혼성 막여과 공정을 이용한 철/망간의 제거 및 막오염 평가

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Fe/Mn Removal and Membrane Fouling in Combined Chlorination/UF Systems for Drinking Water Treatment

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Fe/Mn in Water Sources

- Fe/Mn impart color, and can lead to staining of washing
- They can exist in different oxidation states (Fe^{2+}/Fe^{3+}; Mn^{2+}/Mn^{4+})
- Groundwater and water from the low level of reservoirs often contain the reduced soluble forms
- Current Regulations: Fe/Mn < 0.3 mg/L

How to Control Fe/Mn?

- Oxidation by air; oxidation of Mn^{2+} is relatively slow, so oxidizing agents (O_3, H_2O_2, Cl_2, and $KMnO_4$) are used.
- Biological filtration; depending on HRT and background species
- Use of ion exchange resins; not selective
- Reverse osmosis; nanofiltration; energy-consuming

UF in Combination with Chlorination

- UF can control pathogenic microorganisms and some natural organic matter (NOM)
- However, UF alone can not remove dissolved ions including iron and manganese
- Conjunctive use of chlorination and UF can help enhance iron and manganese removal

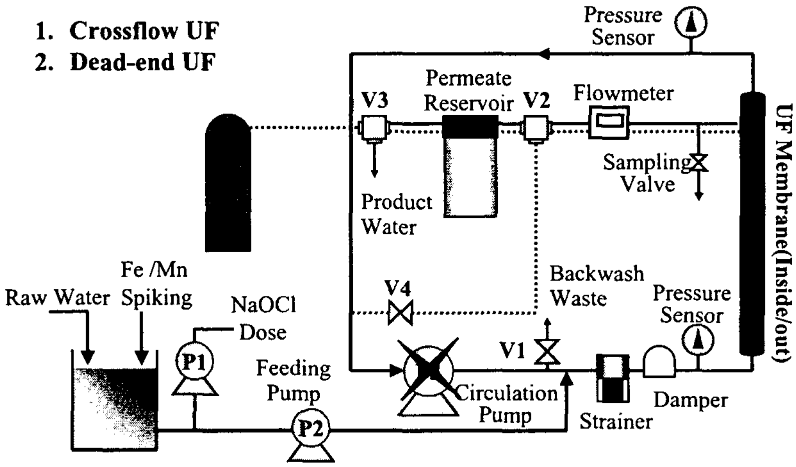
Oxidation of Fe^{2+}/Mn^{2+} by Chorine

- $2Fe(HCO_3)_2 + Ca(HCO_3)_2 + Cl_2$
  $\rightarrow \underline{2Fe(OH)_3}(s) + CaCl_2 + 6CO_2$
- $Mn(HCO_3)_2 + Ca(HCO_3)_2 + Cl_2$
  $\rightarrow \underline{MnO_2(s)} + CaCl_2 + 4CO_2 + 2H_2O$

Outline

- To examine the effect of chlorine dosages on iron and manganese removal in Cl/UF
- To evaluate the effect of UF modes on treatment efficiency and membrane permeability
- To illuminate membrane fouling mechanisms by oxidized Fe/Mn particles

UF System with Prechlorination for On-Site Tests



Characteristics of UF Membrane

Configuration	Hollow Fiber
MWCO, Dalton	100,000
Nominal Pore Size, nm	~10
Material	Cellulose Acetate
I.D. of Membrane Fiber, mm	0.93
Module Length, m	1.2
Number of Fibers per Module	10
Surface Area, m^2	0.035

Membrane Operation

Permeate Flux	69 L/m^2-h (40 mL/min; 58 L/day)
Operation Type	Crossflow (1.0 m/sec) Dead-end Inside/out
Cycle (40 min)	Permeation, 39 min 24 sec Flush, 3 sec Backwash, 30 sec Flush, 3 sec
Water Recovery	91.0%

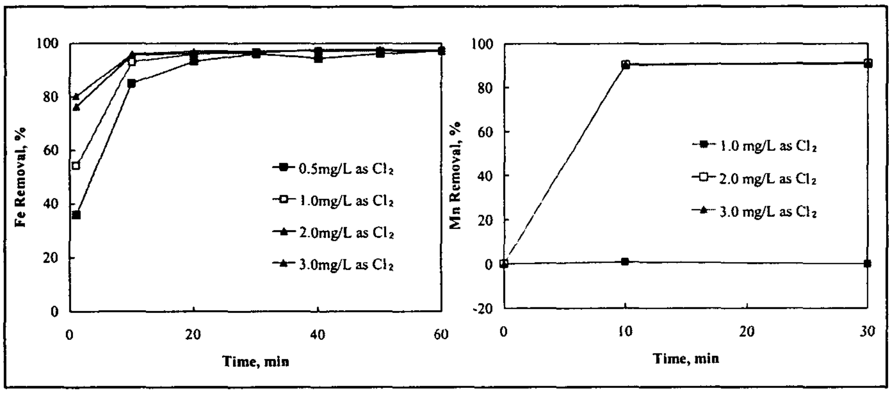
Water Quality of Sources Tested

Parameter	Raw Water	Filtered Water*
pH	6.9-7.3	6.9-7.3
Temperature, ℃	6.9-14.5	7.5-10.9
Turbidity, NTU	1.0-93.0	0.2
Alkalinity, mg/L as $CaCO_3$	12.8-15.4	12.3
Fe, mg/L	<0.1	ND
Mn, mg/L	ND	ND
DOC, mg/L	1.39-3.45	1.14-1.98
UV_{254}, cm^{-1}	0.017-0.033	0.014-0.040
$SUVA_{254}$, L/mg-m	0.64-3.69	0.71-3.34

*Obtained from Sand Filters

Removal of Fe/Mn with Time at Different Chlorine Dosage

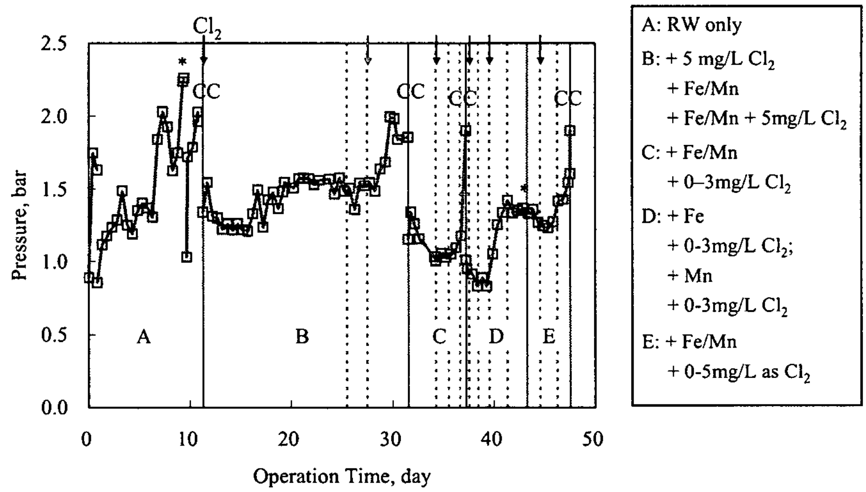
- Initial Fe, 1.0 mg/L; Mn, 0.5 mg/L
- 0.45 μm Filtrate



Summary of Operating Conditions and Removal Efficiency by Crossflow UF

Phase	Time Period day	Feedwater							Chorine Dose mg Cl_2/L	Removal, %				
		Source	pH	Fe mg/L	Mn mg/L	Turb. NTU	UV_{254} cm^{-1}	DOC mg/L		Fe	Mn	Turb.	UV_{254}	DOC
A	0 - 11	RW	7.0	0.0	0.0	2.0	0.022	1.9	0.0	-	-	83	0	14
B1	11 - 25	RW	7.3	0.0	0.0	1.1	0.019	2.2	5.0	-	-	73	19	22
B2	25 - 27	RW	6.9	0.9	0.4	2.4	0.065	1.7	0.0	79	-13	93	66	30
B3	27 - 32	RW	7.0	1.0	0.5	4.2	0.045	2.3	5.5	75	96	98	73	14
C1	32 - 34	RW	7.0	1.0	0.5	5.0	0.049	2.8	0.0	84	4	96	37	19
C2	34 - 36	RW	7.0	0.7	0.4	3.6	0.051	2.2	0.5	75	5	96	47	28
C3	36 - 37	RW	7.1	1.0	0.5	5.9	0.059	2.7	1.3	73	14	96	55	13
C4	37 - 37	RW	7.1	1.0	0.5	5.9	0.059	2.7	3.0	82	81	97	53	24
D1	37 - 38	RW	7.1	1.1	0.0	6.3	0.052	1.6	0.0	86	-	96	34	-
D2	38 - 38	RW	7.1	1.1	0.0	6.3	0.052	1.6	3.0	90	-	97	73	-
D3	38 - 40	RW	7.2	0.0	0.6	8.7	0.025	1.6	0.0	-	8	98	19	27
D4	40 - 41	RW	7.2	0.0	0.5	7.4	0.025	1.2	3.1	-	31	98	31	29
D5	41 - 43	RW	7.0	0.4	0.6	8.6	0.025	1.2	0.0	66	31	98	20	17
E1	43 - 45	RW	6.8	1.0	0.5	6.3	0.062	1.2	0.0	90	2	98	73	27
E2	45 - 46	RW	6.8	1.0	0.5	8.9	0.057	1.9	3.0	92	81	98	74	34
E3	46 - 48	RW	6.8	1.0	0.5	9.9	0.050	1.9	4.8	91	99	99	75	39

Variation of Transmembrane Pressure with Time in Crossflow UF

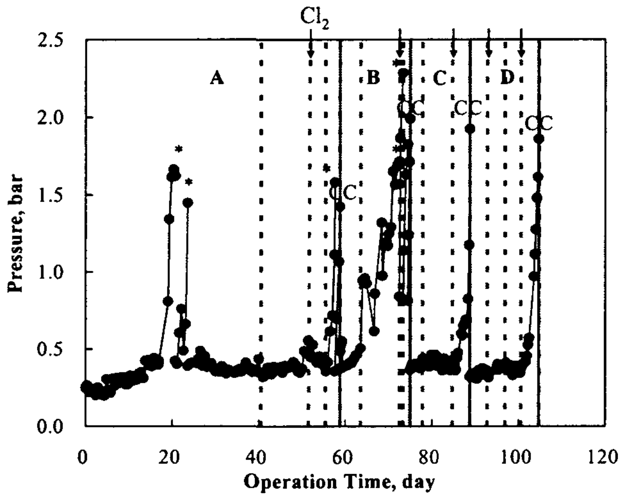


Summary of Operating Conditions and Removal Efficiency by Dead-end UF

Phase	Time Period day	Feedwater							Chorine Dose	Removal, %				
		Source	pH	Fe mg/L	Mn mg/L	Turb. NTU	UV_{254} cm^{-1}	DOC mg/L	mg Cl_2/L	Fe	Mn	Turb.	UV_{254}	DOC
A1	0 - 40	RW	6.9	0.1	0.1	7	0.02	1.5	0.0	-	-	95	9	12
A2	40 - 52	RW	6.6	1.0	0.6	20	0.05	1.8	0.0	97	36	99	39	26
A3	52 - 55	RW	6.7	0.6	0.4	12	0.05	1.8	1.0	97	26	99	55	16
A4	55 - 59	RW	6.7	0.9	0.5	18	0.07	2.2	3.0	87	81	99	63	13
B1	59 - 64	RW	6.5	0.0	0.0	20	0.08	2.4	0.0	-	-	99	65	11
B2	64 - 73	RW	7.0	1.0	0.5	21	0.07	2.5	0.0	98	7	99	47	24
B3	73 - 73	RW	6.9	1.0	0.5	21	0.08	2.8	3.0	-	-	-	-	-
B4	73 - 75	RW	6.9	1.0	0.5	21	0.09	3.8	0.0	-	-	-	-	-
C1	75 - 78	FW	7.1	0.0	0.0	0.2	0.02	1.7	0.0	-	-	-31	-6	8
C2	78 - 85	FW	7.1	1.0	0.5	0.2	0.02	1.2	0.0	100	1	40	7	7
C3	85 - 89	FW	6.8	1.0	0.5	0.7	0.02	1.3	3.0	99	86	50	16	0
D1	89 - 93	FW	7.0	1.0	0.0	0.5	0.05	2.0	0.0	97	-	68	4	15
D2	93 - 97	FW	7.1	1.0	0.0	0.3	0.04	1.6	3.0	99	-	60	10	9
D3	97 - 101	FW	7.1	0.0	0.5	0.2	0.02	1.7	0.0	-	5	63	6	-7
D4	101 - 105	FW	7.0	0.0	0.5	0.2	0.02	1.2	3.0	-	84	36	15	11

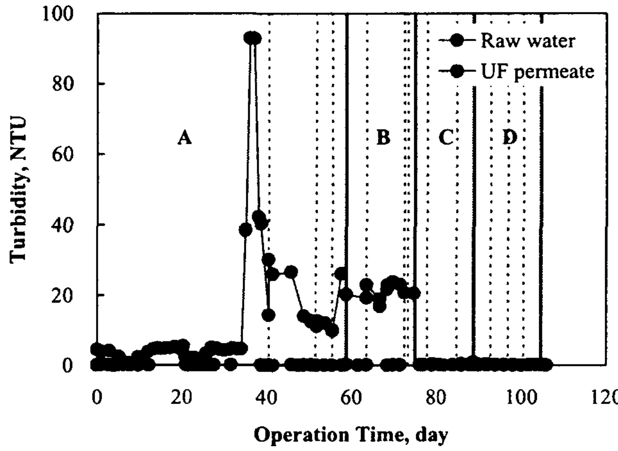
RW: Raw Water
FW: Filtered Water

Variation of Transmembrane Pressure with Time in Dead-end UF



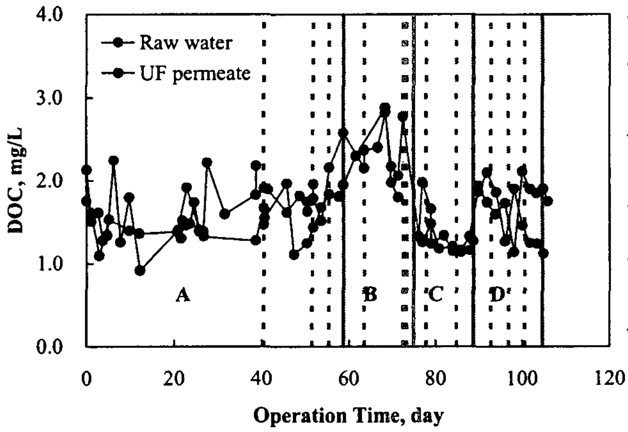
Phase	Feed Water	Fe, mg/L	Mn, mg/L	Chlorine Dose, mg Cl_2/L
A1	RW	No	No	No
A2	RW	1	0.5	No
A3	RW	1	0.5	1
A4	RW	1	0.5	3
B1	RW	No	No	No
B2	RW	1	0.5	No
B3	RW	1	0.5	3
B4	RW	1	0.5	No
C1	FW	No	No	No
C2	FW	1	0.5	No
C3	FW	1	0.5	3
D1	FW	1	No	No
D2	FW	1	No	3
D3	FW	No	0.5	No
D4	FW	No	0.5	3

Variation of Turbidity with Time in Dead-end UF



Phase	Feed Water	Fe, mg/L	Mn, mg/L	Chlorine Dose, mg Cl_2/L
A1	RW	No	No	No
A2	RW	1	0.5	No
A3	RW	1	0.5	1
A4	RW	1	0.5	3
B1	RW	No	No	No
B2	RW	1	0.5	No
B3	RW	1	0.5	3
B4	RW	1	0.5	No
C1	FW	No	No	No
C2	FW	1	0.5	No
C3	FW	1	0.5	3
D1	FW	1	No	No
D2	FW	1	No	3
D3	FW	No	0.5	No
D4	FW	No	0.5	3

Variation of DOC with Time in Dead-end UF



Phase	Feed Water	Fe, mg/L	Mn, mg/L	Chlorine Dose, mg Cl_2/L
A1	RW	No	No	No
A2	RW	1	0.5	No
A3	RW	1	0.5	1
A4	RW	1	0.5	3
B1	RW	No	No	No
B2	RW	1	0.5	No
B3	RW	1	0.5	3
B4	RW	1	0.5	No
C1	FW	No	No	No
C2	FW	1	0.5	No
C3	FW	1	0.5	3
D1	FW	1	No	No
D2	FW	1	No	3
D3	FW	No	0.5	No
D4	FW	No	0.5	3

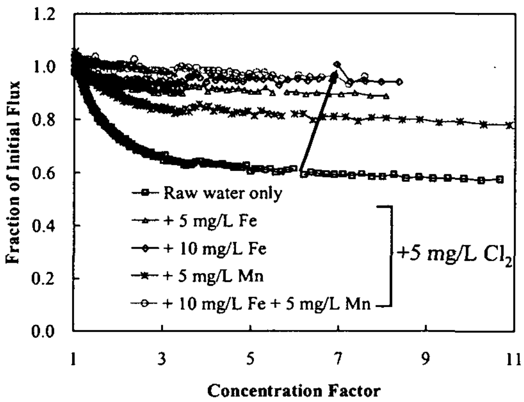
Summary

- Substantial Mn removal (>81%) was achieved at a Cl_2 dosage of > 3 mg/L; Fe removal efficiency was >70% without Cl_2.
- Fe/Mn precipitates formed by chlorination also contributed to an increase in turbidity and NOM removal.
- Oxidized Mn seemed more responsible for membrane fouling in on-site UF than Fe oxides.

Why
Is Mn Causing
Membrane Fouling
More Seriously
than Fe?

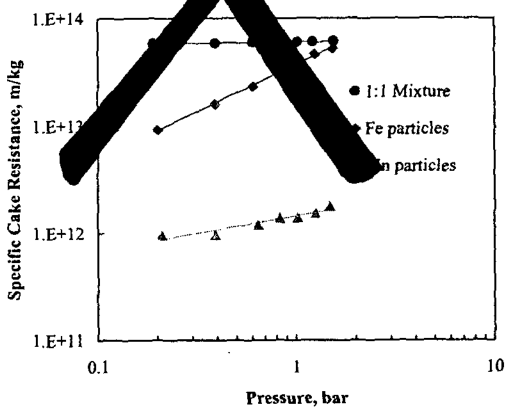
Effect of Fe/Mn on Stirred Flow UF Permeability

- Stirred Cell UF
- Pressure, 1 bar; 160 rpm



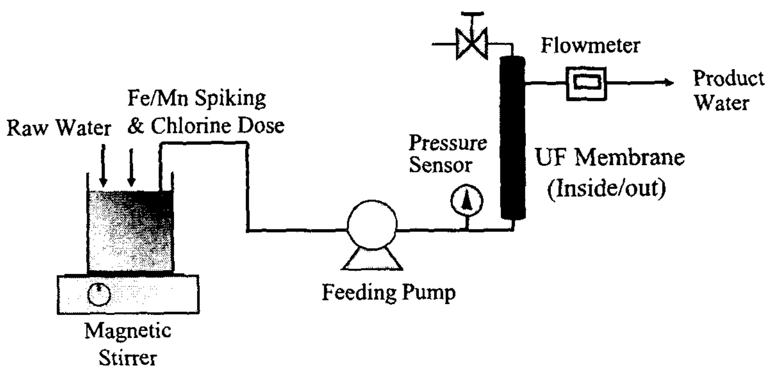
Specific Cake Resistance of Fe/Mn Particles and the 1:1 Mixture

- Cake Mass: Fe, 100 mg; Mn, 100 mg

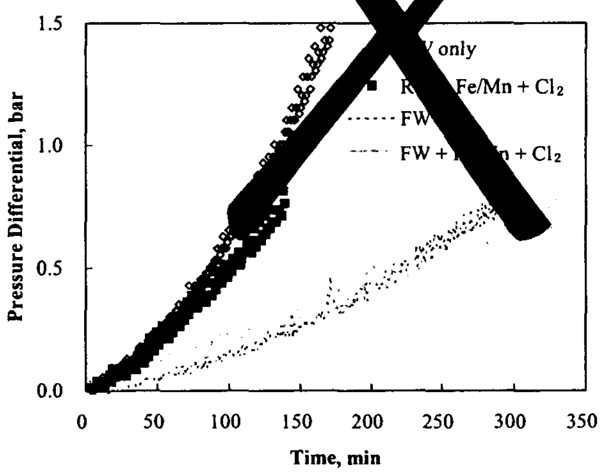


Single Hollow Fiber UF; but Not Backwashed

- Constant Flux: 120 L/m^2-h (1.90 mL/min)
- Dead-end Operation



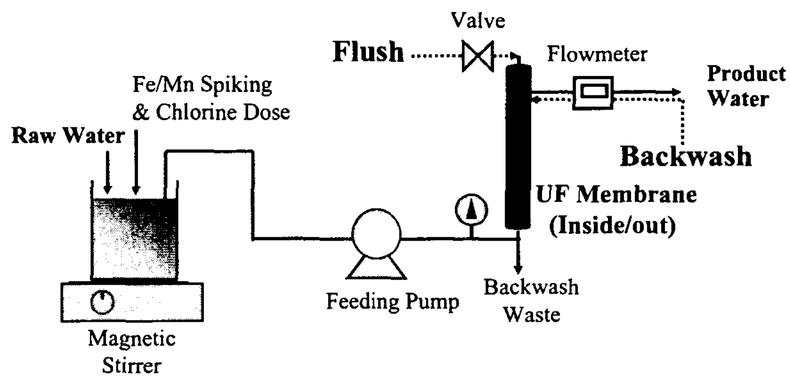
Effect of Fe/Mn on Pressure Build-up during Single Hollow Fiber UF



RW: Raw Water
FW: 0.45-μm MF Permeate
Fe: 1.0 mg/L Fe
Mn: 0.5 mg/L Mn
Cl_2: 5 mg Cl_2/L

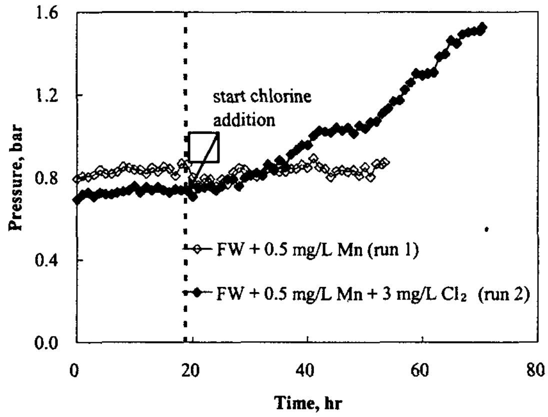
Single Hollow Fiber UF with Backwashing

- Constant Flux: 150 L/m^2-h (1.90 mL/min)
- Backwashing: every 40 min

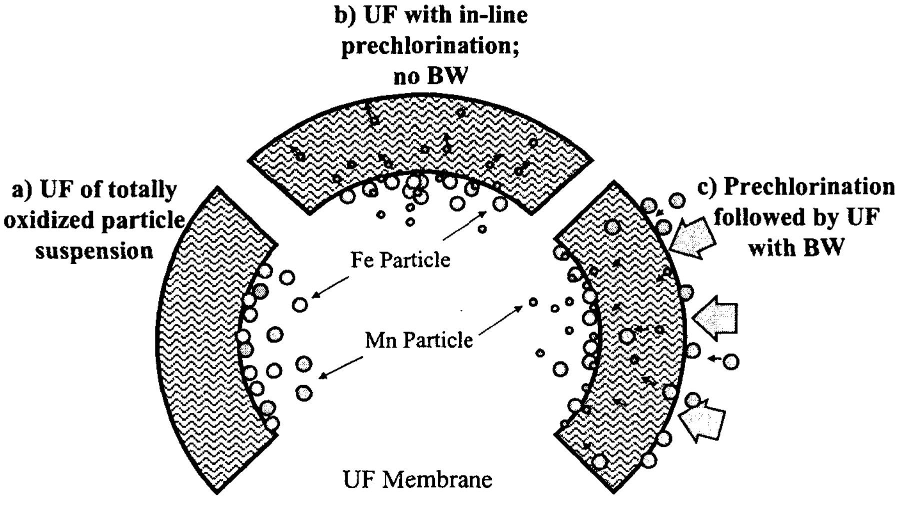


Membrane Fouling Behavior with Backwashing

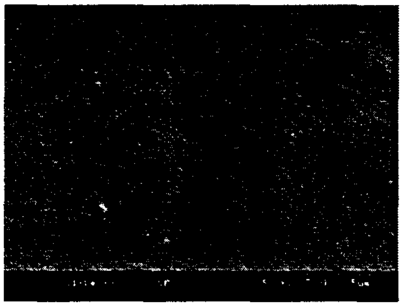
- Flux: 150 L/m²-h; FW: 0.45 μm-MF Perme
- Flush, 3 s; BW, 30 s; Flush, 3 s

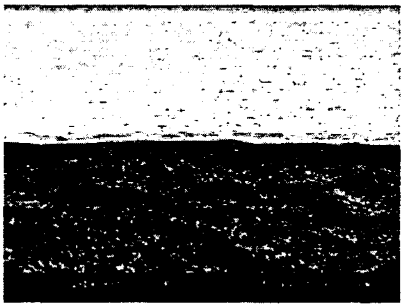


Possible Fouling Mechanisms during Chlorination/UF



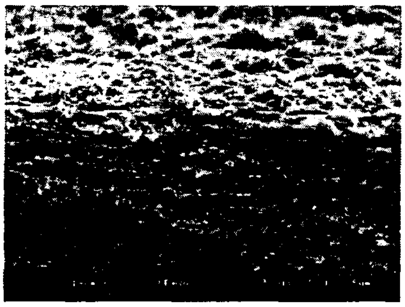
SEM Pictures of Virgin UF Membrane





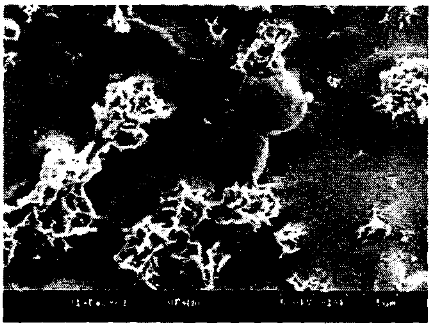
Inside Outside

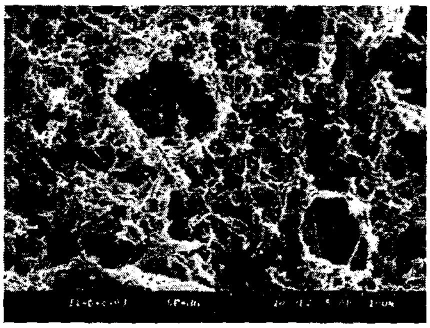
SEM Pictures of Used UF Membrane



Inside Outside

SEM Pictures of Used UF Membrane (Outside)





Summary

- Oxidized Mn and Fe retained by UF did not cause membrane fouling, but reduced it.
- Periodic backwashing rather aggravated fouling due to the deposition of Mn oxides on the outside, which was associated with oxidation kinetics.