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Retention mechanisms of 1.7 nm ZnS quantum dots and sub-20 nm Au nanoparticles in ultrafiltration membranes

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ABSTRACT

Membrane processes are considered to be a very effective and promising method for drinking water and wastewater treatments. However, particle removal mechanisms have not been fully elucidated due to complex surface interactions between colloids and membranes, especially for very small colloidal particles. In this study, a series of systematic filtration tests for eight different types of membrane filters, having nominal pore sizes from 0.005 to 0.1 μm, against 1.7 nm ZnS quantum dots (QDs) and 5, 10 and 20 nm Au nanoparticles (NPs) was performed to understand their retention mechanisms, including rejection in front of the filter surface and adsorption inside the filter. By comparing rejection, adsorption and recovery, it was found that the predominant retention mechanisms for retaining small NPs varied from filter to filter. For instance, electrostatic repulsion played a significant role for the rejection of NPs, i.e. impeding them entering the membrane pores in most membranes. In comparison, the Nylon membrane had a significant adsorption retention ability for Au NPs due to electrostatic attraction. Besides, it was found that filtration flow rate, or flux, was also an important parameter for the final retention because the enhanced hydrodynamic drag could trigger the detachment of deposited NPs or press NPs flowing through the superficial entrance leading to penetration. Tests of 10 nm Au NP retention using five different membranes with the same nominal pore size of 0.1 μm showed large variation of NP retention efficiencies demonstrating that pore size should not be used as the only criterion for rating filter performance, especially for small NPs. Our results provide not only detailed insights into the retention mechanisms of various membranes but also suggestions on how to select membrane filters for different filtration purposes.

1. Introduction

Engineered nanomaterials have been widely applied in various industries and embedded in commercial products due to their extraordinary size-dependent physicochemical properties. Meanwhile, extra concerns have been raised about their unintentional release into the environment and the consequent exposure by living organisms including humans during manufacturing, usage and disposal [1–3]. Many researchers have conducted studies on the effects of the release of nanoparticles (NPs) into water environments, e.g., surface and ground water [4,5] and are trying to develop effective methods to remove NPs from drinking water and industrial wastewater [6–11]. This removal is inevitable because the engineered nanomaterial usage was estimated to be over a half million tons in 2020 and will keep growing [12,13].

Conventional water treatment techniques, e.g., coagulation, flocculation and sedimentation, are often considered to be inefficient for removing well-stabilized NPs due to their slow settling speed [14]. To improve the water treatment efficiency, microfiltration and ultrafiltration processes using membranes have been adopted widely and considered promising techniques for NP removal [15–19]. Especially, membrane technique is now widely applied in virus filtration for biological products [20–22]. However, the filtration mechanisms for NPs have not been totally elucidated yet. Thus, a thorough understanding of the transport and deposition mechanisms is definitely and urgently

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required [23,24].

High-efficiency ultrafiltration membranes have been tested for various purposes. Homaeigohar et al. [25] tested polyethersulfone electrospun nanofibers for the retention performance against polydisperse polystyrene particles. They found the retention of the nanofiber membranes was strongly dependent on the size distribution of the colloidal particles. For example, particles larger than the pore size were retained by size exclusion while smaller ones penetrated. Au NPs with sizes of 5–50 nm were applied to determine the pore size distribution of virus membranes, dedicated for high retention efficiency of virus [21]. It was found that by adding the surfactant, SDS (sodium dodecyl sulfate), to improve the dispersity of Au colloids, the small Au NPs could determine the pore size distribution well as the retention was mainly by size exclusion. For understanding the removal mechanism of very small NPs, polysulfone (30 ~ 300 kDa) and polyvinylidene difluoride (0.22 μm) membranes were challenged by small Ag NPs with a size range from 2 to 20 nm [26]. It was concluded that adsorption and size exclusion were the major retention mechanisms for those membranes. Poynton et al. [27] employed a 10 kDa cutoff membrane to separate ZnO NPs larger than 2 nm to identify the extent of Zn^{2+} dissolution from ZnO suspensions for a toxicity study. Besides, sub-20 nm rated ceramic and polymeric ultrafiltration membranes were successfully applied for oxidized iron and manganese control in water treatment [28]. Gaborski et al. [29] used ultrathin silicon membranes developed by Striemer et al. [30] to remove sub-30 nm Au NPs. Recently, semiconductor nanocrystals, i.e. quantum dots (QDs), have been used for characterizing membranes due to their size-dependent fluorescent properties and small size [31–33]. Liu and Zhang [31] used Cd-based QDs with nominal sizes of 4 and 8 nm to investigate the rejection capability of sub-10 nm membranes. They found that a 3 nm rated membrane filter was the most retentive, followed by 5 and 10 nm rated membrane filters and during loading experiments, a decreasing retention efficiency was observed at high coverage for all three membranes challenged by 4 nm QDs. Another ultrafiltration study was conducted by Wu et al. [32] using sub-5 nm CdTe QDs to evaluate retention and recovery (sum of retentate and permeate) efficiencies of regenerated cellulose membranes. In their study a stirred cell filtration system was applied that provided valuable insights for understanding rejection and fouling mechanisms. In a follow-up study of Le Hir et al. [34], the important effect of polydispersity was in focus. However, above-mentioned researches were mostly focusing on the size effect, i.e., sieving, as the main retention mechanism.

For small particle to pore diameter ratios less than 1.0 (PPD < 1.0), Chen et al. [33] suggested that the diffusion effect of NPs and the feed concentration are very important. They expected a significantly improved filtration performance, i.e., higher retention efficiency when using low feed concentrations. However, detection limits impeded the investigation of lower NP concentrations where NP mass is extremely small. They emphasized the importance of monitoring earlier stages of filtration, i.e., clean filter efficiency, which determines the fate of membrane fouling mechanisms [23]. In addition to this limitation of their study, the retention mechanisms were not fully elucidated due to the nature of the simple dead-end batch type filtration. Agasanapura et al. [35] investigated electrostatic repulsion as important retention mechanism that prevents NPs from entering membrane pores larger than the NPs. The results showed that retention efficiencies of colloidal, negatively charged silica NPs against negatively charged membranes with cylindrical pores were significantly improved with decreasing ionic strength due to the pronounced electrostatic repulsion between NPs and pores. Ladner et al. [23] tested various membranes with a wide range of pore sizes from 0.002 to 0.2 μm by sub-10 nm Au, Ag and TiO_2 NPs. They observed size exclusion, electrostatic repulsion and adsorption as retention mechanisms and concluded that retention was associated with NP types, e.g., material and zeta potential, but independent of the membrane types, e.g., material and structure.

It is expected that performances of different membranes are based on different interactions resulting from material properties, membrane structure and process parameters/filtration conditions, e.g., flux. To shed light on this complex interplay, in this study, rejection, adsorption and recovery efficiencies of eight different membranes with pore sizes ranging from 0.005 to 0.1 μm against commercial sub-20 nm NPs, i.e., 5, 10 and 20 nm Au NPs and self-synthesized 1.7 nm ZnS QDs were investigated. We measured the liquid-borne NP concentration by the electrospray-scanning mobility particle sizer (ES-SMPS) method, which enables the evaluation of clean filter efficiencies (low particle concentration in feed solutions) due to its high sensitivity according to authors' earlier work [36]. We also applied controlled flux conditions, so the effect of low and high fluxes on retention mechanisms was investigated. By employing a stirred cell filtration system, the further understanding in retention mechanisms for small NPs, especially for PPD < 1.0, e.g., adsorption and electrostatic repulsion, became accessible. Our results will pave the way for an in-depth understanding of NP retention mechanisms and, thus, enabling the proper and smart selection of membrane filters for technical NP separation in drinking water and wastewater treatments.

2. Materials and methods

2.1. Particle and filter system

2.1.1. Colloidal particles

The challenging particles in this study include commercially available Au NPs and self-synthesized ZnS QDs. Au NPs with diameters of 5, 10 and 20 nm were purchased from Ted Pella (Ted Pella Inc., Redding, CA, USA). The Au NPs are stabilized by tannic acid and the surfaces of the NPs are negatively charged. The zeta potentials of Au NPs were measured by a Stabino Zeta Potential Analyzer (Particle Metrix GmbH, Meerbusch, Germany) at pH~7 which is the experimental condition of this study, and the average values for 5, 10 and 20 nm Au NPs were −63.1, −63.5 and −70.4 mV, respectively. For filtration experiments the upstream concentrations of 5, 10 and 20 nm Au NPs were controlled at about 0.17, 1.06 and 4.37 μg/mL, which correspond to particle number concentrations of approximately 1.7×10^{11}, 7.8×10^{10} and 5.3×10^{10} particles/mL, respectively, with the density of 19.3 g/cm^3.

For sub-5 nm particles, ZnS QDs were synthesized according to Komada et al. [37] and Segets et al. [38]. The particle size distribution (PSD) of the synthesized ZnS QDs was determined by deconvolution of UV/vis absorbance data measured by a Cary 100 Scan spectrophotometer (Varian, Germany). Therefrom the mean volume weighted particle size was determined as 1.7 nm. The zeta potential of the QDs was −15 mV measured by a Zetasizer Nano ZS (Malvern instruments, Malvern, UK). The synthesized ZnS QDs were stored in the form of powder, which, after a weighing step, could be fully dispersed in 18 MΩ cm resistivity ultrapure water (Milli-Q system, EMD Millipore Corp., Billerica, MA) by the aid of gentle ultrasonication for 10 min. The upstream concentration of QD dispersions used in the experiments was prepared to be 3 μg/mL (~ 2.9×10^{14} particles/mL when assuming the ZnS QD density of 4.09 g/cm^3) by dilution with the aforementioned Milli-Q ultrapure water.

2.1.2. Membranes

As tested filters, polyvinylidene difluoride (PVDF, EMD Millipore Inc., Darmstadt, Germany), Nylon (Tisch Scientific, North Bend, OH), polycarbonate track-etched (PCTE, GE Healthcare Biosciences, Pittsburgh, PA), polytetrafluoroethylene (PTFE, W. L. Gore & Associates Inc., Newark, DE), polyethersulfone (PES, Sterlitech Corporation, Kent, WA), polypropylene (PP, Tisch Scientific, North Bend, OH), mixed cellulose ester (MCE, EMD Millipore Inc., Darmstadt, Germany) membranes and a special customized (SC) small pore size membrane were investigated. Detailed information of membrane filters and filtration conditions is provided in Table 1. Although the exact values of zeta potential of these membranes in water were not available in this study,