of particular concern are membrane fouling caused by ENMs during separation processes. The objective of the present study is to improve the understanding of how ENMs are retained by membranes. An innovative methodology using confocal laser scanning microscopy (CSLM) is developed to locate fluorescent CdTe quantum dots (QDs) in different depths of fouled ultrafiltration membranes. With the help of image analysis software, both qualitative and quantitative information about the distribution of QDs in membranes are obtained. For low molecular weight cut off (MWCO) membranes (1, 5 and 10 kDa), QDs (sizes from 1 to 5 nm) distributed mainly around surfaces or on top of membranes, accompanied with near 100% retention regardless of transmembrane pressure. As membrane MWCO increased (30 and 100 kDa), more QDs could pass through membranes accompanied with decreasing retention efficiencies and the occurrence of QDs was usually in deeper positions of membranes. Distribution results were in agreement with fouling analysis which demonstrated that standard blocking (internal fouling) and/or cake models (external fouling) frequently occurred during filtrations of QDs.

1. Introduction

The rapid development of nanotechnology allows engineered nanomaterials (ENMs) to be widely used in various industrial and commercial products. However, the extensive applications of ENMs will inevitably result in their release into waters, and thereby lead to the exposure of living organisms, as well as humans (e.g. by drinking water consumption and food chain transfer) [1,2]. More and more researchers are concerned about the occurrence, behavior and fate of these emerging contaminants in water environment, as well as their removal/separation technologies.

The use of membrane filtration processes in the study of ENMs is interesting and promising. Membrane filtrations cannot only be used as fractionation techniques prior to further analysis, but also used to remove or separate ENMs from suspensions [2]. Particularly membrane processes are being increasingly used in water treatment processes, such as the extensive applications of ultrafiltration (UF) membranes in drinking water treatment. However, there is still a large knowledge gap on the efficiencies of membrane filtrations in removing ENMs [3,4]. It is urgently needed to investigate the behaviors of ENMs during filtration processes: retention, adsorption onto membrane surfaces, entrapment within membrane pores or passage through membranes, and their impact on membrane fouling or on backwash efficiency.

The separation of ENMs from suspensions through membrane filtration processes are usually challenged by membrane fouling problems [5,6]. Thus, it was decided to study the membrane fouling caused by ENMs, in order to better understand the locations where ENMs are retained (inside membranes or on their surfaces), and to predict the possibility of backwash in removing/reducing membrane fouling. One type of ENMs, the fluorescent semiconductor nanocrystals, also known as quantum dots (QDs), were selected for this study. Because QDs can exhibit size dependent tunable photoluminescence with narrow emission bands, as well as broad absorption spectra [7]. Additionally, QDs are very promising fluorescent markers, due to their good biocompatibility, strong photostability and high quantum yield [8,9].

The fluorescence of QDs can be detected by confocal laser scanning microscopy (CLSM), which is a non-destructive visualization technique without requiring pretreatment of samples. CLSM can provide images at different depths of a 3-dimensional object, and allow the visualization of fouling at membrane surfaces and also inside the porous matrix [10]. To enhance the contrast of

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images, CLSM normally requires that samples are inherently fluorescent or stained with fluorescent reagents. However, the influence of fluorescent dyes on membrane fouling could be significant [11]. The fluorescent properties of QDs allow their application in membrane fouling characterization directly without staining, consequently avoiding the possible influence of fluorescent reagents on the target samples.

Despite that CLSM suffers from low resolution and limited penetration depth, it has been successfully applied in many fields, such as characterization of biofouling in flat sheet membranes [10,12], hollow fiber membranes [13–15] and membrane bioreactor [16]. However, very few studies have been reported on the application of CLSM in membrane fouling characterization during filtration of ENMs, and only qualitative information was obtained [5].

The objective of this study was to apply CLSM to locate fluorescent QDs in different depths of fouled membranes, with the help of image analysis software. Five types of CdTe QDs with different sizes and five UF membranes with different molecular weight cut off (MWCO) were tested in a dead-end filtration system under the conditions of two transmembrane pressures (TMP). The impact of membrane MWCO and TMP on retention and recovery efficiencies of QDs was also assessed. The results obtained improve the understanding of how ENMs are retained by membranes and give more insights into the impact of membrane fouling on separation of ENMs.

2. Materials and methods

2.1. Preparation of QDs suspensions

Hydrophilic CdTe QDs (powders) coated with a proprietary mixture of low-molecular weight thiocarboxylic acid (PlasmaChem GmbH, Germany) were used to prepare suspensions to be filtered. Five types of CdTe QDs with different maximum emission wavelengths at $\lambda = 510 \pm 5$ nm (CdTe-510), $\lambda = 530 \pm 5$ nm (CdTe-530), $\lambda = 580 \pm 5$ nm (CdTe-580), $\lambda = 650 \pm 5$ nm (CdTe-650) and $\lambda = 700 \pm 5$ nm (CdTe-700) were investigated in this study, which correspond to different colors and sizes.

The suspensions were prepared with Milli-Q ultrapure water (pH about 7, conductivity of 0.6 $\mu S\ cm^{-1}$). 50 mL CdTe suspensions were prepared just before the filtration experiments, with a concentration of 100 mg L^{-1}. Among them, 40 mL CdTe were used as feed suspensions to be filtered, and the remaining 10 mL suspensions were used for concentration analysis.

2.2. Characterization of QDs

To obtain information about surface charges of QDs particles in suspensions, zeta potentials were measured using a Zetasizer Nano ZS (Malvern Instruments Ltd., UK). Measurements were performed at 25 °C.

The concentrations of CdTe QDs suspensions before and after filtrations were determined from their fluorescence analyzed by JENWAY 6285 fluorimeter. Relative Fluorescence Units (RFU) were recorded as a function of CdTe concentrations, and these linear relationships were used to determine the QDs concentrations. The excitation wavelength used for RFU analysis was 350 nm, because QDs can be excited with any laser having a wavelength shorter than their maximum emission wavelengths. The emission wavelengths were chosen as a function of nominal maximum emission wavelengths of different CdTe QDs, by changing interference filters in the range from 510 to 700 nm. Since the range of linear relationship between RFU and concentrations was limited, samples with high concentrations which are out of the range of linear relationship, such as retentate and feed, need to be properly diluted before fluorescence analysis.

2.3. Membranes and experimental setup

Five types of flat-sheet disk UF membranes with different MWCO (Ultracel®, Millipore) were evaluated in this study, as shown in Table 1.

Prior to filtration experiments, the membranes were soaked in ultrapure water (Milli-Q) at least 2 h. Then about 50 mL sodium hydroxide (NaOH, pH ≈ 10) solution passed through the membranes, under different pressures according to membrane MWCO. This stage was carried out to remove glycerin on membrane surfaces, which might last about 30 min to more than 1 h. Finally, the membranes were rinsed by ultrapure water (Milli-Q) until the pH of rinsing water being neutral, which was driven by the same pressure as alkaline cleaning procedure. This procedure is in agreement with Millipore requirements.

The filtrations of five QDs were carried out by 1, 5, 10 and 30 kDa membranes at constant TMP of 2 bar, and by 10, 30 and 100 kDa membranes at constant TMP of 0.6 bar. Ultrafiltration experiments were carried out using a lab scale filtration system (Fig. 1), which consists of an air-pressurized feed tank connected to an Amicon 8050 stirred filtration cell (Millipore Corporation, Bedford, MA). The volume and effective filtration area of filtration cell are 50 mL and 13.4 cm^2 respectively. To prevent concentration polarization at the membrane surface, dead-end filtration cell was stirred at 200 rpm using a speed adjustable magnetic stirrer (FB15001, Fisher Scientific). This stirring rate was arbitrary selected as a compromise between the shear stress at the membrane surface and the turbulence in the filtration cell [4]. Filtration was carried out at constant TMP (0.6 and 2 bar). All runs were carried out in a clean white room with air conditioning, where room temperature can be maintained at 20 ± 2 °C. The filtration processes lasted from 3 min (e.g. 100 kDa) to more than

Table 1
Characteristics of membranes (Millipore).

MWCO[a] (kDa)	Code[a]	Estimated pore size[b] (nm)	Permeability ($L\ h^{-1}\ m^{-2}\ bar^{-1}$)[c]	Surface charge at pH 8 (mV)[d]	Other information[a]
1	PLAC	1.58	3.3 ± 0.3	−11.6	– **Membrane material:** regenerated cellulose
5	PLCC	3.72	12.6 ± 1.3	−14.3	– **Support material:** polypropylene nonwoven
10	PLGC	5.37	69 ± 3	−7.5	– **Thickness:** 230 μm
30	PLTK	9.61	335 ± 10	−16.4	
100	PLHK	18.20	607 ± 53	−17.3	

[a] Information supplied by Millipore.
[b] Pore sizes were determined from reference [17].
[c] Membrane permeability was determined using the dead-end filtration apparatus (Amicon 8050, Millipore). Permeate flux was measured as a function of feed pressure from 0.5 to 4 bar. The reported permeability value is the average of results from six separate membrane samples ($T = 20$ °C).
[d] Surface charges were taken from reference [18].