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Determining Brownian and shear-induced diffusivity of nano- and micro-particles for sustainable membrane filtration

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Abstract

Membrane filtration for sustainable wastewater reuse has been encountering particle deposition (i.e., particle cake fouling) with mostly micron-sized particles including bacteria, and nano-sized colloids/particles as well. Particle size may influence membrane fouling and flux decline through cake formation as particles with different sizes exhibit different back diffusivity and packing density of the cake. A theoretical diffusivity equation was proposed by Einstein (1906) [1]; thermodynamic and drag (i.e., resistance or mobility relation) forces were compared in equilibrium. The diffusivity relationship, ratio of thermodynamic and drag forces, was combined with steady-state convection and diffusion equation and finally came up with a relationship between retention times from flow field-flow-fractionation (fl-FFF) and diffusivity of a particle. An asymmetric fl-FFF system (Postnova, Germany) equipped with a regenerated cellulose membrane with molecular weight cutoff of 1,000 molecular mass and a micro-channel employing both laminar channel and cross flows, was used to obtain chromatography using an UV detector. A wide range of colloids and particles were used; both traceable polymer and latex microsphere colloids/particles with nominal diameters of 0.09 (i.e., 90 nm), 0.152, 0.2, 0.5, 0.701, 0.82, 0.993, 1.0 μm (Duke Scientific, US), and micro silica particles with nominal diameters of 3.0, 6.0, 10.0 μm (Nanotech, Korea). Each colloid or particle was characterized in terms of either its size or diffusivity with analyses of chromatography obtained from fl-FFF. It was found in this work that ca. 0.5 μm is a critical size below and above which diffusivity of a particle increases (i.e., particle of 0.5 μm has a minimum diffusivity). An empirical equation for the shear-induced diffusivity will be suggested in the presentation based on the results obtained from the fl-FFF. There may be many important implications on this observation; for example, bacteria with a 0.5 μm size may provide significant cake deposition and subsequently flux decline and possibly bio-fouling. These nano-/micro-size and diffusivity information is being investigated in conjunction with membrane filtration with the corresponding particles and various membranes.

Keywords: Diffusivity; Nano colloid; Micro particle; Sustainable membrane filtration

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1. Background and related theories

Diffusion is one of the most important influencing factors for particles (including colloids) transport including cake formation and their transmission through the membrane pores, if any. It is obvious that particles (or colloids) having higher diffusivity should have less cake fouling propensity. The only problem remained to be determined is how the diffusivity of either particles or colloids is resulted: i.e., Brownian- [1] vs. shear-induced one [4]. Wiesner and Chellam [3] also pointed out that the diffusivity of particles is a function of particle size and has a minimum value around 0.1 μm; i.e., in particle size ranges lower than and higher than approximately 0.1 μm particle diffusivity increases as its size decreases and increases as Brownian and shear-induced diffusivity increases, respectively. It is filed-flow fractionation (FFF) apparatus that can measure both Brownian and shear-induced diffusivity of particles and colloids, which employs two crossing flows (channel laminar and cross flows), a micro channel, and an accumulation membrane wall [2]. The schematic of the FFF system is described in Fig. 1.

Theories for FFF in terms of retention parameter (λ), channel geometries (channel thickness w, channel volume V^0), volumetric rate of crossflow V_c, peak times ratio (R), and particle diffusivity (D), can be described as follows [2]:

$$\lambda = \frac{V^0 D}{V_c w^2} \quad (1)$$

$$\lambda = \frac{R}{6(1-R)^{1/3}} \quad (2)$$

where $R = t_0/t_r$, and t_0 and t_r represent retention times of unretained (void) and retained peaks from the FFF system, detected by the UV detector at 254 nm, respectively. It is not revealed yet how the diffusivity of particles is resulted (i.e., by either Brownian or shear induced).

Equating Eqs. (1) and (2) gives the following Eq. (3) that estimates diffusivity (or size) of particles.

$$\frac{R}{6(1-R)^{1/3}} = \frac{V^0 D}{V_c w^2} \quad (3)$$

Here the diffusivity can be substituted in two ways: Brownian diffusivity [Eqs. (4) and (5)] [1] and shear-induced diffusivity [Eqs. (6) and (7)] [4].

$$D = \frac{kT}{6\pi\mu a} \quad (4)$$

$$\frac{R}{6(1-R)^{1/3}} = \frac{V^0}{V_c w^2}\frac{kT}{6\pi\mu a} \quad (5)$$

for particles of the size less than approximately 0.1 μm, according to Wiesner and Chellam [3]. Here k is the Boltzmann's constant, T is the absolute temperature, μ is the viscosity of fluid, and a is the particle radius.

When shear-induced diffusivity [Eq. (6)] is inserted in Eq. (3), Eq. (7) can be derived:

$$D = D'\gamma a^2 \quad (6)$$

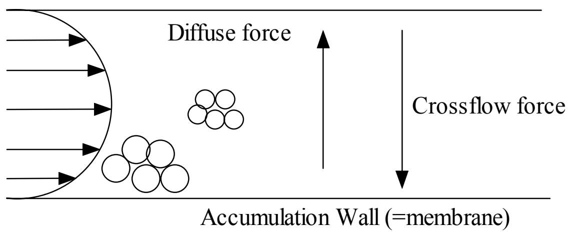

Fig. 1. Schematic of the FFF system. There are two flows inside the micro channel of the FFF, the first is the laminar flow channel (direction to the right), and the second is the crossflow one (downward direction). A larger particle is more affected by the crossflow rather than a smaller particle thus accumulated near the accumulation wall, while smaller particles can be towards the center of the channel and reach the exit earlier. UV detector is placed at the right end side.

$$\frac{R}{6(1-R)^{1/3}} = \frac{V^0}{V_c w^2} D'\gamma a^2 \tag{7}$$

Here D' and γ are the dimensionless diffusivity coefficient and shear rate, respectively, and $\gamma = 3Q/2BH_0^2$, Q, B, and H_0 are the channel flow rate, the channel width, and the channel half height, respectively [5].

Eqs. (5) and (7) will be used to estimate diffusivity (D) and dimensionless diffusion coefficient (D') for particles predominantly influenced by the Brownian and shear-induced diffusion, respectively.

2. Hypotheses

It is hypothesized that the diffusivities of particles or colloids with different sizes under different conditions can be determined by the FFF system with the same flowing conditions; i.e. the same flowing conditions are applied for the FFF system but particles with different sizes are hypothesized to behave differently to provide their different diffusivities. Similar to the notion suggested by Wiesner and Chellam [3], it is also hypothesized that there is a boundary particle size having a minimum diffusivity. Finally, particles containing lower diffusivities are hypothesized to provide a grater cake layer and subsequently greater membrane fouling.

3. Methods

An asymmetric fl-FFF system (Postnova, Germany) equipped with a regenerated cellulose membrane with molecular weight cutoff of 1,000 molecular mass (Postnova, Art No. Z-MEM-AQU-005) and a micro-channel employing both laminar channel and cross flows (1.5 mL/min and 0.1 mL/min, respectively), was used to obtain chromatography using an UV detector at 254 nm. Eluent used was FL-70 solution which contained anionic and neutral surfactants. A wide range of colloids and particles were used; both traceable polymer and latex microsphere colloids/particles with nominal diameters of 0.09 (i.e., 90 nm), 0.152, 0.2, 0.5, 0.701, 0.82, 0.993, 1.0 μm (Duke Scientific, US), and micro silica particles with nominal diameters of 3.0, 6.0, 10.0 μm (Nanotech,

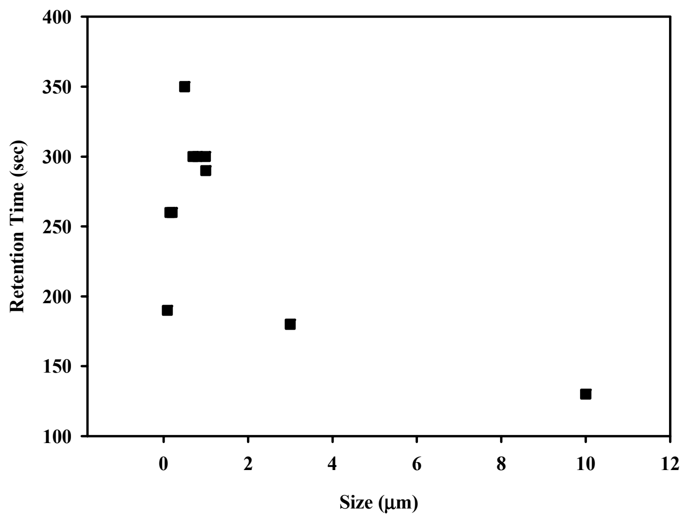

Fig. 2. Retention time trends for various different particles with different sizes, obtained from the FFF system with the UV detector. Every point is an average value calculated from triplicate measurements. Higher retention time exhibits lower diffusivity according to the FFF theory.

Korea). Membrane filtration tests were conducted using a bench-scale unit equipped with a membrane holder, a gear pump, various flow-control valves, and a digitalized flow meter and a pressure gauge.

4. Preliminary results and discussion

As shown in Fig. 2, two different diffusion trends were clearly found, supporting the first hypothesis; the boundary particle size having a minimum diffusivity was 0.5 μm, differently from the size of approximately 0.1 μm calculated by Wiesner and Chellam [3]. Corresponding diffusivity or dimensionless diffusion coefficient are being estimated and other measurements with the same particles but different membranes are also being conducted to demonstrate the effect of membrane properties such as the membrane surface charge on particle diffusivity.

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References

[1] A. Einstein, Investigations of the Theory of the Brownian Movement. Dover Publication Inc., New York, 1956.

[2] M.R. Schure, M.E. Schimpf and P.D. Schettler, Retention — normal mode, Ch. 2, in: M. Schimpf, K. Caldwell and J.C. Giddings, eds., Field-Flow Fractionation Handbook. Wiley-Interscience, John Wiley & Sons, New York, 2000.

[3] M.R. Wiesner and S. Chellam, Mass transport considerations for pressure-driven membrane processes, J. AWWA, 84(1) (1992) 88–95.

[4] R. Davis and D.T. Leighton, Shear-induced transport of a particle layer along a porous wall, Chem. Eng. Sci., 42(2) (1987) 275–281.

[5] R.H. Davis, Modeling of fouling of crossflow microfiltration membranes, Separ. Purif. Methods, 21(2) (1992) 75–126.