

Characterization and Assessment of Fouling Resistant Membrane Surfaces for Water and Wastewater Treatment

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Presentation Outline

- Introduction
 - Water Treatment
 - Membranes
 - Membrane Fouling
 - Objective
- Materials and Methods
 - Characterization
 - Physical
 - Chemical (XDLVO)
 - Membrane performance
- Results and Discussion
- Conclusion

Introduction – Water Treatment

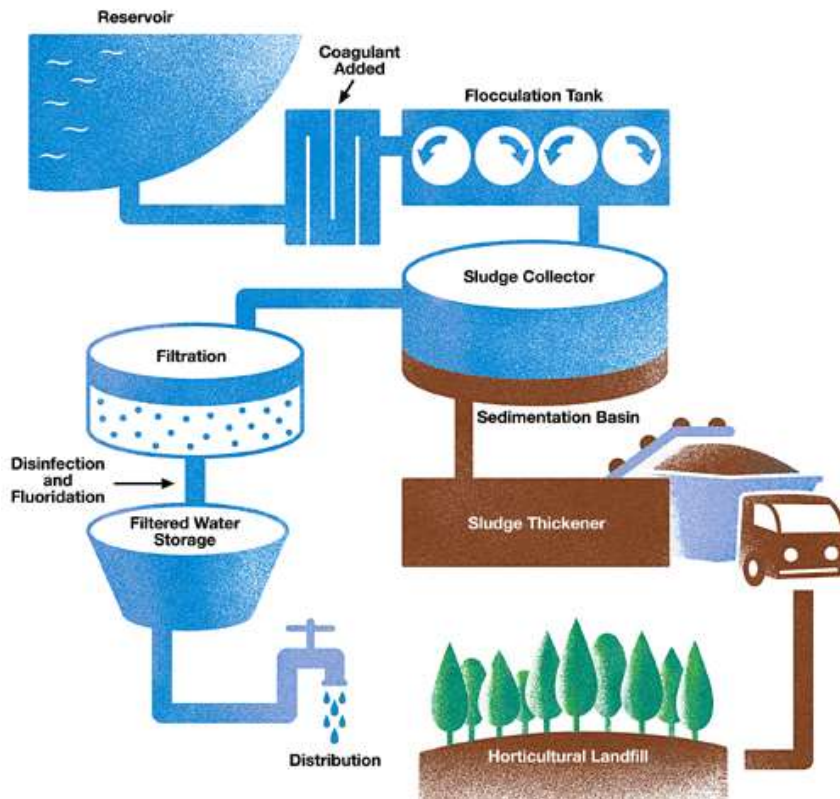
- The world faces a global water crisis as a result of continued population growth and the contamination of existing freshwater supplies
- It has been necessary to find ways of maximizing water utility, recycling being the most effective
- Treatment of wastewaters is widely applied across the globe to recycle contaminated water

Introduction – Water Treatment

- Drinking water supply involves treatment of water from fresh water sources like rivers and lakes
- Harmful substances are removed to comply with municipal or EPA drinking water standards
- Ocean waters also undergo a process known as desalination where salty water is converted to drinking water

Introduction – Water Treatment

- Water treatment involves a series of steps
- Filtration is the final step and removes any suspended particles left from previous steps
- The most common filtration media used is sand



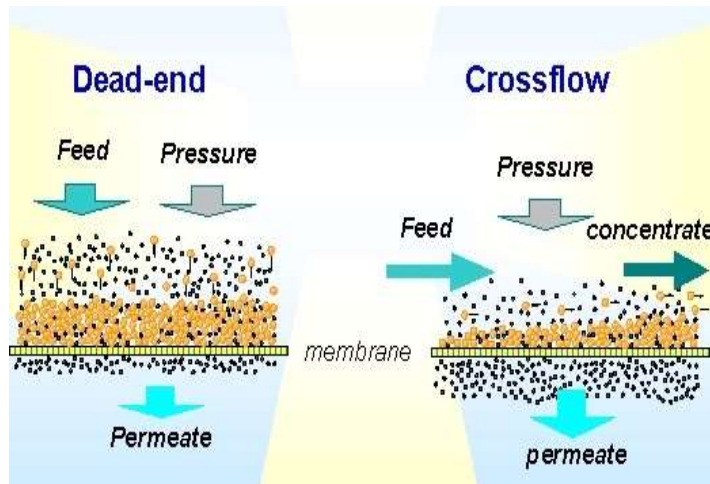
Introduction – Membranes

- In recent years, membranes have been introduced as an alternative to conventional filtration in drinking water and reuse systems
- Membranes are thin materials capable of separating substances when driving force is applied across them
- Advantages membranes have over conventional filtration are;
 - Lower capital costs
 - Superior product water quality
 - Lower chemical requirements
 - Smaller equipment footprint

Introduction – Membranes

- Membrane processes have been found to more easily meet new and more stringent drinking water regulations e.g. arsenic and disinfection by products
- Membrane separation processes are differentiated on the basis of;
 - Pore size
 - Molecular weight cut off (MWCO)
 - Mechanism by which solute is separated

Introduction – Membrane Fouling



- A major challenge facing membrane processes is fouling
- Fouling results from the deposition, adsorption and/or accumulation of rejected species on the surface
- Fouling results in the deterioration of permeate water flux and quality

Introduction - Fouling

- Fouling mechanisms vary based on physical and chemical properties of the membrane
- Chemical properties include
 - Surface charge
 - Hydrophobicity/ Hydrophilicity
- Physical properties include;
 - Pore size
 - Surface roughness

Introduction - Membranes

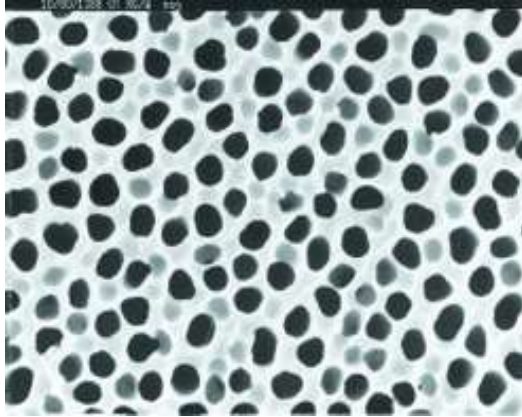
- Two general approaches can be used to alleviate fouling;
 - Pretreatment of the feed waters to get rid of substances that are known to dominate fouling in the system
 - Development of materials and surfaces that are less susceptible to fouling
- However, fouling mitigation is further complicated by the great diversity of foulants and characteristics that exist in any system

Introduction - Objective

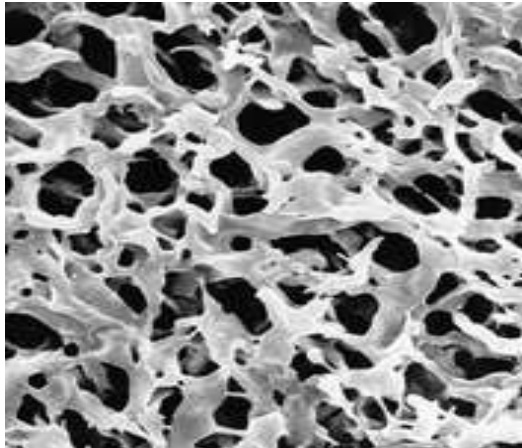
- This project evaluated the abilities of two new nanostructured surface coatings, diamond-like carbon (DLC) and hydroxyapatite, for mitigating fouling of ceramic membranes (alumina)

Materials and Methods

Alumina



Durapore



- Anodized alumina membranes were used as the support substrate onto which HA and DLC were deposited
- Pulsed laser deposition (PLD) was used to deposit the coatings
- Durapore membranes made from polyvinylidene fluoride (PVDF)
- Bovine serum albumin (BSA) was used as the model foulant

Materials and methods

Surface properties and their associated measuring equipment

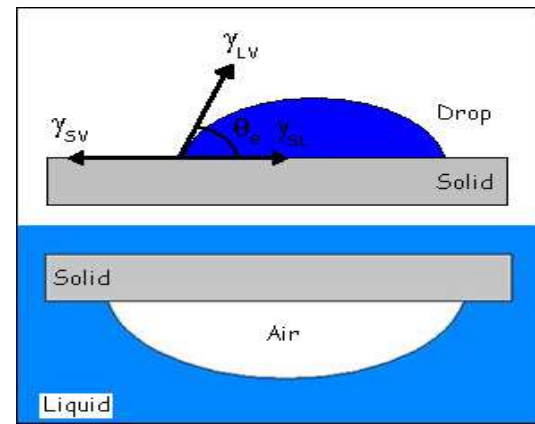
Properties	Measuring Equipment
Surface Roughness / Pore Size	Atomic Force Microscopy (AFM)
Hydrophobicity / Hydrophilicity	Geniometer (KrÜss Scientific)
Surface Charge	Streaming Potential Analyzer
Membrane Performance	Dead-end stirred filtration cell (Sterlitech)

Materials and Methods

- Contact angle measurements were taken using 3 probe liquids; DDW, formamide and diiodomethane
- The surface energy parameters for each of the surfaces of interest, calculated using the Extended Young equation:

$$(1 + \cos \theta) \gamma_l^{TOT} = 2 \left(\sqrt{\gamma_s^{LW} \gamma_l^{LW}} + \sqrt{\gamma_s^+ \gamma_l^-} + \sqrt{\gamma_s^- \gamma_l^+} \right)$$

- The free energy of interaction determined from these parameters can then be used to judge the hydrophobicity/hydrophilicity of the samples



Materials and Methods

- Using the contact angle measurements, the following interaction energies between the foulant and surfaces were determined;
 - Lifshitz-van der Waals (LW)
 - Electrostatic (EL)
 - Acid-base (AB)
- The total interaction forces between membranes and colloids are calculated as follows using the extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory:
$$U^{\text{Tot}} = U^{\text{EL}} + E^{\text{LW}} + U^{\text{AB}}$$
- Force plots were then generated based on the XDLVO theory

Materials and Methods



- Dead end filtration was used to evaluate membrane performance
- Permeate flux was observed as a function of time
- The mass balance and pressure transducer were interfaced with a computer allowing real time monitoring
- Membrane fouling was investigated at a fixed ionic strength ($I=0.01\text{M NaCl}$) and constant BSA concentration (100mg/L)

Materials and Methods

- Doubly deionized water (DDW) was first run through the system to determine the pure water flux of the membranes
- A constant flux at which to run fouling tests on all the membranes was determined – each membrane had a unique operating pressure at this flux
- Fouling tests were then run for each individual membrane at its predetermined operating pressure
- The performance of the membrane was judged by how much the permeate flux changed after fouling

Results and Discussion

Select physical properties of the studied membranes

Membrane	Thickness nm	Average Pore Size μm	Material(s) of Construction
Durapore	150	0.22	PVDF
Unmodified Anodisk	100	0.20	Alumina
HA	100	0.12	Alumina/HA
DLC	100	0.12	Alumina/DLC

Results and Discussion

AFM membrane surface roughness statistics for each of the studied membranes

	Unmodified Anodisk	HA	DLC	Durapore®
Avg. Roughness (nm)	102.97	48.03	57.15	45.32
Root Mean Square Roughness (nm)	127.98	62.96	73.92	55.41
Surface Area (μm^2)	81.01	48.19	53.95	53.88
Surface Area Difference (%)	225.30	93.89	116.22	116.78

Results and Discussion

Surface potentials for the protein and membrane surfaces

Colloid/Membranes	Surface Charge (mV)
BSA	-9.7
DLC ¹	-14
HA ²	-8
Durapore	-20

Results and Discussion

Contact angle results for the protein and membrane surfaces

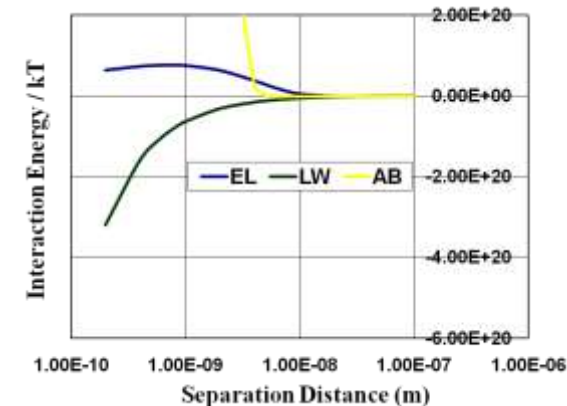
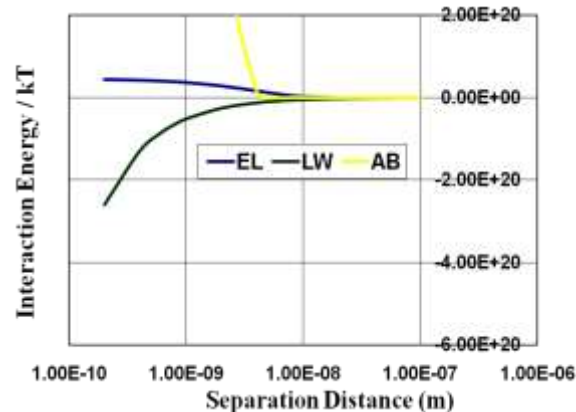
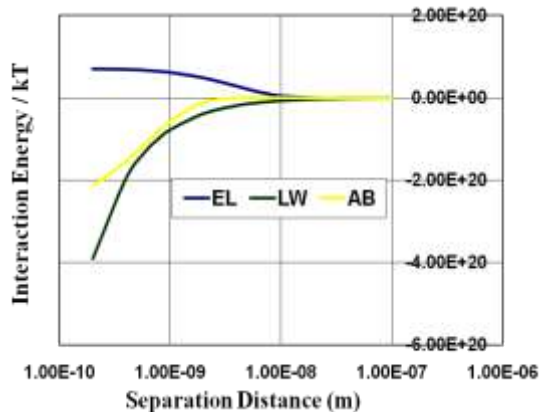
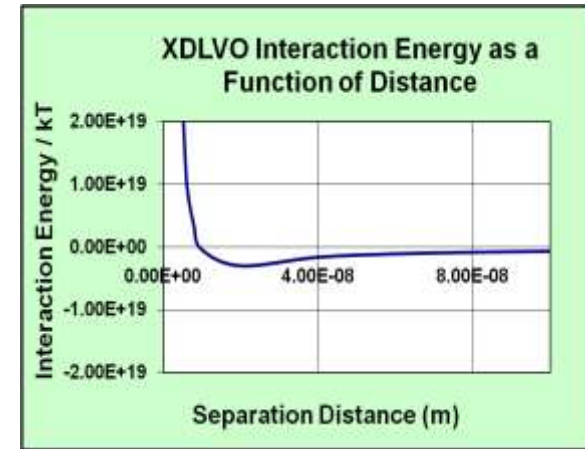
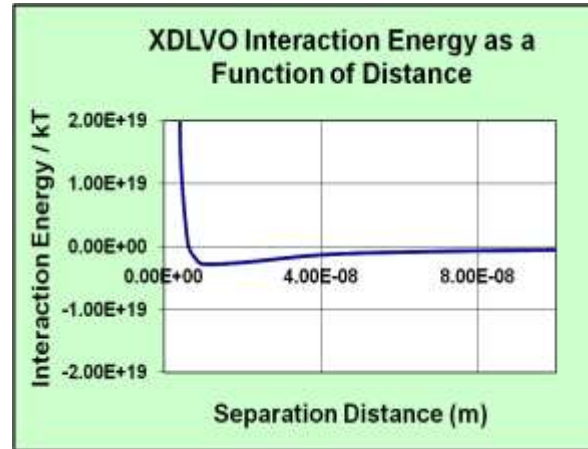
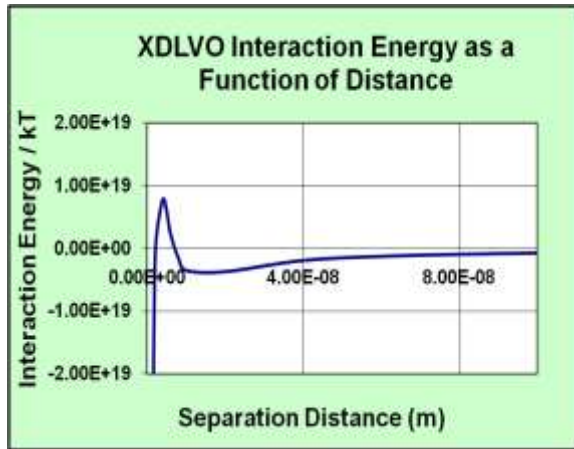
	DDW	Diiodo-methane	Form-amide
BSA protein	18.0°	39.0°	31.0°
DLC	70.8°	42.7°	43.4°
HA	61.1°	53.6°	55.4°
Durapore	31.9°	48.9°	40.6°

Membrane and protein surface energy parameters (mJ/m²) at 20°C

	γ^{LW}	γ^+	γ^-	γ^{AB}	γ^{TOT}	ΔG^{SWS}
BSA protein	40.1	0.2	61.0	6.3	46.4	45.7
DLC	38.2	1.4	7.2	6.3	44.5	-41.2
HA	32.2	0.1	25.7	3.8	36.0	-1.7
Durapore	34.9	0.2	54.7	7.0	41.9	39.9

Results and Discussion

Interfacial interaction energies as a function of separation distance for the membranes and BSA protein ($I = 0.01$ M NaCl; $\text{pH} = 5.9$; $T = 20^\circ\text{C}$)



DLC

HA

Durapore

Results and Discussion

Summarized membrane performance and fouling results

Membrane	Operating pressure psig	Initial Pure Water Flux m³/m².day	Final Pure Water Flux m³/m².day	Flux Loss %
Unmodified Anodisk	33.33	256.63	167.65	-34.67
Diamond-like Carbon	25.64	202.19	110.87	-45.17
Hydroxyapatite	24.07	190.03	158.24	-16.73
Durapore	19.90	202.50	182.29	-9.98

* All membranes were operated at a starting flux of 200 m³/m².day prior to each fouling test

Conclusion

- Based on the XDLVO models obtained for each membrane surface, DLC would be expected to be most susceptible to protein fouling
- The hydroxyapatite surface coating appears to improve the resistance to protein fouling of the alumina anodisks studied
- This is attributed to an improvement in the interaction between the membrane surface and the BSA molecules

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QUESTIONS?

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