PART 1

Filtration Efficiency of 1.9-30 nm Nanoparticles through Eight Different Membrane Filters

PART 2

CFD Simulation of Liquid Filtration in Different Conditions

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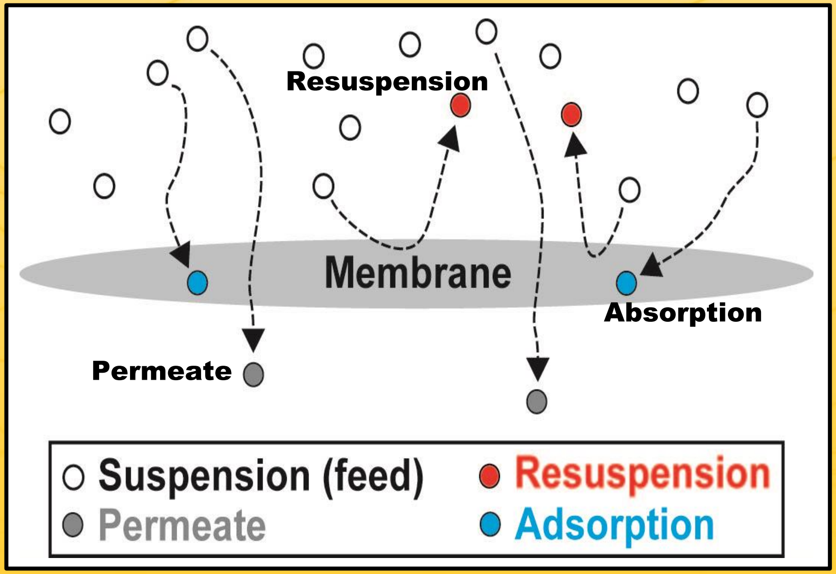
PART 1

Filtration Efficiency of 1.9-30 nm Nanoparticles through Eight Different Membrane Filters

Introduction

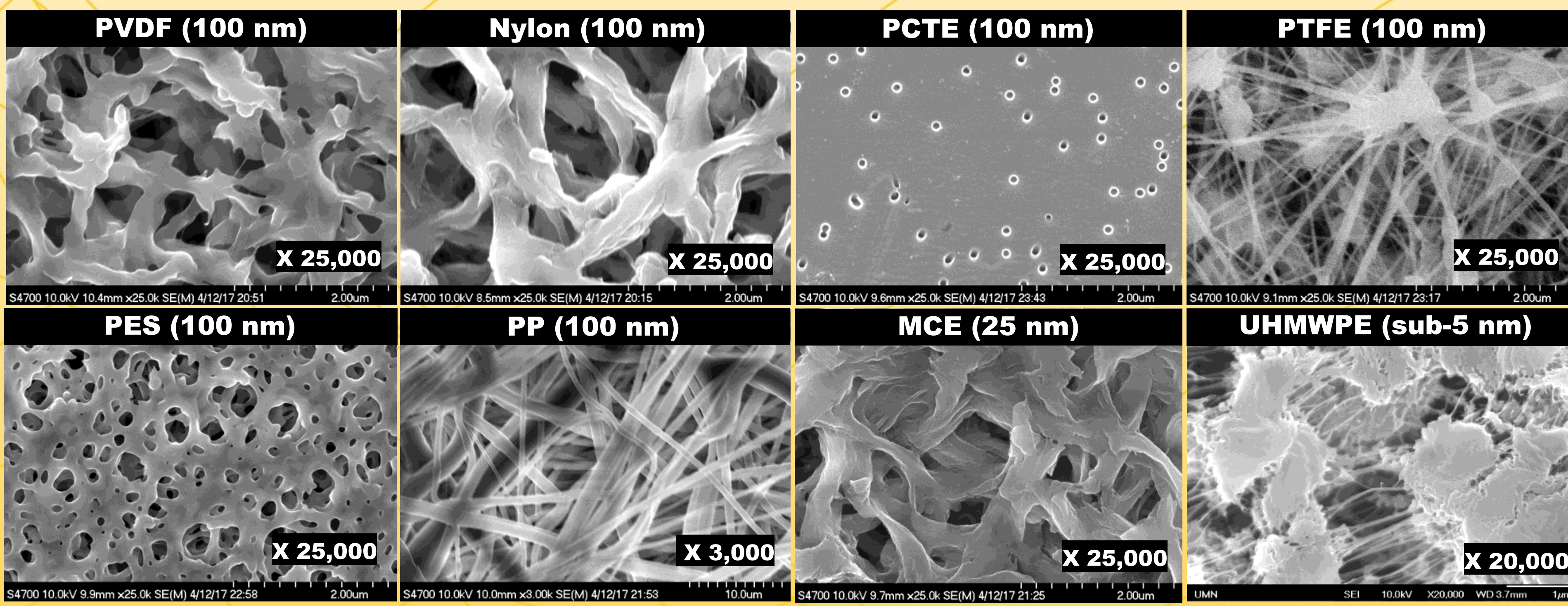
- **Micro- (100 nm ~ 1 μm)** and **ultra-filtration (10 nm ~ 100 nm)** using membranes have been widely applied as an effective technique to separate suspended particles from liquid in many industries.
- It is important to investigate the **filtration behaviors** of nanoparticles against different membranes.
- Filtration behaviors vary with **interaction energy** between particle and filter surfaces.
- Particles can be rejected by a membrane and **re-suspension**, **adsorption** and **penetration** can occur.



Objectives

- **Investigating filtration behaviors for different filters with different materials, structures and pore sizes**
- **Obtaining filtration efficiencies of nanoparticles with sizes of 1.9 nm quantum dots and 5, 10 and 20 nm Au particles**
- **Understanding particle rejection (retention) mechanisms and the fraction of each mechanism (e.g., percentages of re-suspension, adsorption and penetration)**

SEM Images of Membranes



PVDF: Polyvinylidene difluoride

PCTE: Polycarbonate track-etched

PTFE: Polytetrafluoroethylene

PES: Polyethersulfone

PP: Polypropylene

MCE: Mixed cellulose ester

UHMWPE: Ultra-high-molecular-weight polyethylene

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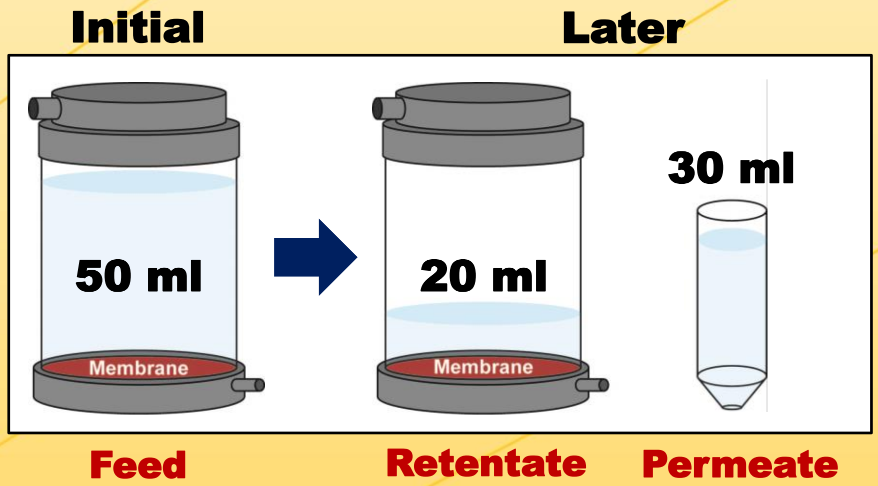
Filtration Process

- Stirred cell filtration system (constant pressure)



- Stop filtration when permeate volume reaches 30 ml
- Measure concentration of each sample using ES-SMPS
  - ✓ Feed (upstream, F)
  - ✓ Permeate (30 ml downstream, P)
  - ✓ Retentate (20 ml, R)

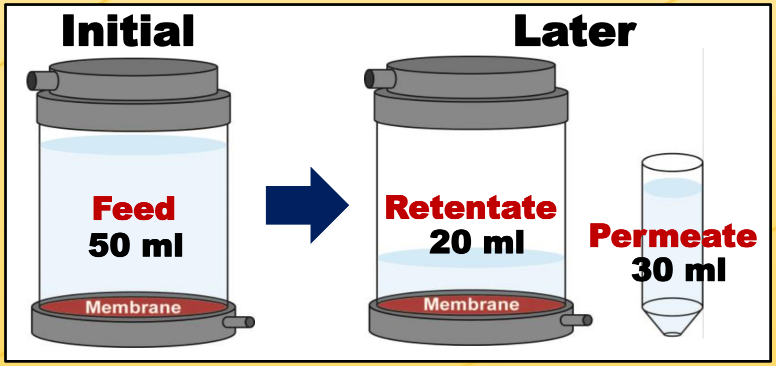
Filtration Efficiency

- **Retention efficiency ($E_{retention}$) = $1 - \dfrac{C_P}{C_F}$**
- **Recovery efficiency ($E_{recovery}$) = $\dfrac{C_R V_R + C_P V_P}{C_F V_F}$**

$C_F V_F$: Number of particles in **feed**

$C_R V_R$: Number of particles in **retentate**

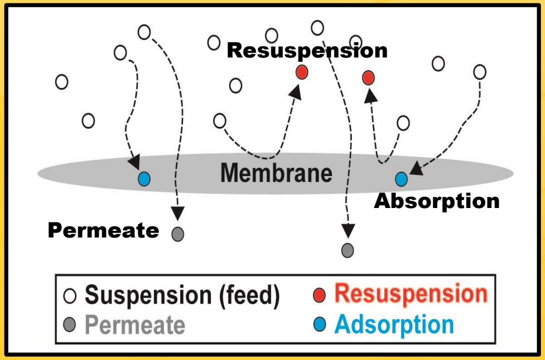
$C_P V_P$: Number of particles in **permeate**



ex) 100% adsorption without re-suspension into upstream ($C_P = 0$)

$E_{retention} = 1$

$E_{recovery} = \dfrac{\cancel{C}_R V_R}{\cancel{C}_F V_F} = 20/50 = 0.4$ (**minimum** value)

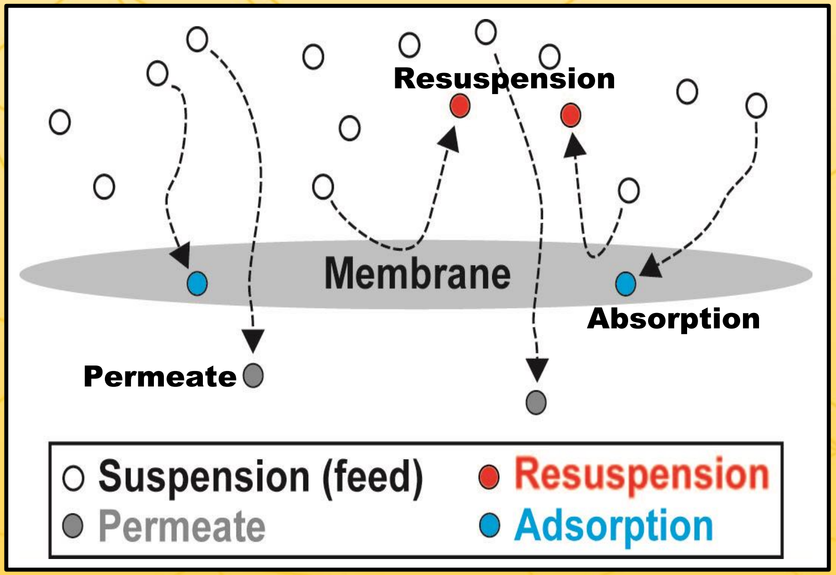


ex) 0% adsorption ($C_R V_R + C_P V_P = C_F V_F$)

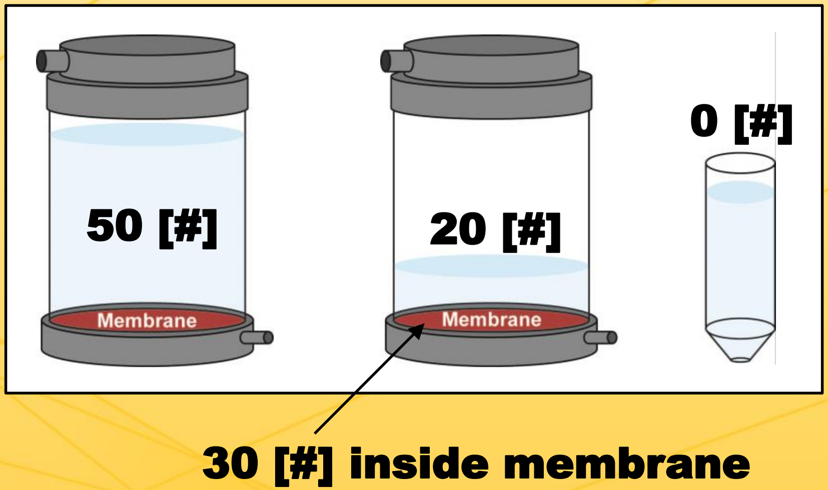
$E_{recovery} = (C_R V_R + C_P V_P)/C_F V_F = 1$ (**maximum** value)

Filtration Efficiency

- **Retention efficiency ($E_{retention}$) = $1 - \frac{C_P}{C_F}$**
- **Recovery efficiency ($E_{recovery}$) = $\frac{C_R V_R + C_P V_P}{C_F V_F}$**



Ex 2)



Ex 1) If $E_{recovery}$ = 1, all particles are in upstream and downstream (no particles in membrane).

Ex 2) If $E_{recovery}$ = 0.4, all particles passing membrane are adsorbed into the membrane (no re-suspension).

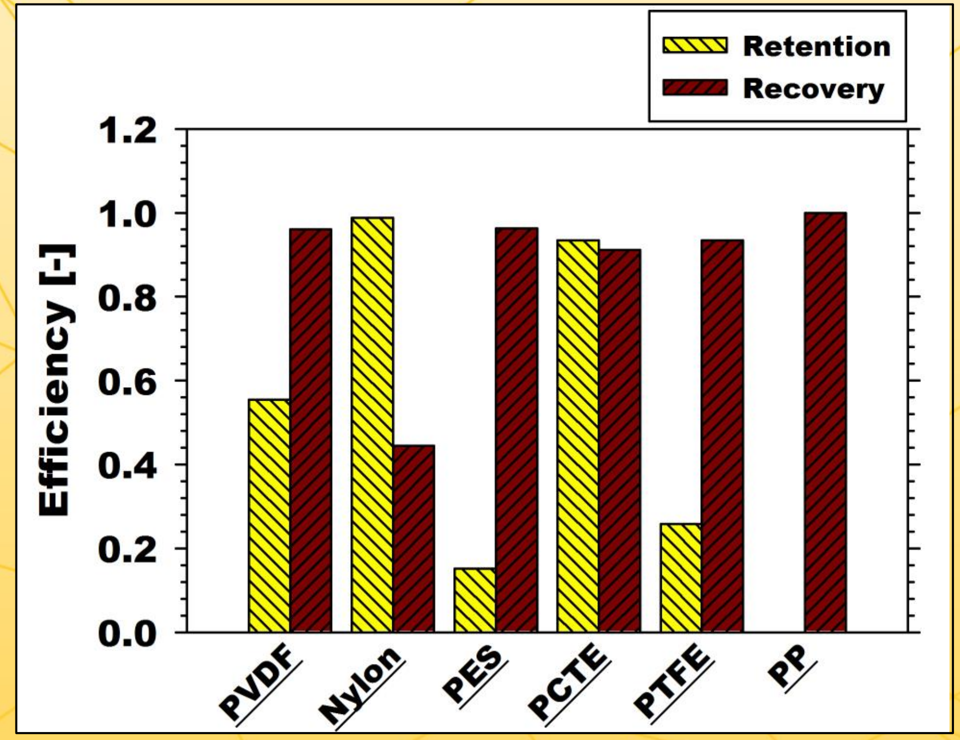
Permeability of Membranes

	Filtration time [min]	Filtered solution [ml]	Applied pressure [Inch of H_2O]	Permeability [L/m^2h]
PVDF (100 nm)	28	30	1	47.97
Nylon (100 nm)	25	30	0	53.73
PCTE (100 nm)	34	30	10	39.51
PTFE (100 nm)	10	30	0	134.32
PES (100 nm)	11	30	0	116.81
PP (100 nm)	7	30	0	191.90
MCE (25 nm)	30	30	90	44.78
PES (30 nm)	22	30	0	61.06
PCTE (15 nm)	66	30	1107	20.35
UHMWPE (sub-5 nm)	35	30	70	38.38

- **Effective filtration area: 13.4 cm^2**
- **Permeability calculated from flow rate and filtration area**
- **Pressure drop**

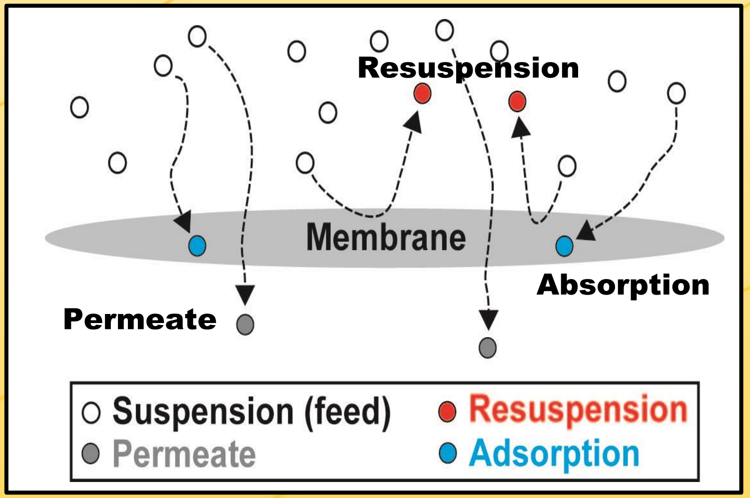
PCTE (15 nm) > MCE (25 nm) > UHMWPE (sub-5 nm) > PCTE (100 nm) > PVDF (100 nm) > Nylon (100 nm) > PES (30 nm) > PES (100 nm) > PTFE (100 nm) > PP (100 nm)

Au 10 nm through 100 nm rated membranes



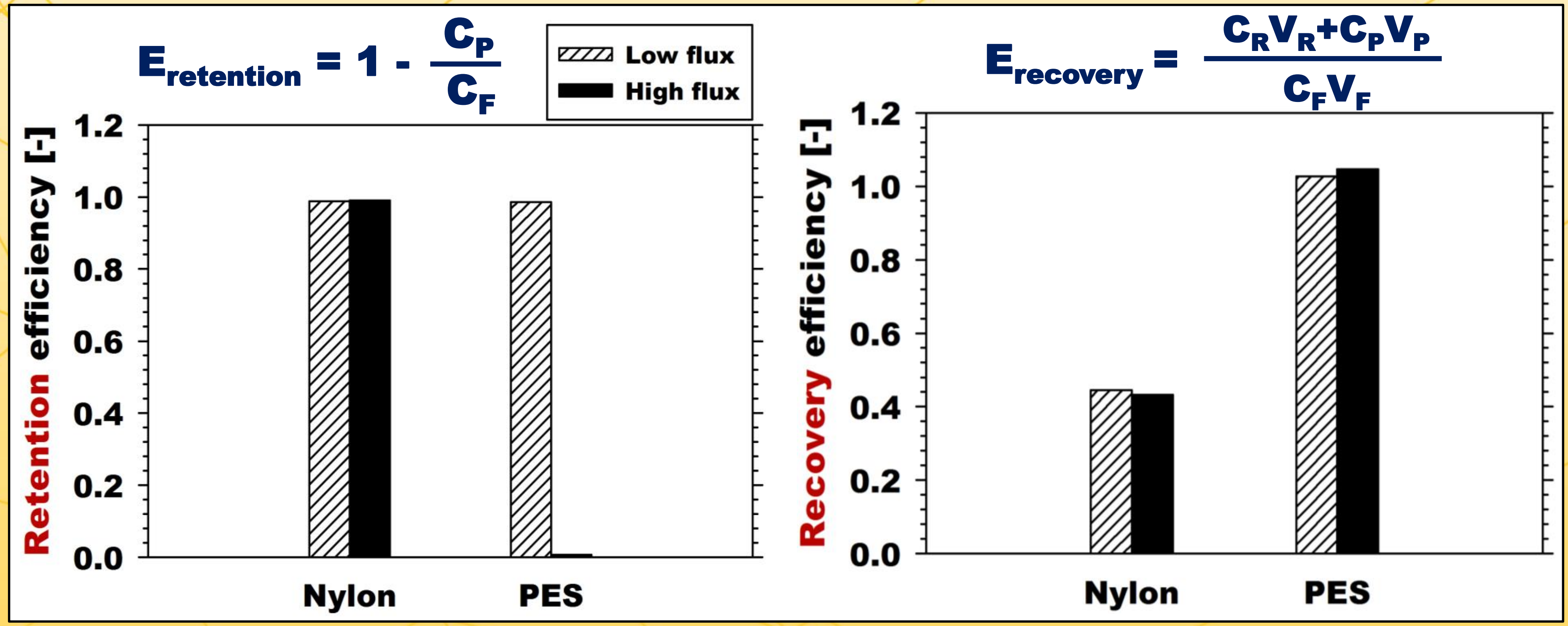
$$E_{retention} = 1 - \frac{C_P}{C_F}$$

$$E_{recovery} = \frac{C_R V_R + C_P V_P}{C_F V_F}$$



- Nylon and PCTE have the highest retention.
- Nylon rejects particles by adsorption (minimum recovery ~ 0.4) and PCTE rejects particles by preventing particles from entering pores of the membrane (high recovery).
- PVDF has around 50% retention and 95% recovery so it rejects particles by repulsing or re-suspending the particles.
- PP has almost 100% penetration for 10 nm Au particles.

Flux (Face Velocity) Effect



- **Nylon (100 nm rated – Au 10 nm) has high retention at low and high flux, but PES (30 nm rated – Au 5 nm) has very low retention at high flux (high flow velocity).**
- **Retention mechanisms for Nylon and PES are adsorption and rejection to entering pores (resuspension), respectively.**
- **Higher flow drag force than repulsion results in carrying particles into the membrane.**

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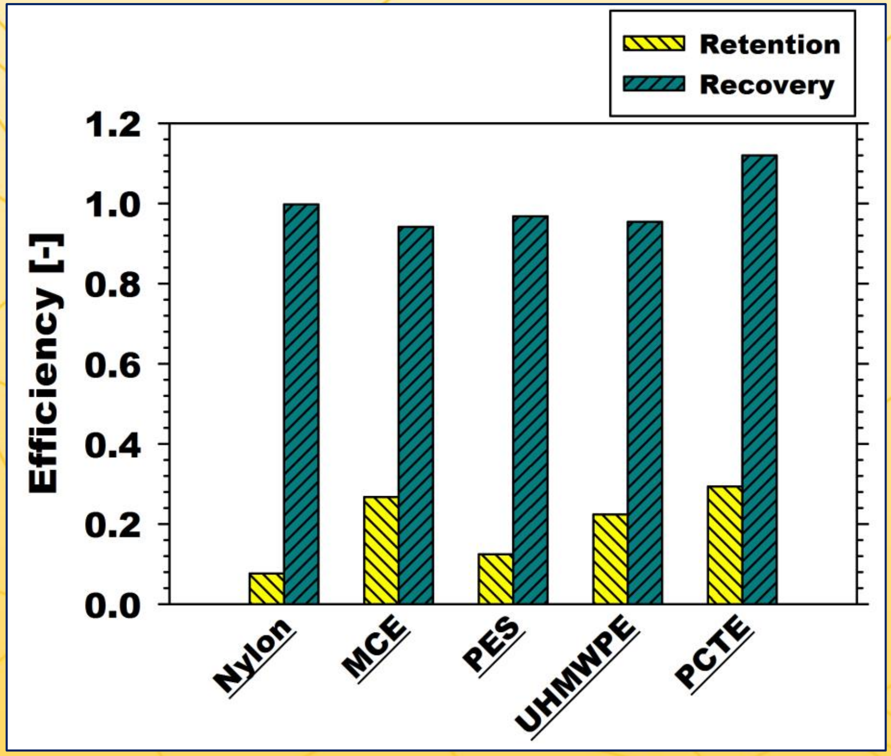
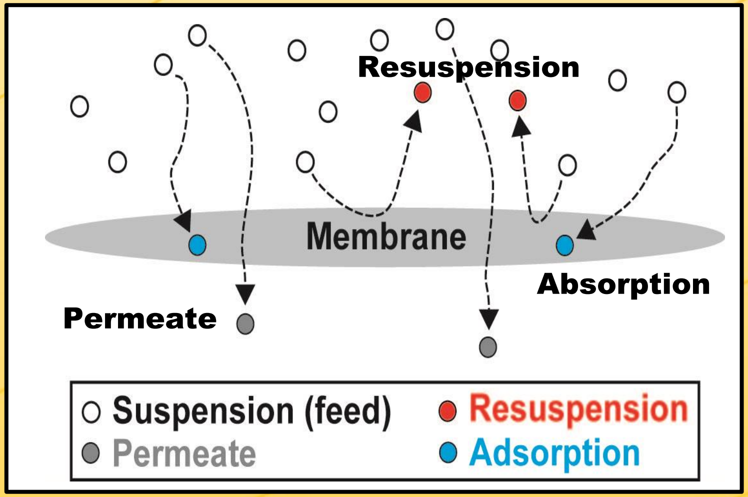
Ultrafiltration of 1.9 nm Quantum Dots



$$E_{retention} = 1 - \frac{C_P}{C_F}$$

$$E_{recovery} = \frac{C_R V_R + C_P V_P}{C_F V_F}$$



- Nylon (100 nm), MCE (25 nm), PES (30 nm), UHMWPE (sub-5 nm) and PCTE (15 nm) membranes were challenged by 1.9 nm QD.
- Retention efficiencies of QD are generally low with high recovery efficiency, which means that QD is not easily rejected by both adsorption and repulsion, compared to Au nanoparticles.
- The pore size does not have the significant effect on retention efficiency but interaction energy might be more important.

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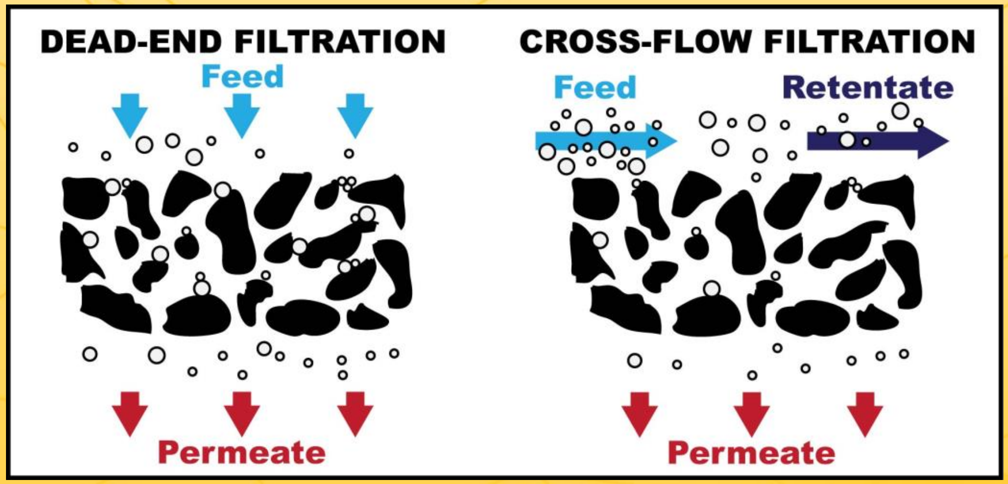
Conclusion

- **Different structures and materials of membranes result in different rejection mechanisms.**
- **Therefore, it would be important to choose a proper membrane according to types of filtration systems.**
  - ✓ **Dead-end filtration: membranes with high retention / low recovery**
  - ✓ **Cross-flow filtration: membranes with high retention / high recovery**



- **For very small nanoparticles with specific materials (e.g., QD), the effective rejection mechanism would be sieving due to the weak adsorption to membrane.**

PART 2

CFD Simulation of Liquid Filtration in Different Conditions

Introduction

- The performance (efficiency) of liquid filtration is hard to predict due to complex interactions between solid surfaces in liquid.
- Unlike air filtration, particle detachment can easily occur due to high viscosity flow and repulsion energy between surfaces.
- From the valid and proper simulation of particle behaviors through filters, one can predict the membrane efficiency under specific conditions.

Objectives

- CFD simulation to predict filtration performance of filter media with different structures, e.g., fibrous, granular filters

- Validation of CFD simulation by comparing with existing empirical equations and experimental data
  - ✓ Single sphere efficiency (favorable / unfavorable)
  - ✓ Single fiber efficiency (favorable)

- 2-D fibrous filter media (many fibers) simulation
  - ✓ Solution chemistry (ionic strength / zeta potential)
  - ✓ Flow velocity (hydrodynamic drag)
  - ✓ Fiber and particle (size / material)

Overall Methods

- **Solve continuity, momentum and energy equations using ANSYS Fluent**
- **Track particles in a Lagrangian reference frame using discrete phase model (DPM)**

✓ $$\frac{d\vec{v}_p}{dt} = \frac{1}{m_p}\sum \boxed{\vec{F}}$$ **: Gravitational, Brownian and Stokes drag forces**

✓ **Trap by interception, impaction and Brownian diffusion**

✓ **User Defined Function (UDF) to implement interaction energy between particle and filter surfaces for adhesion criteria**

✓ **UDF to implement adhesion and drag torques for detachment criteria**

1) **TRANSPORT: How many particles get close to filter surface**
2) **ADHESION: How many particles near filter attach to the filter surface**
3) **TORQUE: How many attached particles remain onto the filter surface**

Calculations in UDF

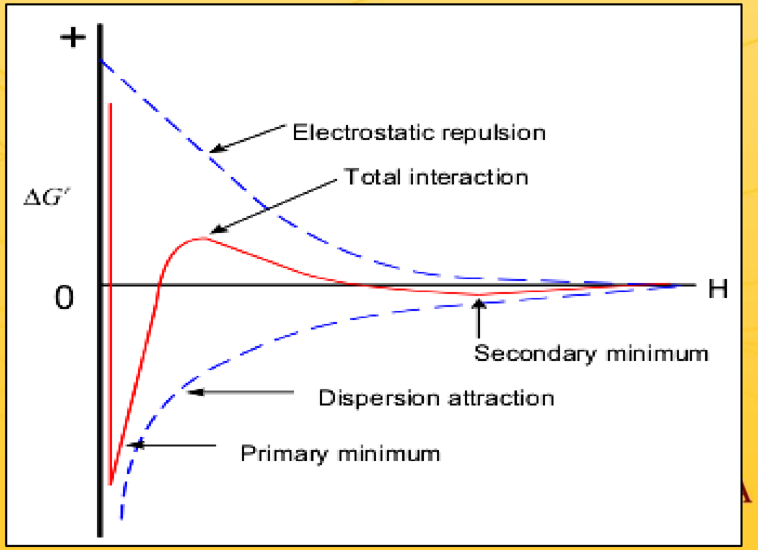
- **Distance between particle and fiber surfaces**
- **Total interaction energy between particle and filter surfaces in every time step based on DLVO theory**

  ✓ **Van der Waals energy:** $\Phi^{VDW}(H) = -\frac{Aa_p}{6H}\left(\frac{1}{1+14H/\lambda}\right)$

  ✓ **Double layer energy:** $\Phi^{DL}(H) = \pi\varepsilon\varepsilon_0 a_p\left\{2\psi_p\psi_s \ln\left[\frac{1+\exp(-\kappa H)}{1-\exp(-\kappa H)}\right] + \left(\psi_p^{\ 2}+\psi_s^{\ 2}\right)\ln\left[1-\exp(-2\kappa H)\right]\right\}$

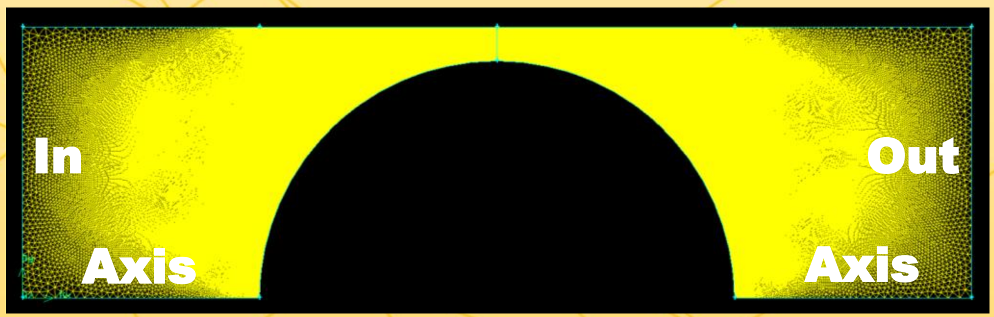
  ✓ **Born energy:** $\Phi^{BR}(H) = \frac{A\sigma^6}{7560}\left[\frac{8a_p+H}{(2a_p+H)^7}+\frac{6a_p-H}{H^7}\right]$

- **Collision efficiency (α) at primary and secondary minimum based on Maxwell approach**
- **Torque acting on particles due to hydrodynamic drag force and adhesion force**



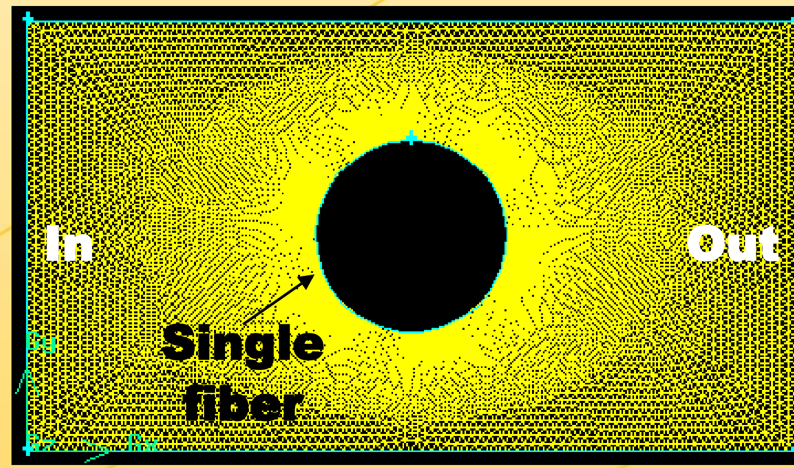
Calculation Domain for Validation

Single sphere efficiency



Half sphere

Single fiber efficiency



	Collector size [μm]	Porosity	Approach velocity [m/s]
Single sphere	328	0.67	1.2E-5
	400	0.6	4E-5
	600	0.6	2.8E-3
Single fiber	0.5	0.8	5E-4
	2	0.8	
	20	0.8	

Single Collector Theory (Hydrosol)

- **Single sphere efficiency** (Tufenkji and Elimelech, 2004)

$$\eta_{favor} = \underbrace{2.4A_S^{1/3}N_R^{-0.081}N_{Pe}^{-0.715}N_{vdW}^{0.052}}_{\text{Diffusion}} + \underbrace{0.55A_S N_R^{1.675}N_A^{0.125}}_{\text{Interception}} + \underbrace{0.22N_R^{-0.24}N_G^{1.11}N_{vdW}^{0.053}}_{\text{Gravity}}$$

- **Single fiber efficiency** (Choo and Tien, 1992)

$$\eta_{favor} = \frac{\pi d_f}{4(1-\varepsilon_0)} \times (\lambda_0 + \lambda_{BM})$$

Interception / gravitation / London-van der Waals

$$\lambda_0 = \left(\frac{6}{\pi}\right)\frac{1-\varepsilon_0}{d_f}A_S\left[0.216 \times 10^{-0.41\varepsilon_0}N_R^{1.55}N_{LO}^{0.1542} + 2.99 \times 10^{-4} \times 10^{3\varepsilon_0}N_G^{1.1}N_R^{-0.3}\right]$$

Diffusion

$$\lambda_{BM} = \left(\frac{9.2}{\pi}\right)(c_1 + c_2)^{1/3}\left[(1-\varepsilon_0)/d_f\right]N_{Pe}^{-2/3}$$

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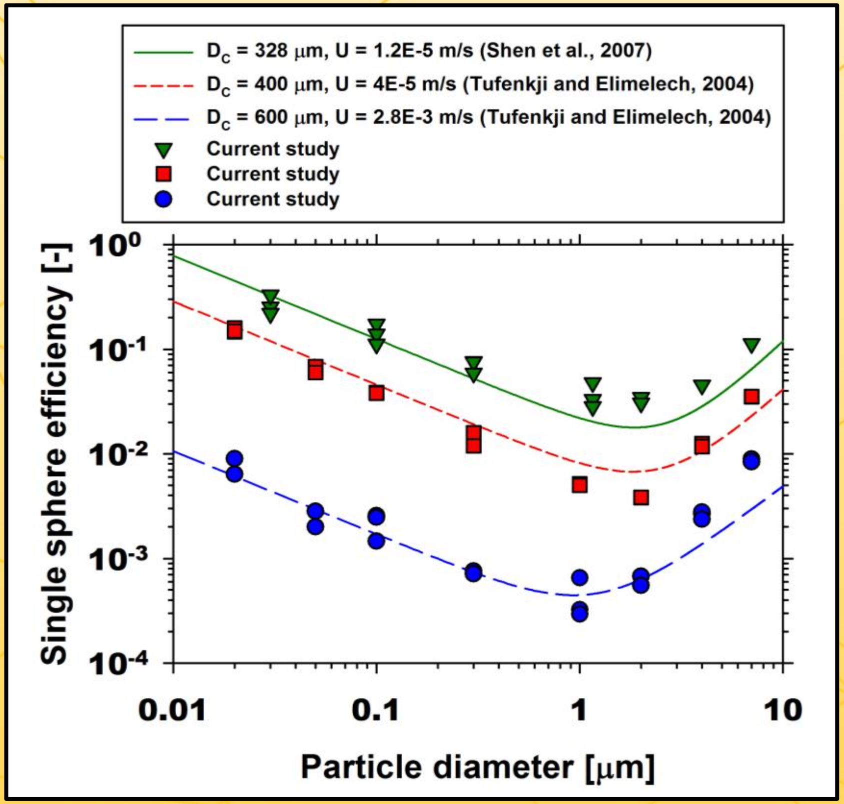
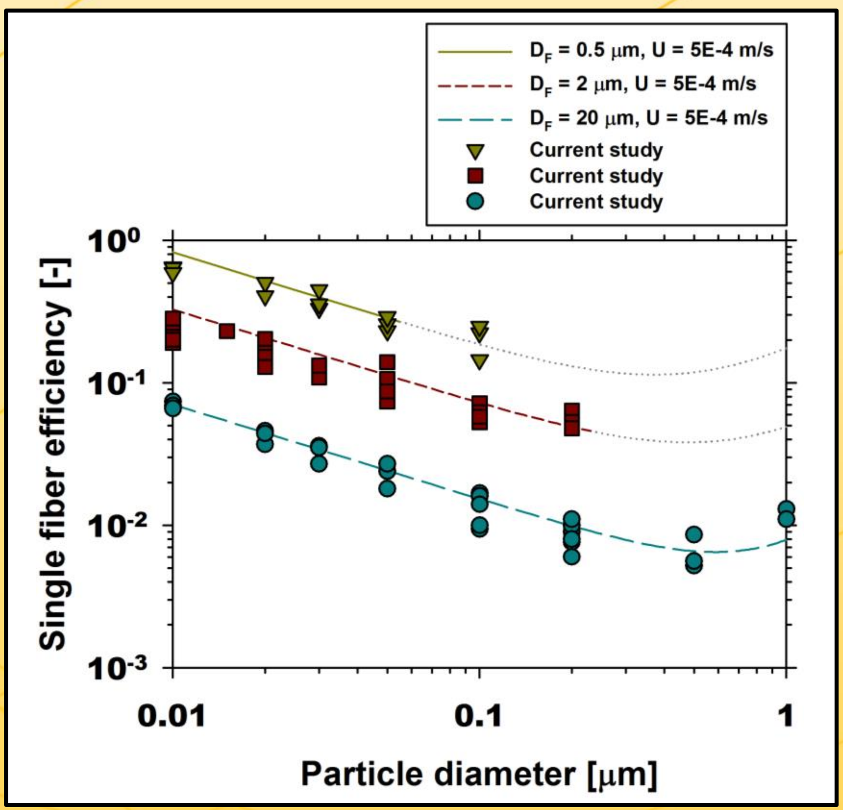
Favorable (Interception & Diffusion)

Single sphere efficiency



Single fiber efficiency



- CFD results were obtained for the valid particle size range, i.e., $D_P/D_F < 0.1$.
- Good agreement between CFD and empirical results of both single sphere and single fiber theory in liquid medium under favorable (no detachment) condition.

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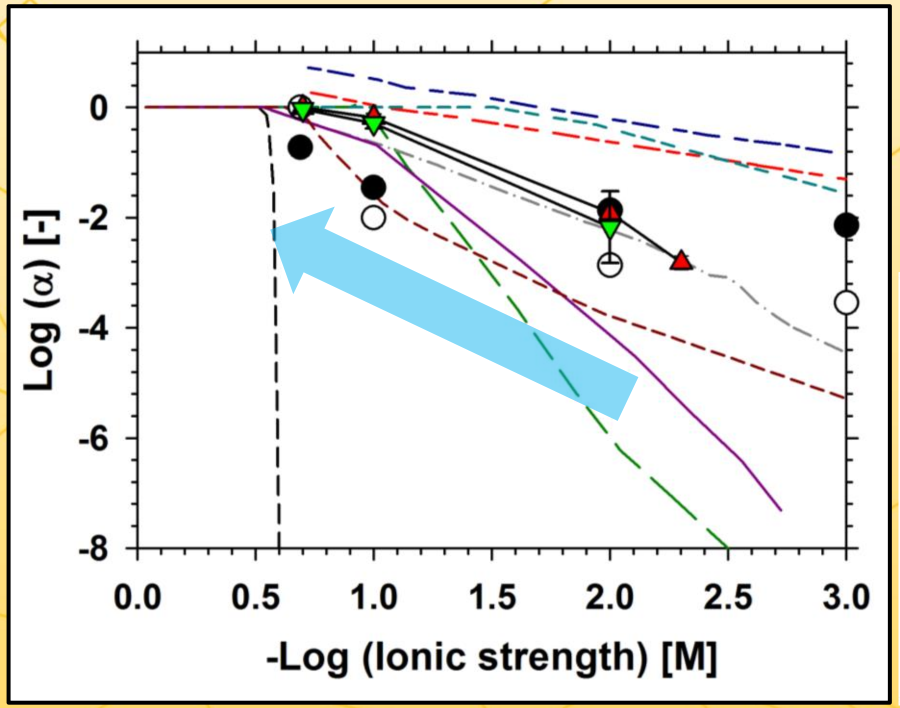
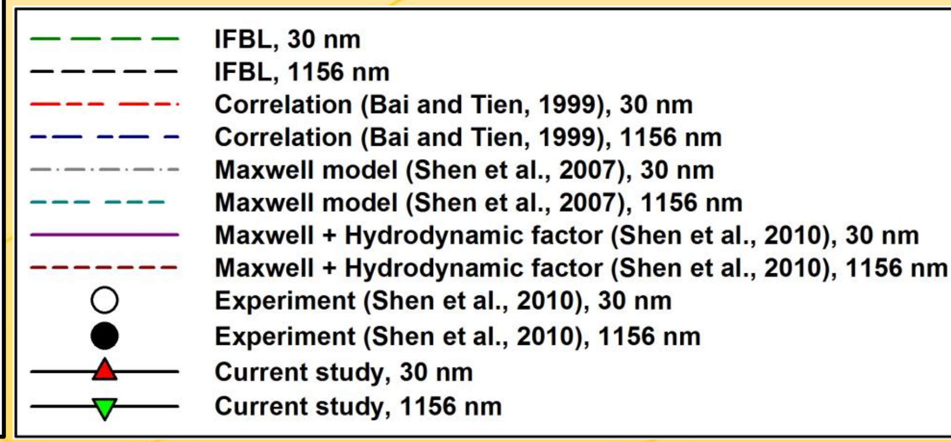
Validation of Unfavorable Condition (Repulsion)





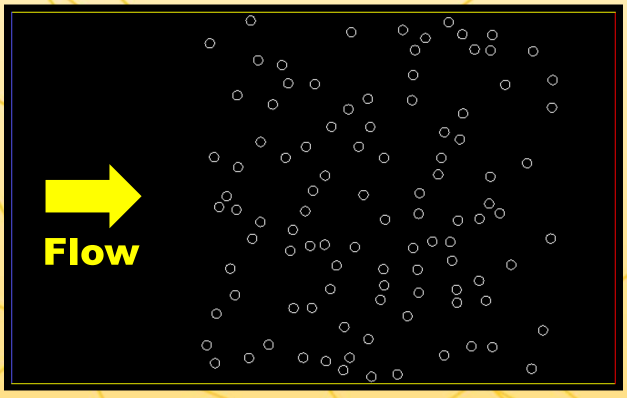
- **30 and 1156 nm PSL particles and 300 ~ 355 μm Quartz sand experiments (Shen et al., 2010)**
- **Ionic strength with different zeta potentials**
- **Collision efficiency (α) is the rate of successful collisions resulting in attachment of colloidal particles.**

$$\alpha = \frac{E_{unfavorable}}{E_{favorable}} \leq 1$$

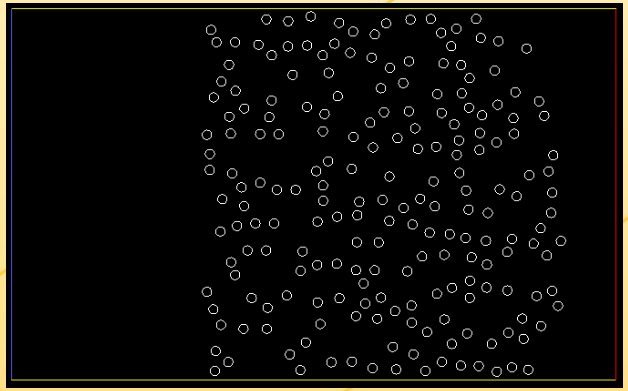
- **Increasing ionic strength – increasing collision efficiency**

Simulation of 2-D Fibrous Filter Media

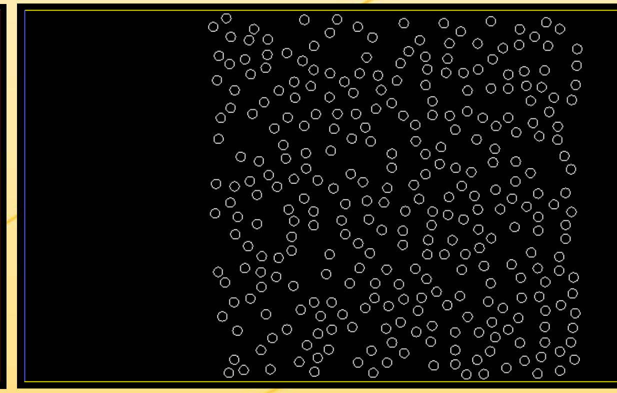
Solidity 5%



Solidity 10%



Solidity 15%

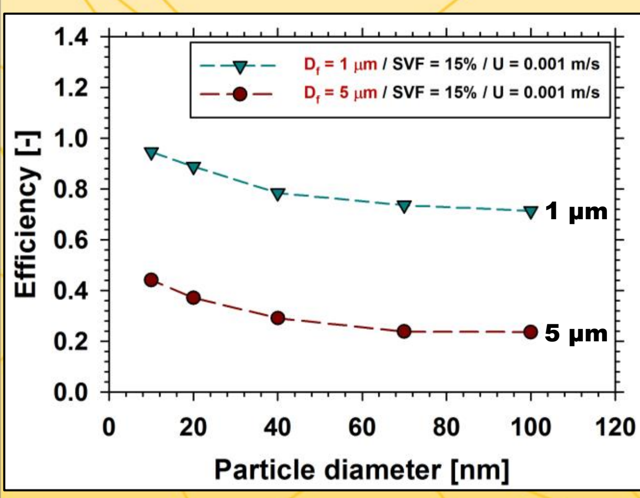


Fiber diameter	Solidity [%]	Flow velocity [m/s]
1 µm	5%	0.001 m/s
	10%	0.0001 m/s
5 µm	15%	0.00001 m/s

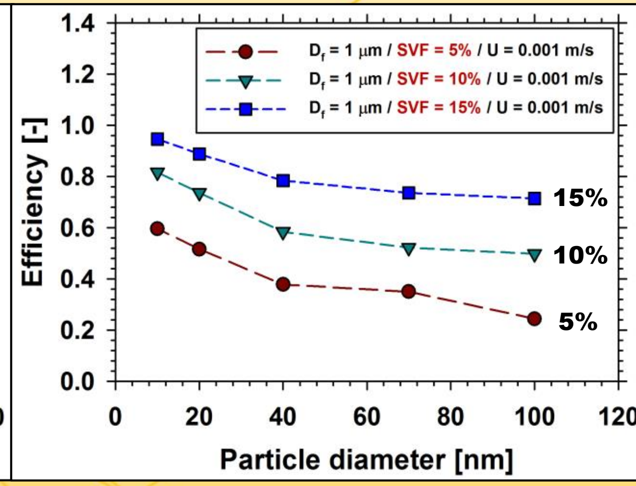
- Filtration performance under favorable and unfavorable conditions
- Considering various parameters, e.g., fiber diameter, solidity, flow velocity, Hamaker constant, zeta potential and ionic strength

Effects of Fiber Diameter, SVF and Fluid Velocity

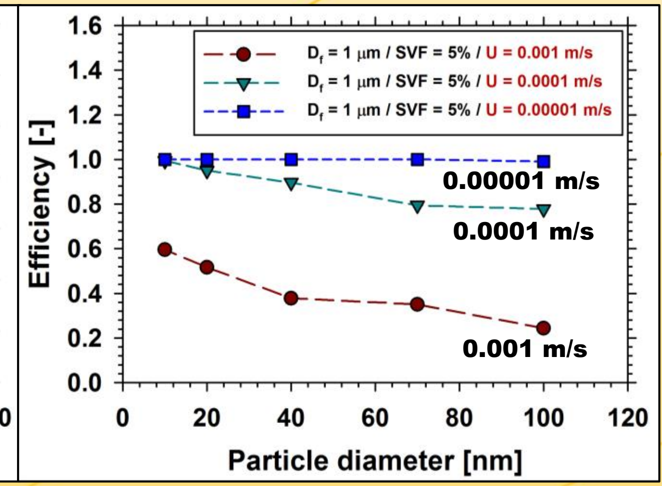
Fiber diameter



Solid volume fraction

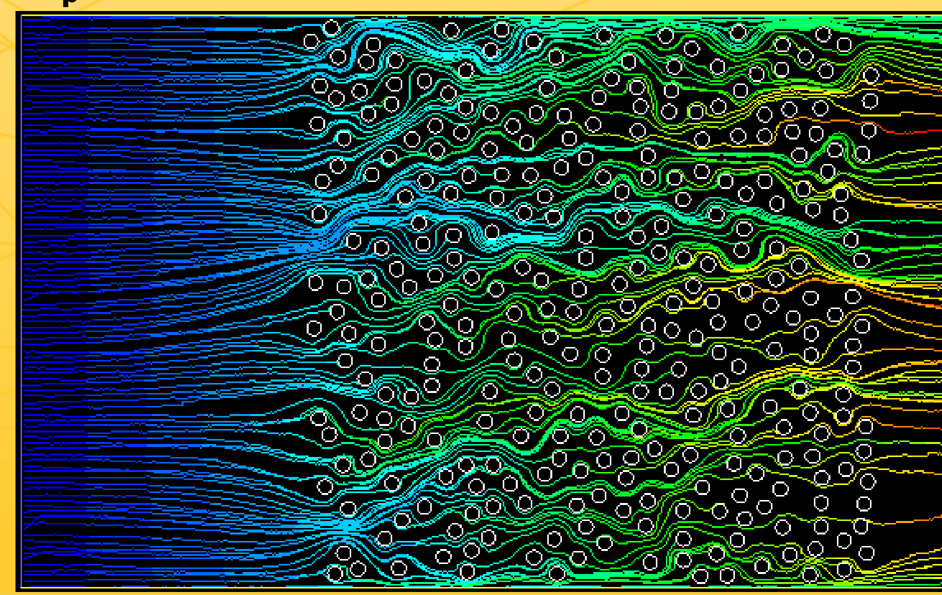


Fluid velocity



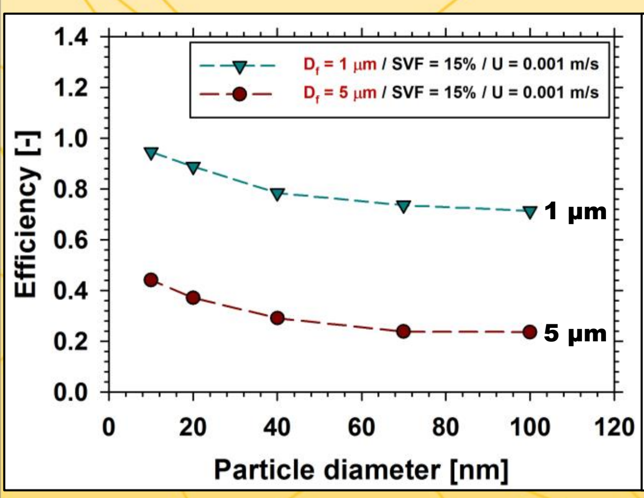
D_f = 1 μm
D_p = 100 nm

D_f = 5 μm
D_p = 100 nm

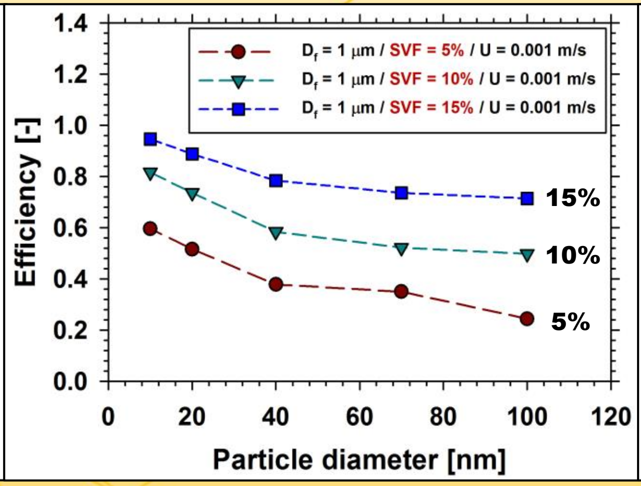


Effects of Fiber Diameter, SVF and Fluid Velocity

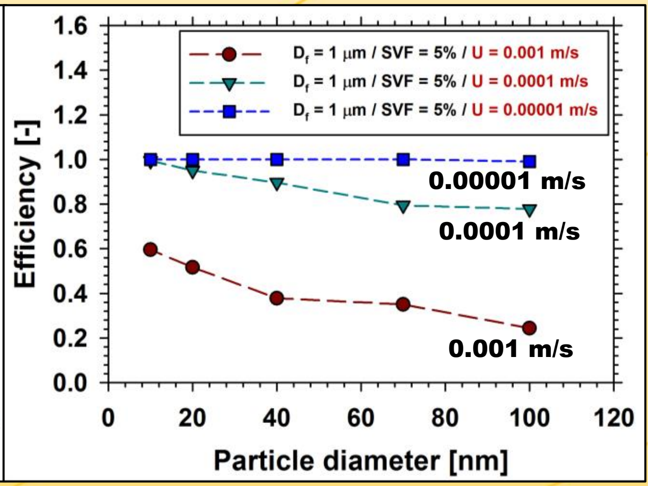
Fiber diameter



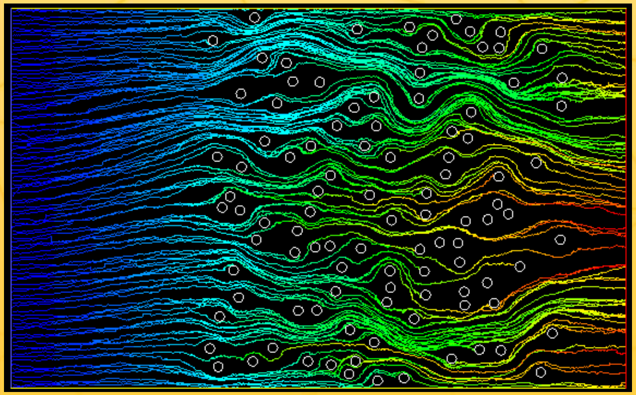
Solid volume fraction



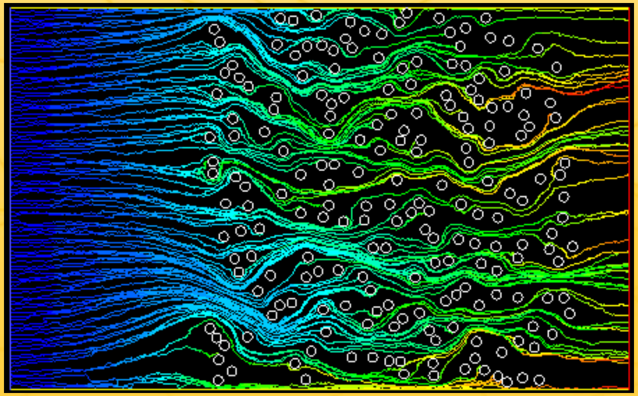
Fluid velocity



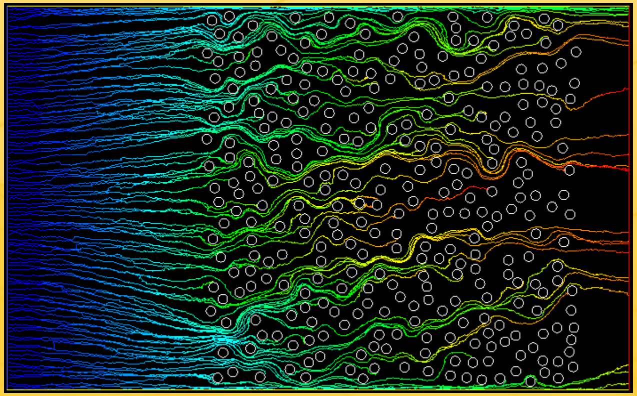
SVF = 5%
D_p = 100 nm



SVF = 10%
D_p = 100 nm



SVF = 15%
D_p = 100 nm



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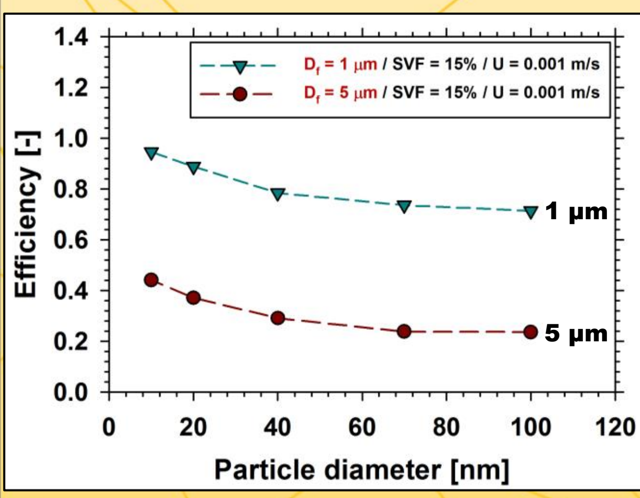
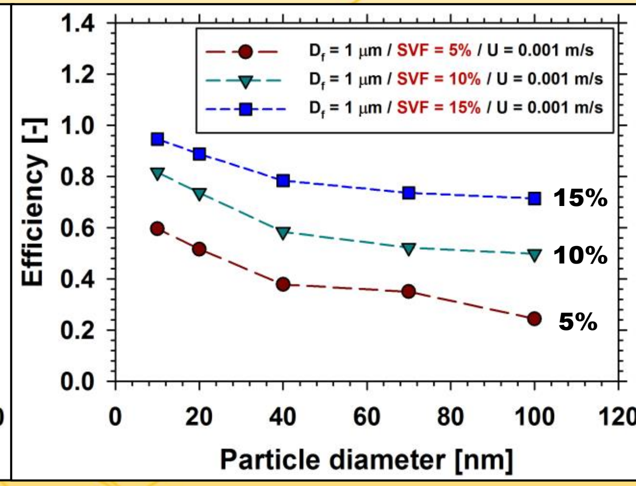
Effects of Fiber Diameter, SVF and Fluid Velocity

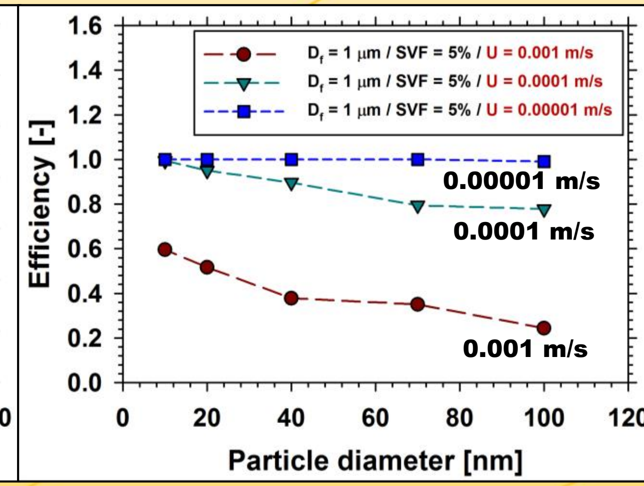
Fiber diameter



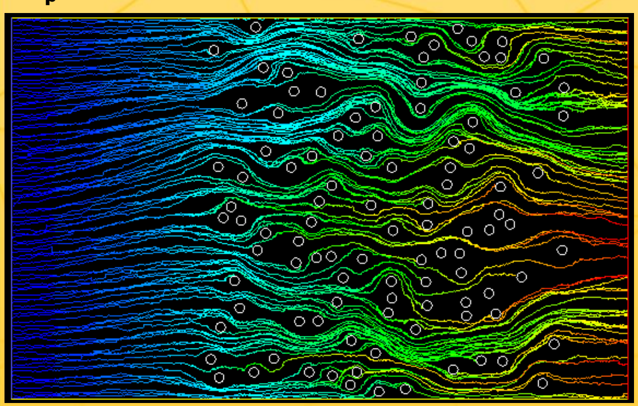
Solid volume fraction



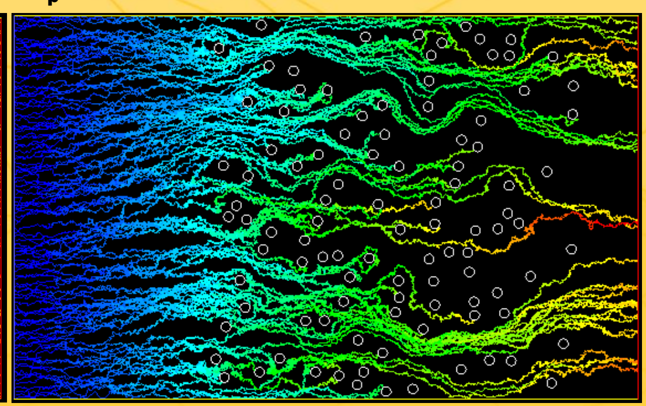
Fluid velocity



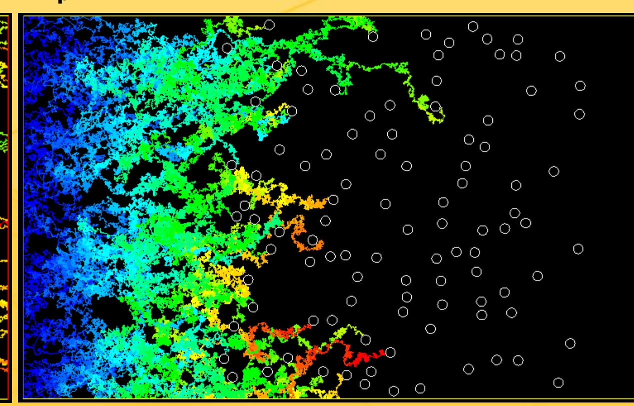
U = 0.001 m/s
D_p = 100 nm



U = 0.0001 m/s
D_p = 100 nm



U = 0.00001 m/s
D_p = 100 nm



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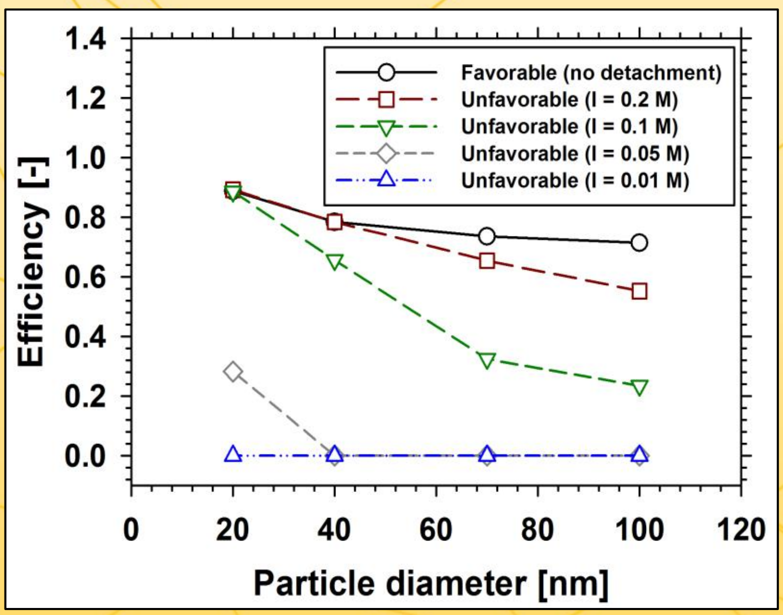
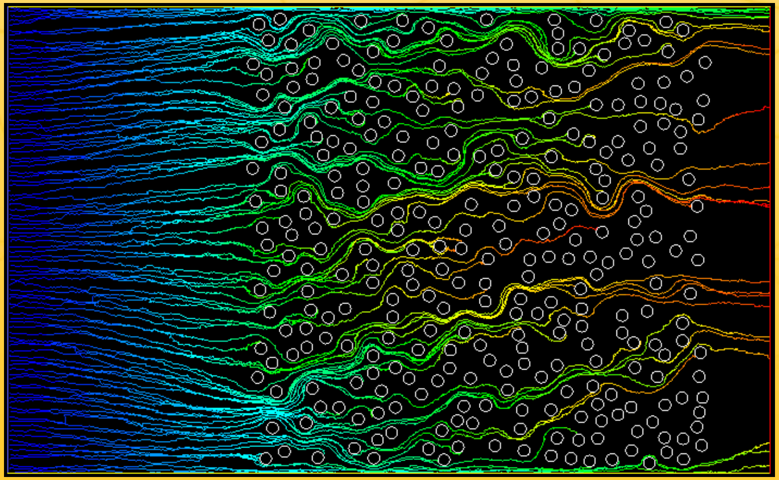
Effects of Ionic Strength

D_f = 1 μm / SVF = 15% / U = 0.001 m/s

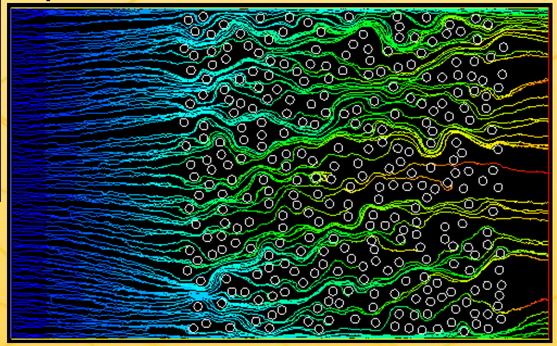


- Higher efficiency for smaller particles
- As ionic strength decreases, efficiency deceases due to the repulsion between particle and filter surfaces.
- Energy barrier decreases with higher ionic strength.

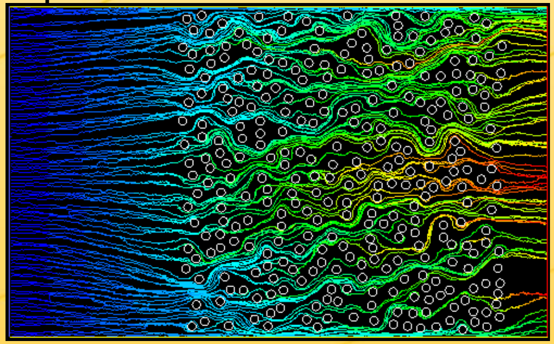
Favorable
D_p = 100 nm



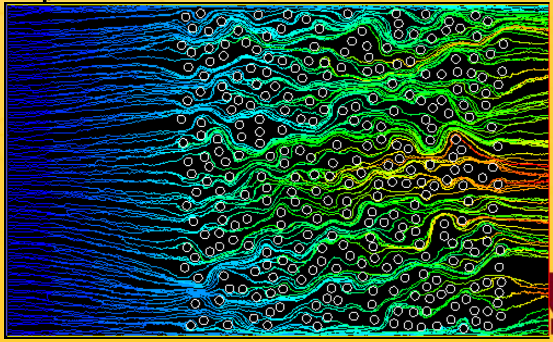
I = 0.2 M
D_p = 100 nm



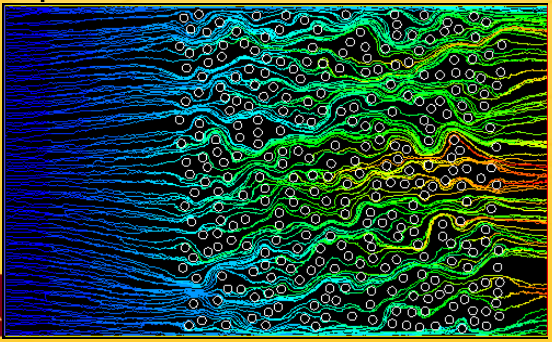
I = 0.1 M
D_p = 100 nm



I = 0.05 M
D_p = 100 nm

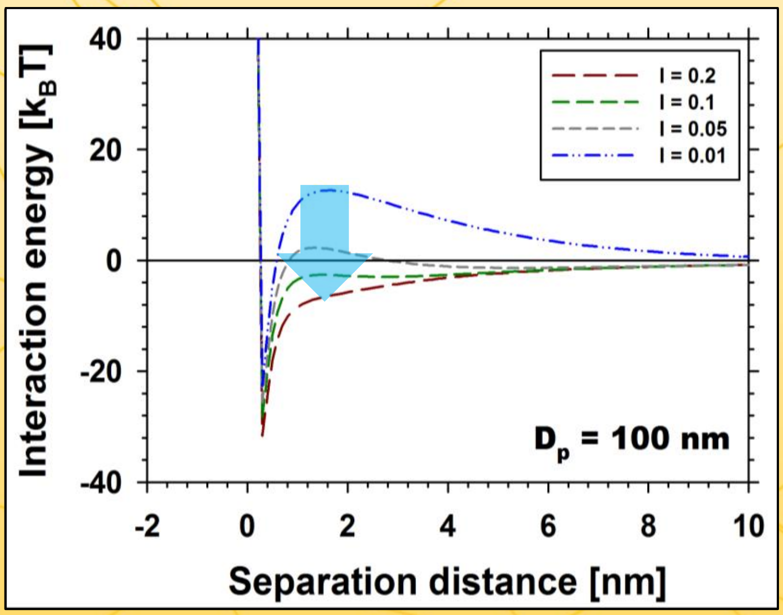


I = 0.01 M
D_p = 100 nm



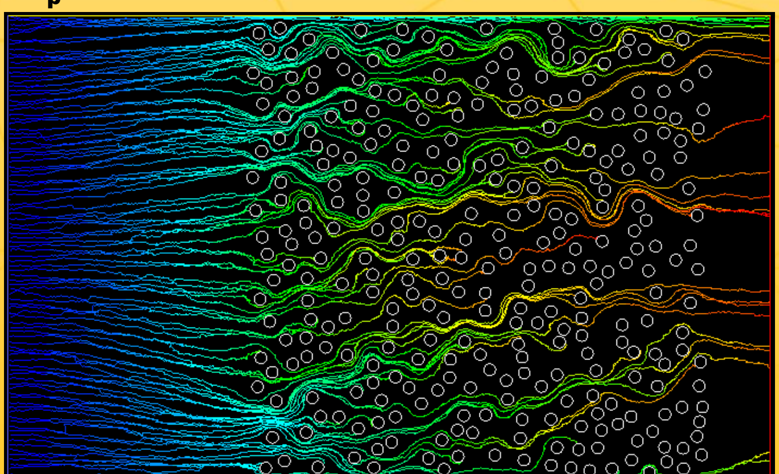
Effects of Ionic Strength

D_f = 1 µm / SVF = 15% / U = 0.001 m/s

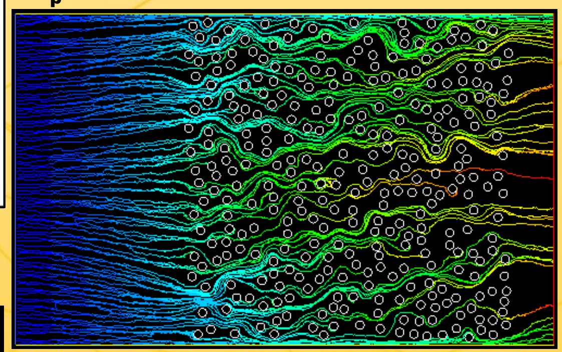


- **Higher efficiency for smaller particles**
- **As ionic strength decreases, efficiency deceases due to the repulsion between particle and filter surfaces.**
- **Energy barrier decreases with higher ionic strength.**

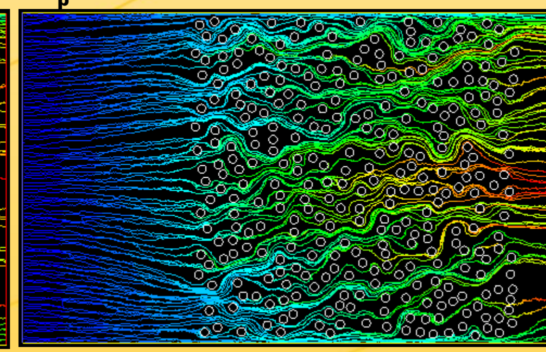
Favorable
D_p = 100 nm



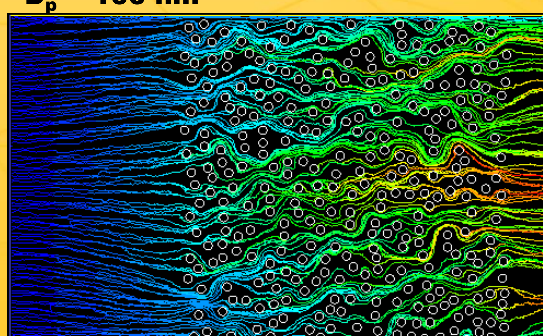
I = 0.2 M
D_p = 100 nm



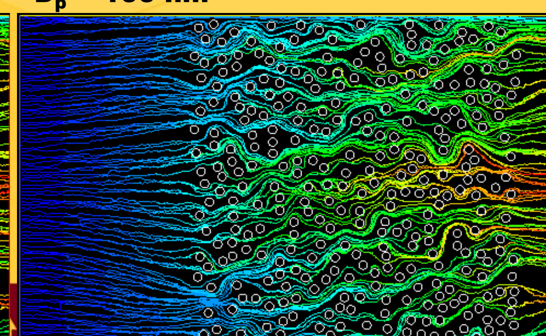
I = 0.1 M
D_p = 100 nm



I = 0.05 M
D_p = 100 nm

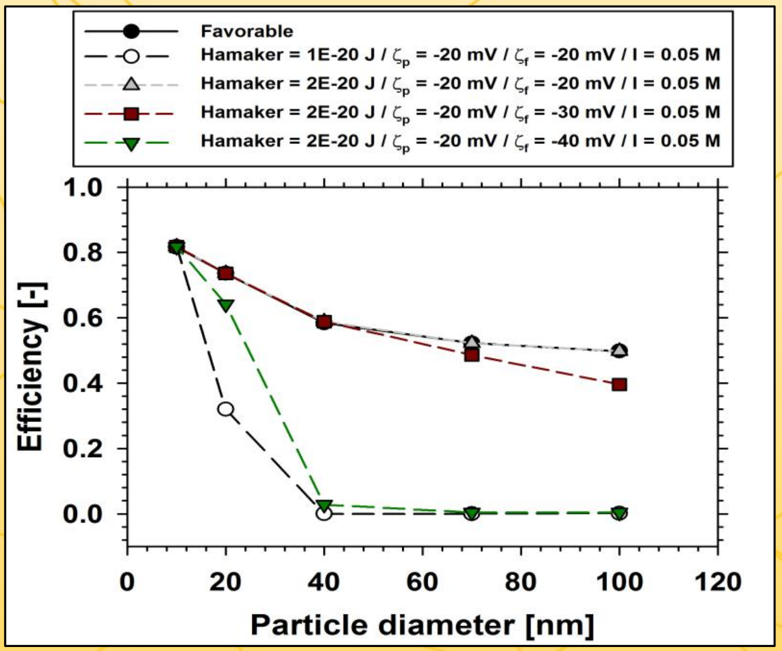


I = 0.01 M
D_p = 100 nm



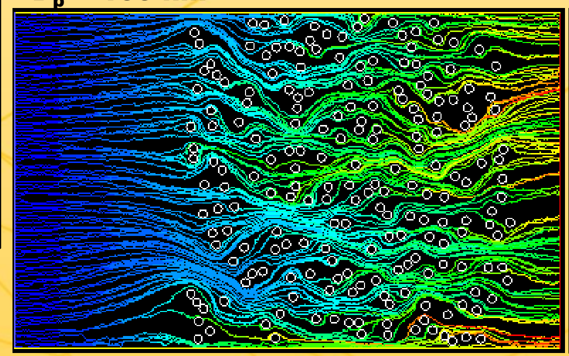
Effects of Hamaker constant and zeta potential

D_f = 1 μm / SVF = 10% / U = 0.001 m/s



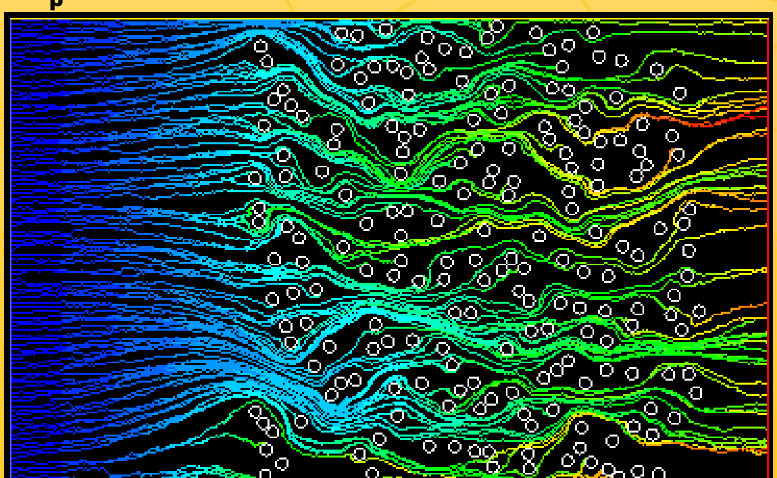
- **Higher Hamaker constant increases van der Waals attraction resulting in higher efficiency.**
- **Increasing zeta potential results in stronger repulsion between particle and filter surfaces (higher double layer force).**

Hamaker = 1E-20 J
ζ_p = -20 mV
ζ_f = -20 mV
D_p = 100 nm

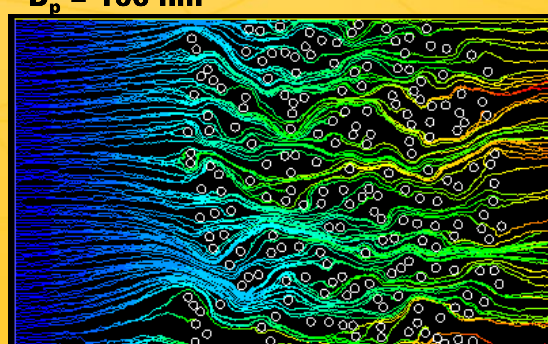


Hamaker = 2E-20 J
ζ_p = -20 mV
ζ_f = -20 mV
D_p = 100 nm

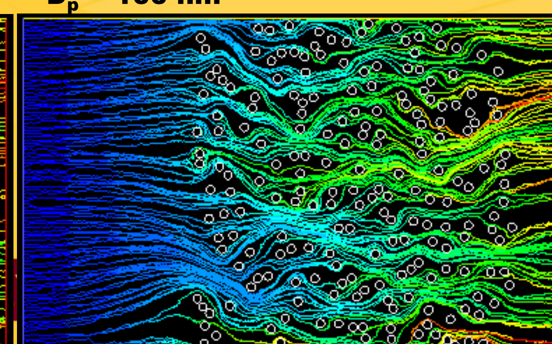
Favorable
D_p = 100 nm



Hamaker = 2E-20 J
ζ_p = -20 mV
ζ_f = -30 mV
D_p = 100 nm



Hamaker = 2E-20 J
ζ_p = -20 mV
ζ_f = -40 mV
D_p = 100 nm



Conclusion

- **Low flow velocity increases filtration efficiency due to enhanced Brownian motion and reduced hydrodynamic drag.**
- **Hydrodynamic drag significantly affects filtration efficiency due to detachment of already deposited particles.**
- **High Hamaker constant and low zeta potential increase attraction energy, which results in higher filtration efficiency.**
- **With different solution conditions and material types, filtration performance can change significantly (Efficiency can vary from 0 to 100%).**

Future Work

- **Polydisperse fiber diameters**
- **3-D CFD simulation under unfavorable condition**

THANK YOU

Q/A

APPENDIX

PART 2

CFD Simulation of Liquid Filtration in Different Conditions

Single Collector Theory

Single sphere efficiency

$$A_S = \frac{2\left(1-p^5\right)}{w}$$

$$w = 2 - 3p + 3p^5 - 2p^6$$

$$p = (1-\varepsilon_0)^{1/3}$$

Single fiber efficiency

$$A_S = \frac{(2/3)(4c_1 + c_4)}{c_1[(1/\varepsilon_s) - 2 + \varepsilon_s] + (c_4/2)(\varepsilon_s - 1 - \ln \varepsilon_s)}$$

$$c_1 = \frac{-\varepsilon_s c_4}{4} \qquad c_3 = c_1 + \frac{c_4}{2}$$

$$c_2 = -c_1 - c_3 \qquad c_4 = \frac{-4}{2\ln \varepsilon_s + 3 - 4\varepsilon_s + \varepsilon_s^2}$$

$$N_R = \frac{d_p}{d_g}$$

$$N_{Pe} = \frac{U d_g}{D_{BM}}$$

$$N_G = \frac{2\left(\rho_p - \rho_0\right) a_p^2 g}{9\mu U}$$

$$N_{vdW} = \frac{A}{k_B T}$$

$$N_{LO} = \frac{A}{9\pi\mu a_p^2 U}$$

$\varepsilon_0\,(porosity) = 1 - \varepsilon_s$

$d_g\,(or\ d_f)$

University of Minnesota