Journal of Membrane Science 524 (2017) 682–690

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Liquid filtration of nanoparticles through track-etched membrane filters under unfavorable and different ionic strength conditions: Experiments and modeling

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ARTICLE INFO

Keywords:
Track-etched polycarbonate membrane filter
Microfiltration
Derjaguin-Landau-Verwey-Overbeek (DLVO) theory
Adhesive and hydrodynamic torque
Short range hydration effects

ABSTRACT

Nanoparticle deposition experiments under unfavorable conditions were conducted experimentally and theoretically. The 0.2 and 0.4 µm rated track-etched membrane filters were challenged with 60, 100, 147, 220, 350 and 494 nm polystyrene latex (PSL) particles with different ionic strengths ranging from 0.005 to 0.05 M. The capillary tube model, with replacing the viscosity of air to water, was used to estimate the initial efficiency, or the transport efficiency of the particles to the filter surface, which was corrected in a second step by allowing the detachment of the nanoparticles according to the sum of adhesive and hydrodynamic torques. The adhesive torques were derived from surface interactions accessed by the extended DLVO theory. Calculation results showed that the adhesive torque of a particle located in the calculated primary minimum was slightly larger than the hydrodynamic torque, resulting in particle deposition. However, experimental data clearly indicated that detachment occurred. This could only be explained by the presence of additional hydration forces, leading to a larger separation which became relevant at high ionic strengths. By including hydration into our theoretical framework, experiment and theory were in very good agreement under all different ionic strength conditions. The findings allow a basic understanding of surface interactions between nanoparticles and membranes in micro- and ultra-filtration applications for drinking water production, wastewater treatment and particle free water production in industries.

1. Introduction

Membranes, including symmetric, asymmetric, non-woven fabric and composite types, for micro- (0.1–1 µm pore diameter) and ultra-filtration (< 0.1 µm pore diameter), are being widely used. Applications are ranging from particle removal in municipal water and wastewater treatments as well as process water in various industries such as semiconductor, pharmaceuticals, food and beverage [1–5]. Currently, the quality of these small pore size membranes is usually graded by their mean pore size under the assumption of sieving as the major removal mechanism. However, the evolution of the deposition efficiency with particle size and load usually does not correlate well with sieving characteristics [6]. Therefore detailed theoretical studies are needed to find out the reason for the discrepancy between the state of the art modeling and experiments and to provide a theoretical framework that allows an accurate prediction of particle deposition efficiency. Noteworthy, herein we do not focus on the topic of membrane rejection or cross-flow filtration which is the so-called size and charge-based exclusion of nanoparticles by controlling pH and ionic strength. In such way the particles are retained in the upstream solution of the membrane or at the membrane surface [2,5,7–11]. In our study we focus on applications of e.g. non-woven and asymmetric membranes where particle deposition on the surface and inside the membrane is intended and expected [1,12]. Therefore, a dead-end batch type filtration setup was used in this study.

Deposition (or adhesion) of colloidal particles in packed-bed-type granular bead collectors has been found to include two sequential processes. First, transport of the particles to the vicinity of the filter

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http://dx.doi.org/10.1016/j.memsci.2016.11.023
Received 6 August 2016; Received in revised form 5 November 2016; Accepted 13 November 2016

surface, which is then followed in a second step by particle deposition onto the bead surface. Regarding liquid filtration in general, transport models of particles were mainly derived based on those originally developed for air filtrations [13–17]. For example, Logan et al. extended aerosol filtration models to aquasols and confirmed that they were applicable for several types of filter media [17]. Regarding the second deposition step, it was determined by the total interaction energy between particle surface and collector interaction energies derived by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and therefrom based extensions [13,14]. The typical total interaction energy curve described by classical DLVO theory consists of the superposition of van der Waals interaction (usually attraction) and electrostatic repulsion. It mostly results in a deep primary minimum approaching negative infinity at a distance of 0 nm, a shallow secondary minimum at larger separation distance, and a maximum known as energy barrier situated in between. The energy barrier usually determines the fraction of effective collisions between particles and filter media that result in successful attachments. The ratio between attached particles and the total amount of incoming particles is defined as attachment coefficient which has been conventionally described only with chemical factors such as solution chemistry (or ionic strength) and surface potentials between particles and collectors [18,19]. However, recent studies showed that in the specific case of filtration, hydrodynamic drag on colloidal particles may have a significant impact on both, attachments at primary minimum and secondary minimum. Thus, also detachment potentially might occur [20–23]. For the time being, most of these studies are limited to the packed-bed filtration system using granular collectors [19,24]. Only limited research has extended the experimental and theoretical examinations of particle deposition to micro- and ultra-filtration membranes.

In addition to the finding that hydrodynamic drag can affect the filtration efficiency, researchers found that classical DLVO theory often does not accurately describe the surface interaction energies [25,26]. Therefore, some studies have shown discrepancies between experimental data and predictions by the DLVO theory [27,28]. To overcome these limitations, in a first instance, the Born repulsion, representing the short-range repulsion caused by the overlap of electron orbitals at very short distances, has been introduced and combined with the classical DLVO as the so-called extended DLVO theory (xDLVO). It allows a better description of the interactions when the particles come close to the collector surface with distances of a few nanometers and less. Thus, Born repulsion severely influences the primary minimum [29]. The existence of short-range interactions has been confirmed by direct measurements of interaction forces using atomic force microscopy (AFM) which further recognized few types of additional short-range interactions (non-DLVO forces) beyond the Born repulsion, i.e. solvation and hydration forces as well as steric interactions. In particular the specific surface conditions determine physi- or chemisorbed ligands at the particle surface [30–32]. Thus, in the context of filtration, many open questions are remaining and a lot of research is needed to clarify, e.g. the effects of additional short-range interactions on the deposition of colloidal particles.

In this study, the filtration (or deposition) efficiencies of track-etched, straight-through polycarbonate membrane filters against PSL particles were investigated experimentally and theoretically under unfavorable filtration conditions and different ionic strengths. It is to be noted that the reason for using such a straight-through pore filter is due to its relatively simple structure that allowed the establishment of well-defined air filtration models [33–37]. Throughout all investigations unfavorable filtration condition, which means particle and filter surfaces are like-charged, was used. In some applications, e.g. photoresist filtration, it is usually impossible to modify the composition of chemicals or pH value in such a way that favorable conditions between particle and filter surface are achieved. Therefore, it is very important to evaluate the filter performance under unfavorable condition that results in repulsion between particles and filters.

Theoretical depositions, calculated by considering particle transport and subsequent short range surface interactions by means of xDLVO with and without additional hydration forces, were compared with experimental data to understand the filtration of colloidal PSL nanoparticles between 60 and 500 nm in more detail. The necessity of including a defined hydration force in addition to xDLVO was clearly recognized. Finally, the effect of ionic strength on the interaction between particle surface and filter surface as well as the effect of hydrodynamic drag on the detachment of colloidal particles were analyzed. Our findings provide important insights to the deposition mechanism of electrostatically stabilized nanoparticles between 60 and 500 nm. The results pave the way to a future knowledge-based design of dead-end deep-bed membrane filtrations for drinking and particle-free process water and chemical productions and wastewater treatments.

2. Materials and methods

2.1. Theoretical considerations

2.1.1. Particle transport to a filter surface

Polycarbonate straight-through membranes, or so-called Nuclepore filters, are filters with an array of microscopic cylindrical holes and uniform diameters as shown in Fig. S1 of Supporting Information A (SI A). Nuclepore filters were chosen due to their defined geometric structure, the existence of a well-established filtration model and the broad range of applications at least on a laboratory scale. As mentioned earlier, during the liquid filtration, particles are firstly transported to the vicinity of the filter surface by convection and/or diffusion prior to deposit onto the filter surface (front and tube wall surfaces). In the gas phase, capillary tube models have been developed and the size-dependent deposition by superposition of different transport mechanisms was accurately predicted [33–37]. In this study, the capillary tube model was only used to describe the transport efficiency of colloidal nanoparticles to the vicinity of the filter surface. As discussed in the next section, whether attachment occurs is defined in the next step by the local torque (or force) balance considering particle-filter surface interactions. The considered transport mechanisms were (i) diffusion on the front surface of the Nuclepore filter (E_{DS}), (ii) interception on the pore opening (E_R) and (iii) diffusion on the walls inside the pores (E_{DP}). Impaction and settling on the filter surface were not considered due to the negligible inertia and gravity of colloids [17]. Expressions for calculating each mechanism can be found in SI B.

2.1.2. DLVO Theory

The classical DLVO theory balances two interaction energies: van der Waals (VDW) interaction (φ_{VDW}) and electrical double layer (EDL) repulsion (φ_{EDL}). In this study, the VDW attraction using the sphere-plane Hamaker approximate expression for the retarded VDW energy was employed:

$$\varphi_{VDW} = -\frac{Aa_x}{6h}\left(1 + \frac{14h}{\lambda}\right)^{-1} \tag{1}$$

where A is the Hamaker constant calculated on the basis of the Lifshitz theory [25]: A value of 1.74×10^{-20} J was obtained for the PSL-water-polycarbonate system; a_x is the radius of the colloids; h is the separation distance between particle and filter surface; λ is a characteristic wavelength of interaction. Noteworthy, retardation is often addressed in terms of a length of electromagnetic interactions which was found to be around 100 nm for most materials [14,38,39]. Besides, retardation effects need to be considered at larger separation distances which is the case for this study. Moreover, we confirmed that the results of Eq. (1) coincide with the classical Hamaker term found for the system sphere-plate at short separation (Fig. S2 of SI C) [39]. Thus, Eq. (1) is applicable for both short and large separation distance