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A Hybrid (Membrane/Biological) System to Remove Perchlorate From Drinking Waters

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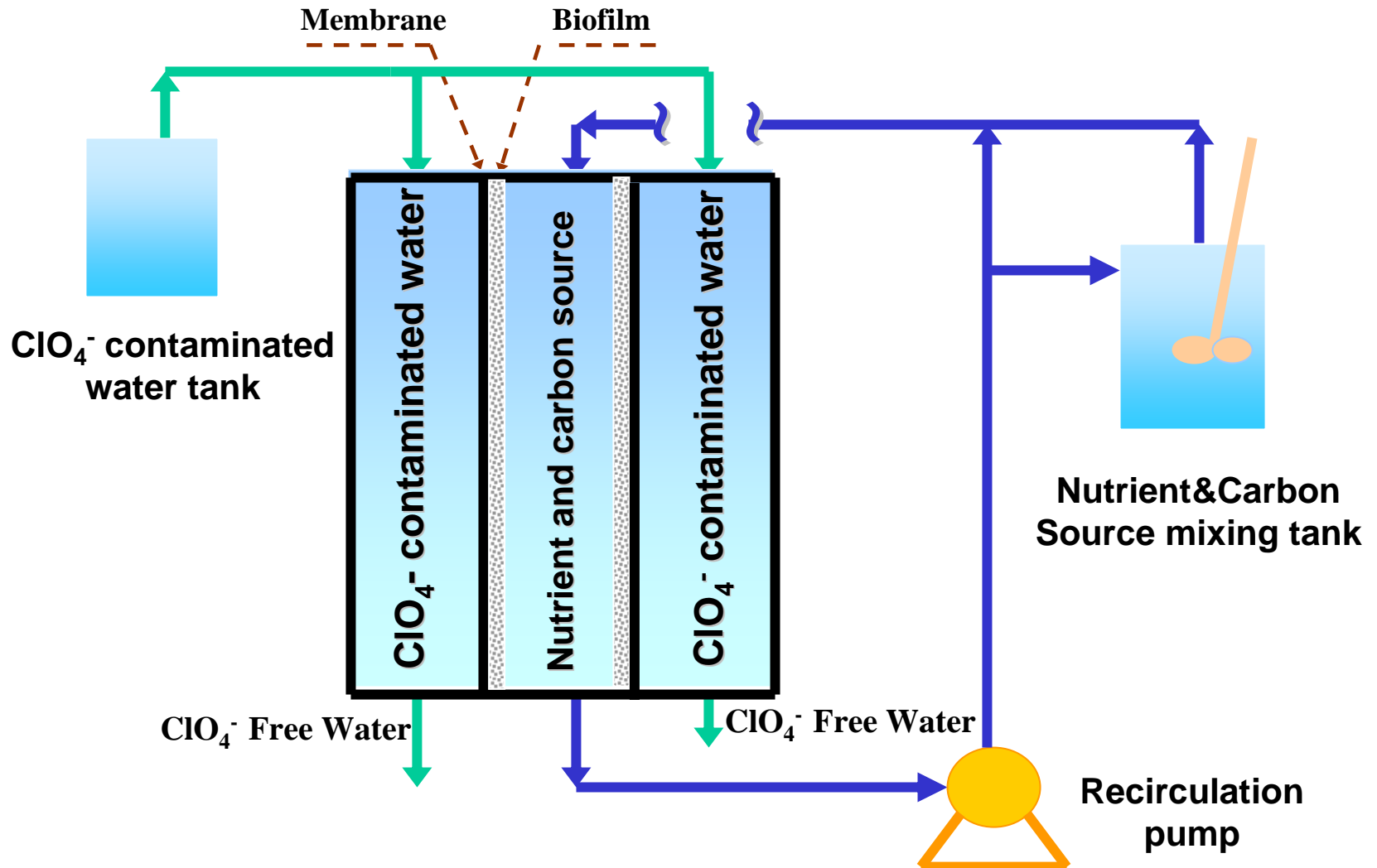
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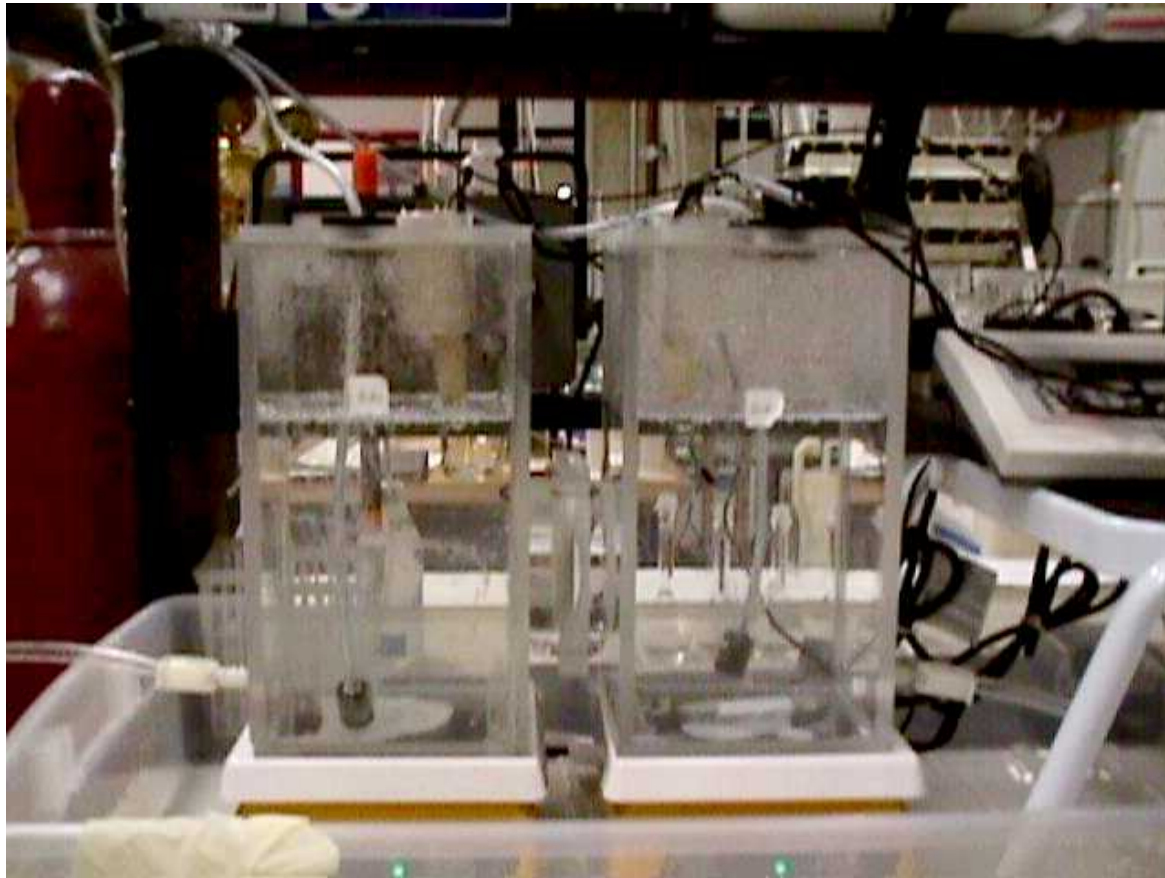
BACKGROUND

- **Perchlorate is readily biodegradable.**
- **Perchlorate can diffuse through membranes.**
- **Perchlorate degrading biofilms can attach to membranes.**
- **Reactor design separates microbes from treated drinking water.**
- **Studies on the suitability of different reactor designs to biologically remove perchlorate from waters is needed.**

Potential Process Flowsheet for Perchlorate Removal using a Membrane-Immobilized Biofilm



MEMBRANE-IMMOBILIZED BIOFILM REACTOR SET-UP



EXPERIMENTAL INVESTIGATION

- **Enrichment of perchlorate biodegrading culture.**
- **Diffusion coefficient of perchlorate and other anions (nitrate and sulfate).**
- **Perchlorate biodegradation rates.**
- **Carbon source limitation.**
- **Factors affecting ClO_4^- biodegradation.**

ENRICHMENT CULTURE FROM WWTP, LV (“BALI”)

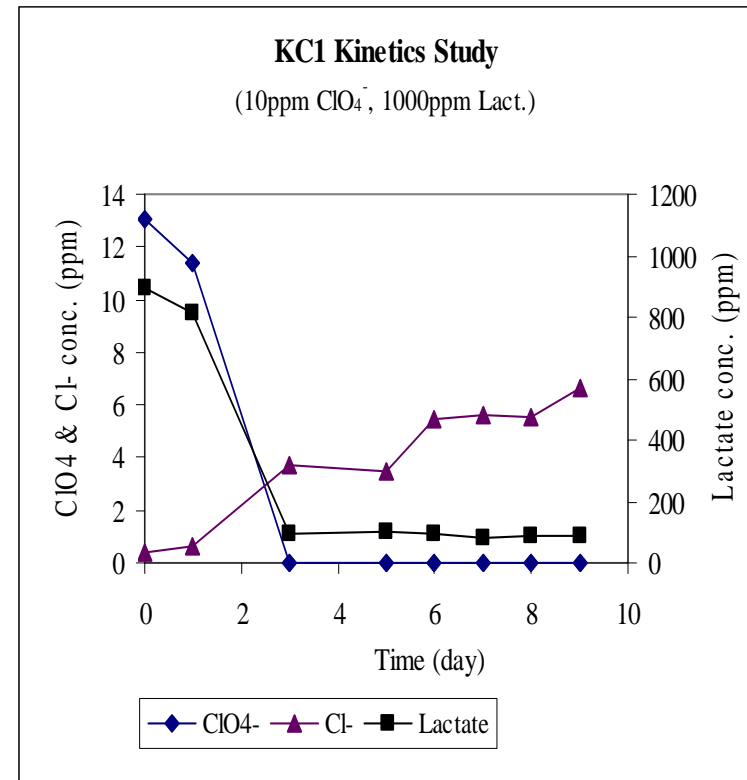
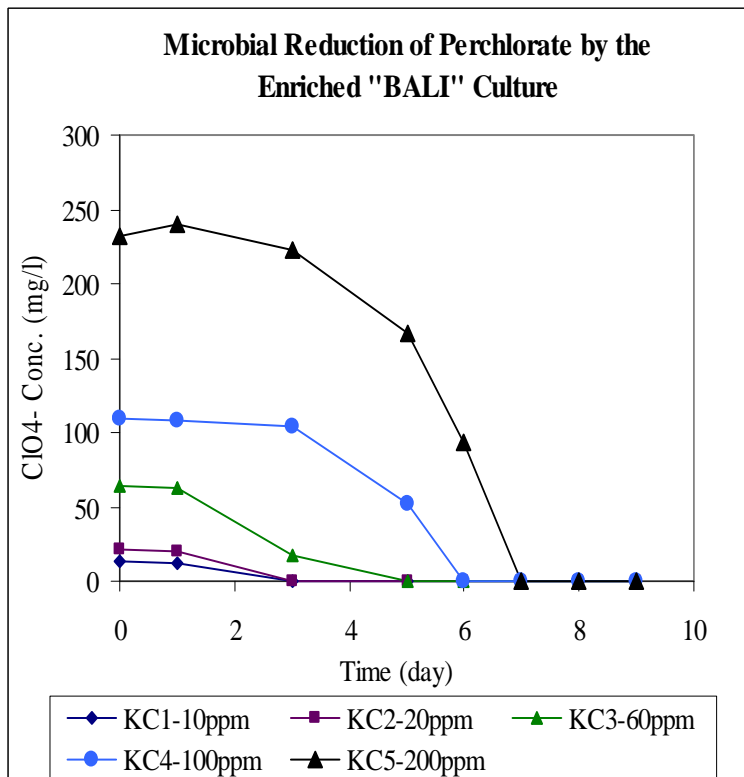


CARBON LIMITATION TESTING



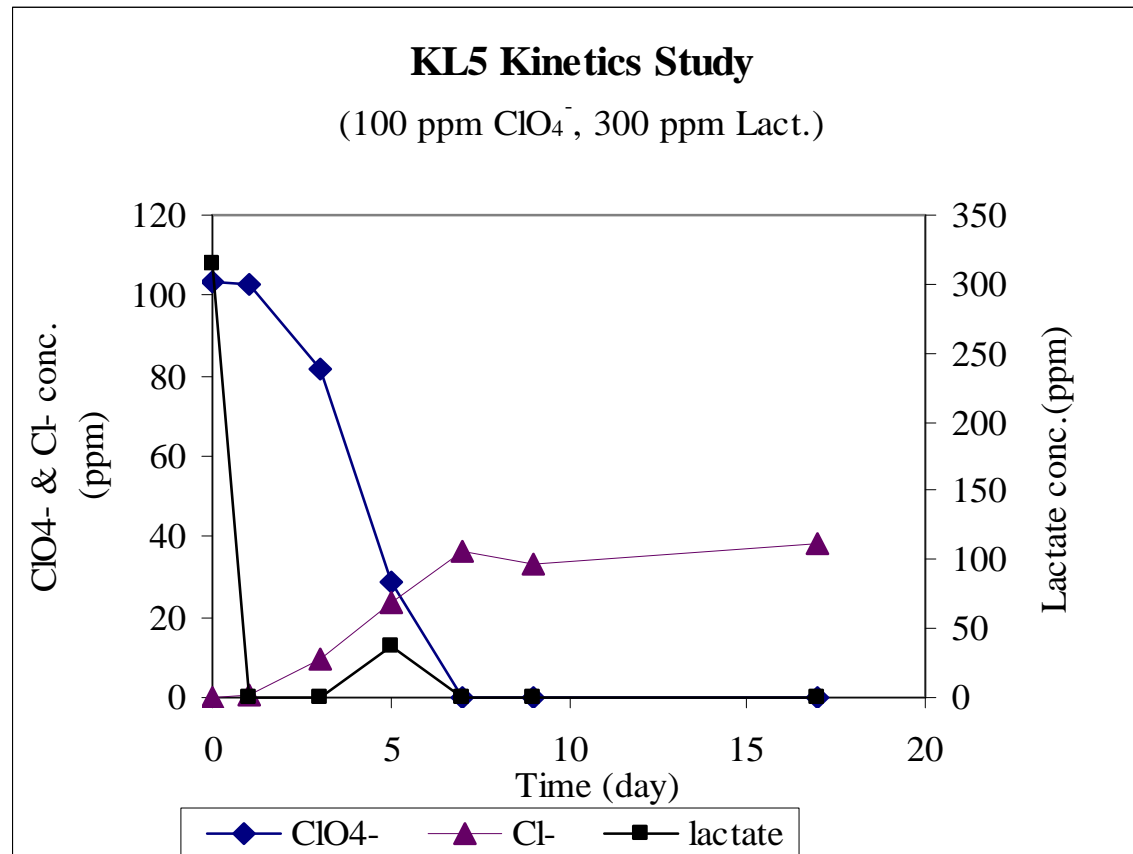
KINETICS EVALUATION

Perchlorate Limited Testing



KINETICS EVALUATION

Lactate Limited Testing

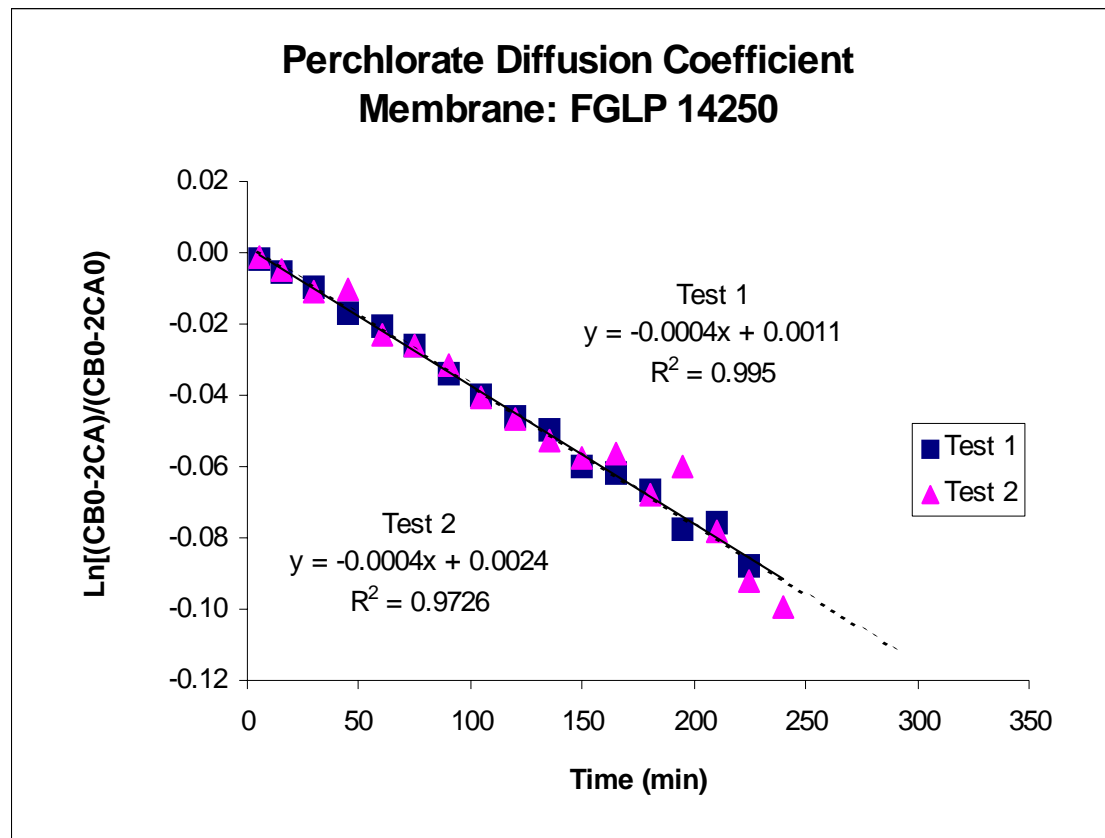


CONCLUSIONS

Kinetics study of “BALI” indicates that a lactate to perchlorate ratio of at least 3:1 is needed for perchlorate biodegradation to occur, and acclimation time varies with the concentrations of perchlorate.

RESULTS

Perchlorate Diffusion Coefficient Testing (1)



RESULTS

Perchlorate Diffusion Coefficient Testing (1)

$$V_{BR}(dC_{BR}/d t) = - (D_M A_M)/(\Delta L_M)(C_{DR} - C_{BR})$$

$$\ln[(C_{DR0} - 2C_{BR})/(C_{DR0} - 2C_{BR0})] = - (2A_M D_M t)/(V_{BR} \Delta L_M)$$

$$K = -0.0007 = -2A_M D_M / (V_{BR} \Delta L_M)$$

$$A_M = 3.14 r^2 \times E \quad E = 70\% = 0.7, \quad \Delta L_M = 125 \text{ um}$$

$$V_A = 5 L = 5 \times 10^{-3} \text{ m}^3 \quad r = 0.05 \text{ m}$$

$$\begin{aligned} \text{so, } D_M &= K V_{BR} \Delta L_M / (2A_M) \\ &= 0.0007 \times 5 \times 10^{-3} \times 125 \times 10^{-6} / (2 \times 3.14 \times 0.05^2 \times 0.7) \\ &= 3.98 \times 10^{-8} \text{ m}^2/\text{min} = 6.64 \times 10^{-6} \text{ cm}^2/\text{sec} \end{aligned}$$

RESULTS

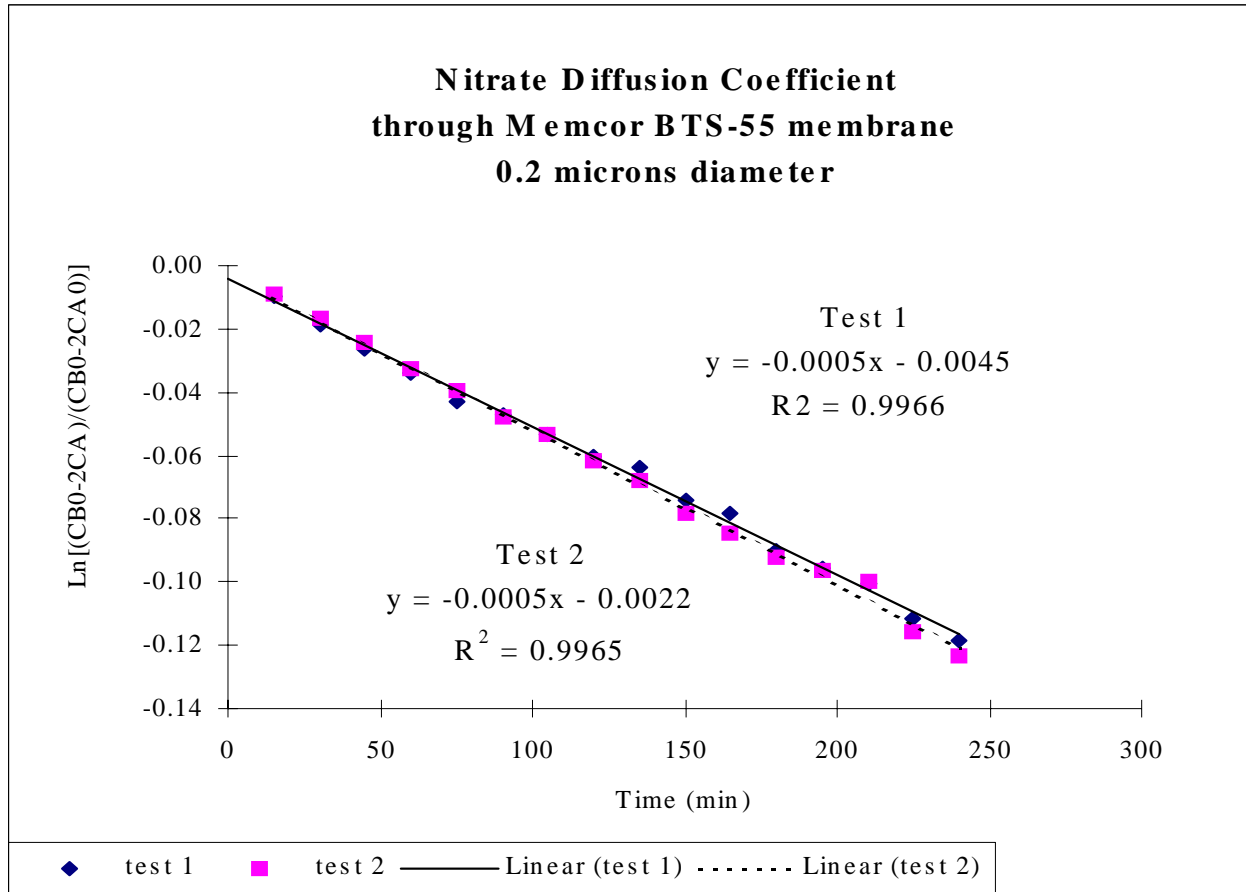
Perchlorate diffusion coefficient through 3 different types of membrane

Membrane Type	BTS-55	PVDF	FGLP
Pore Size, μm	0.2	0.45	0.2
Thickness, μm	125	99	220
Pore Fraction, %	70	70	70
Diffusion coeff. $\text{cm}^2/\text{sec.}$	6.64×10^{-6}	3.75×10^{-6}	6.67×10^{-6}

Diffusion coefficient calculated by Wilk-Chang
method: $1.53 \times 10^{-5} \text{ cm}^2/\text{sec.}$

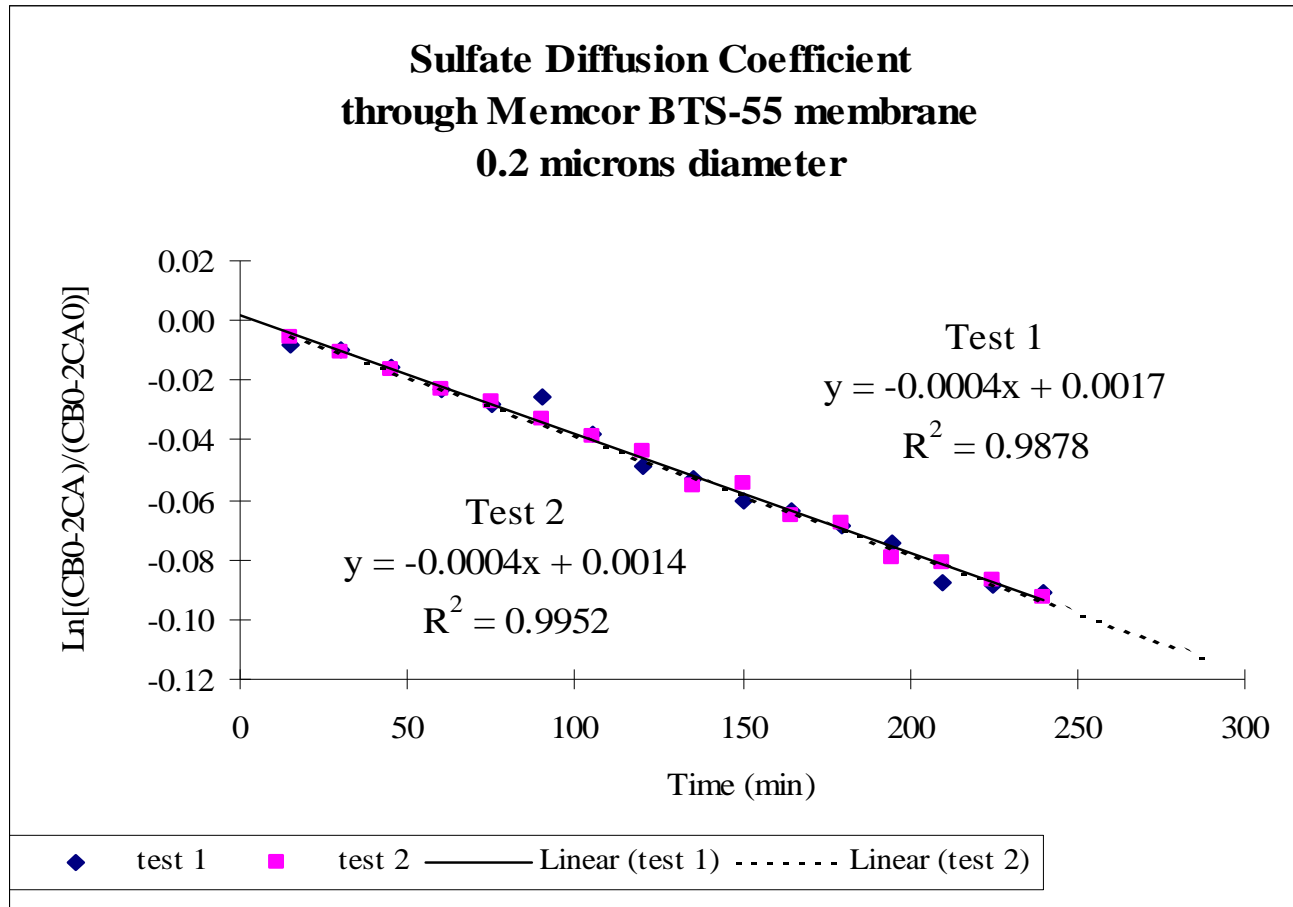
RESULTS

Nitrate Diffusion Coefficient Testing



RESULTS

Sulfate Diffusion Coefficient Testing



RESULTS

Table: The Diffusion Coefficients of Perchlorate, Nitrate and Sulfate in Water and Through Memcor BTS-55 Membrane

	Perchlorate	Nitrate	Sulfate
With BTS-55, cm²/sec (Testing Data)	6.64 x 10⁻⁶	4.74 x 10⁻⁶	3.79 x 10⁻⁶
Without BTS-55, cm²/sec (Calculated by Wilke- Chang's Method)	1.53 x 10⁻⁵	2.12 x 10⁻⁵	1.47 x 10⁻⁵

CONCLUSIONS

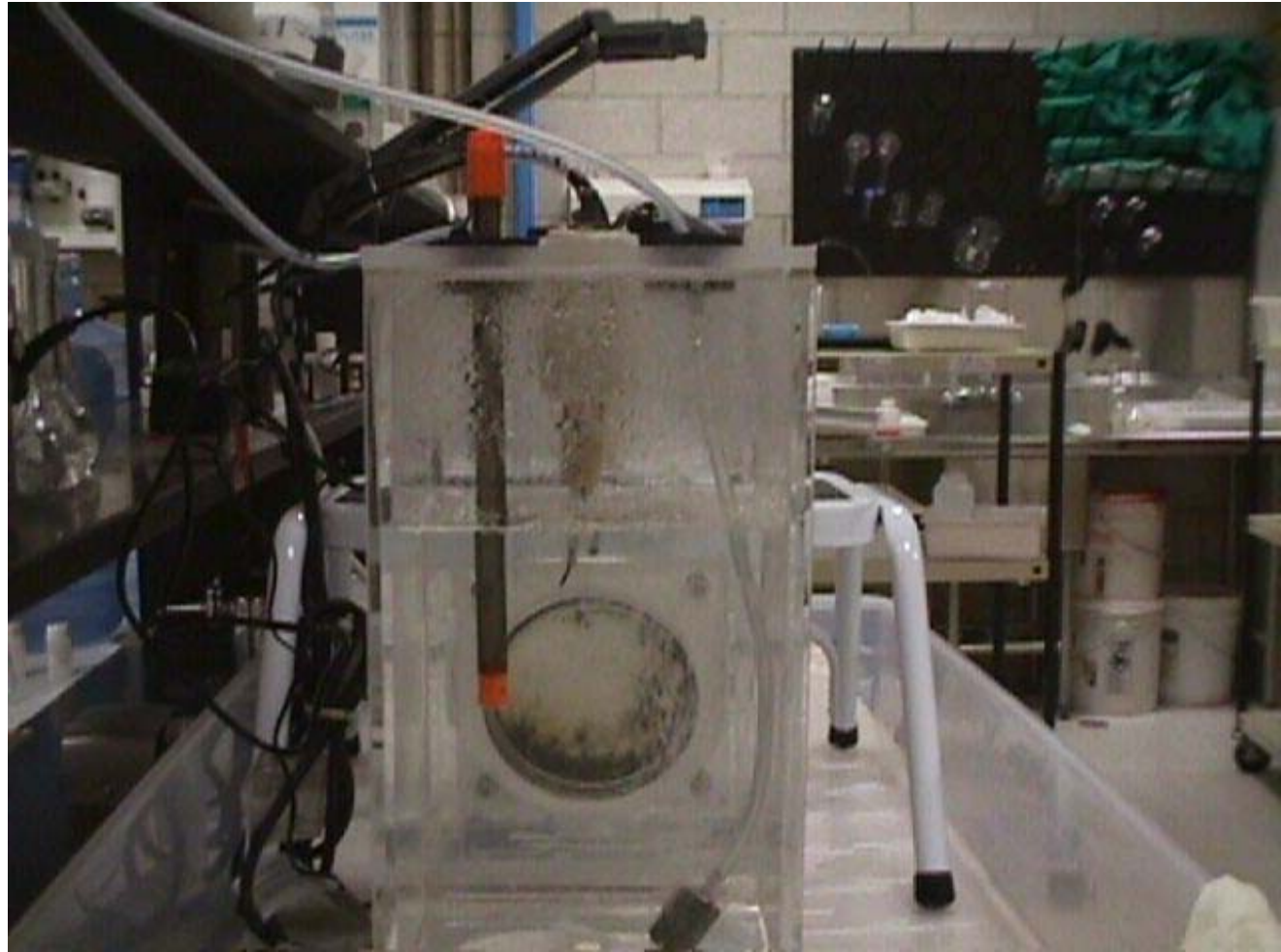
- ClO_4^- , NO_3^- , and SO_4^{2-} easily migrate through a semipermeable membrane by diffusion, eliminating the need of energy input.
- The diffusivity in water follows:



While diffusivity through the BTS-55 Membrane follows:

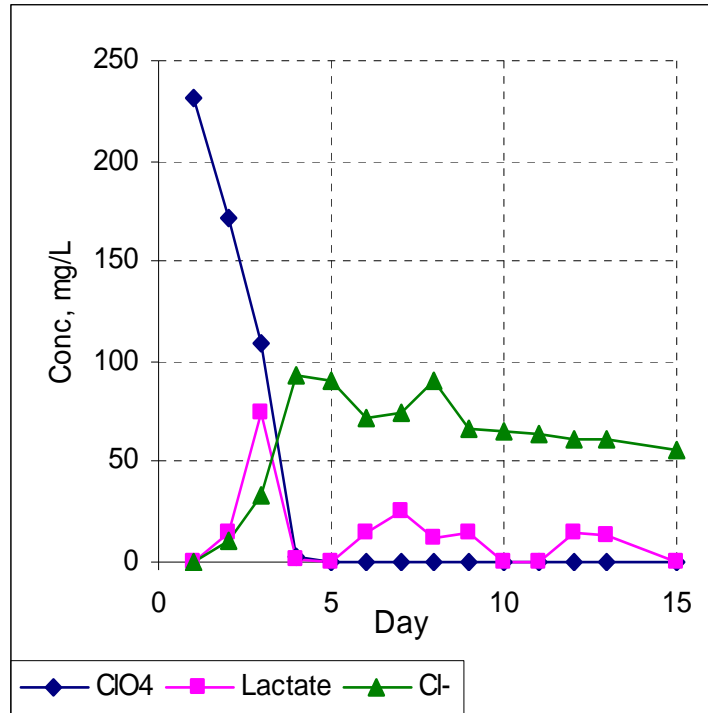


Membrane - Immobilized Biofilm

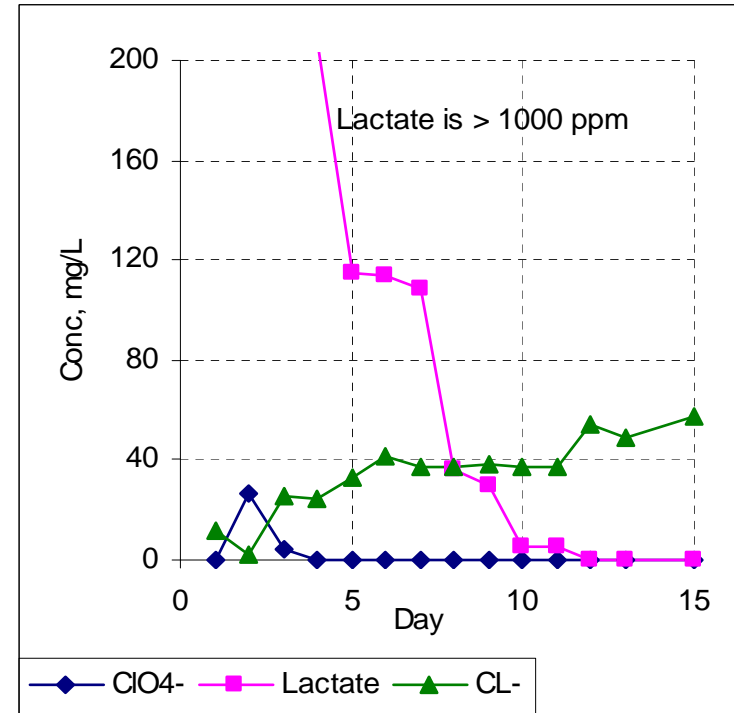


RESULTS---BTS-55 (1st Cycle)

DR Reactor



BR Reactor



$$\text{ClO}_4^- / \text{Cl}^- = 0.82$$

ClO₄⁻ biodegradation rate = 1.95 moles/day

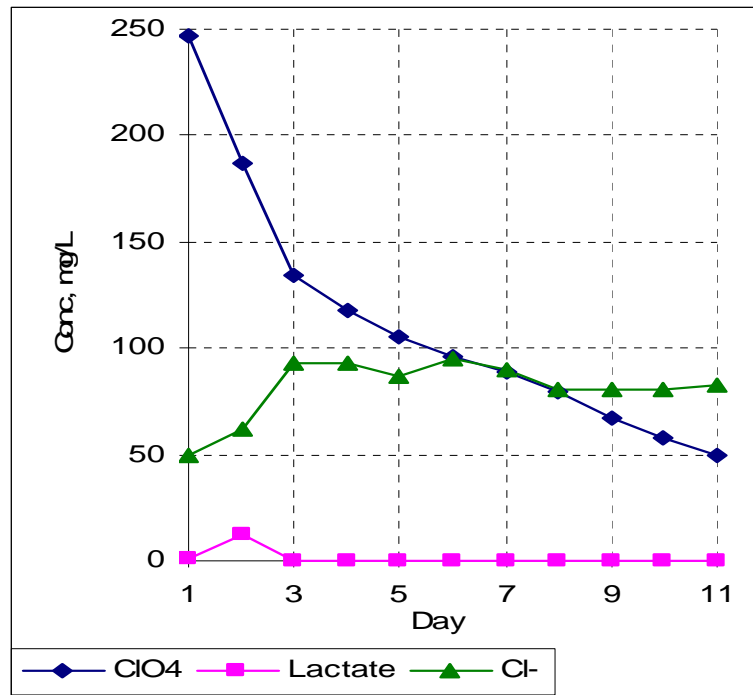
RESULTS

Table: Perchlorate Biodegradation by a Biofilm Immobilized on a BTS-55 Membrane (2nd cycle)

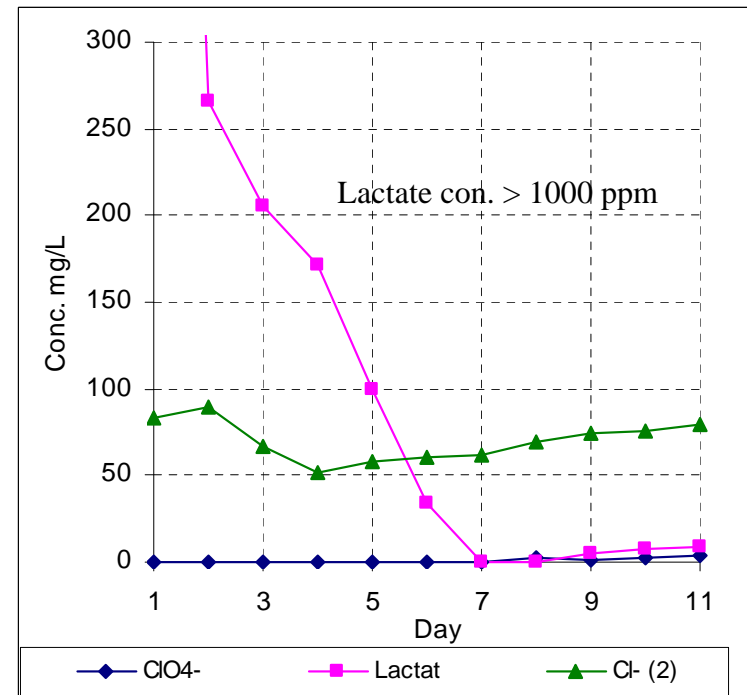
Day	DR Reactor (ClO ₄ ⁻ only)			BR Reactor (Lact., Nutri./Minerals, and Buffer)		
	ClO ₄ ⁻ (mg/l)	Lactate (mg/l)	Cl- (mg/l)	ClO ₄ ⁻ (mg/l)	Lactate (mg/l)	Cl- (1) (mg/l)
1	246.96	0.94	49.89	0.19	1058.9	44.71
2	187.08	12.73	61.6	0.35	266.54	64.86
3	134.21	0	93.22	0.055	204.93	72.14
4	117.74	0	93.25	0.024	172.05	78.91
5	105.58	0	86.69	0.003	99.22	80
6	96.42	0	95.37	0	33.66	84.65
7	89.24	0	89.58	0	0	88.47
8	79.82	0	80.99	3.09	0	69.02
9	67.6	0	80.3	1.43	5.44	74.7
10	57.88	0	80.81	2.26	7.06	75.16
11	50.07	0	82.73	3.25	9.28	79.12

RESULTS---BTS-55 (2nd Cycle)

DR Reactor



BR Reactor



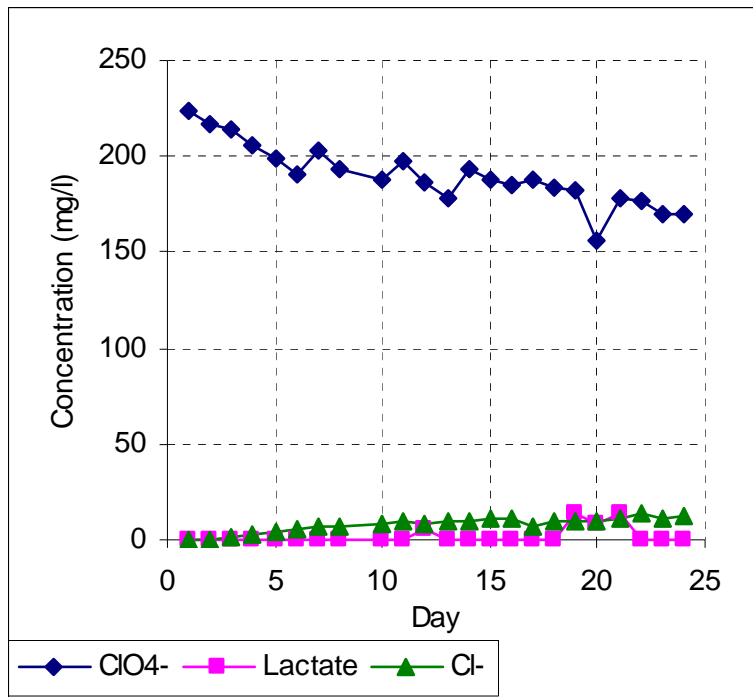
$$\text{ClO}_4^- / \text{Cl}^- = 1.03$$

ClO₄⁻ biodegradation rate = 0.90 moles/day

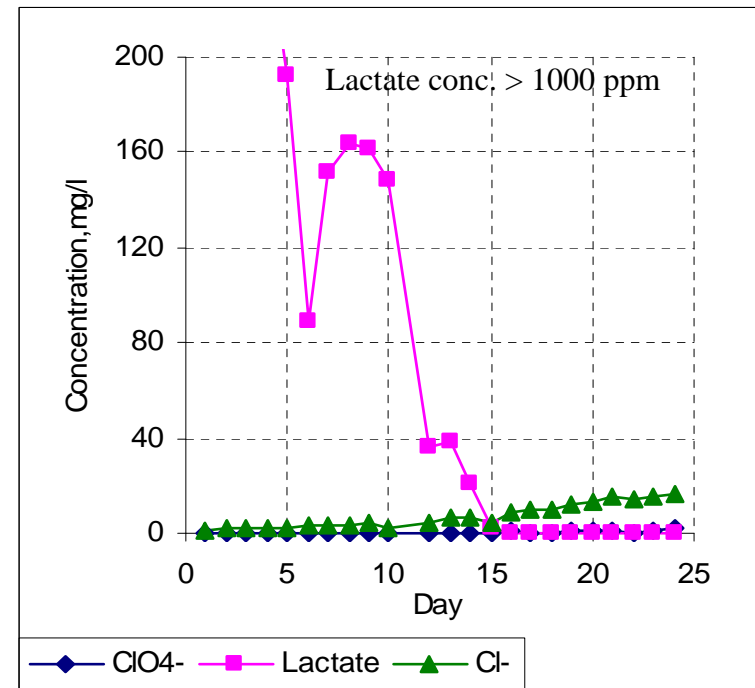
RESULTS

Perchlorate Biodegradation By Membrane (FGLP) Immobilized Biofilm

DR Reactor



BR Reactor



CONCLUSIONS

Table: Parameters Calculated for the Biofilms Immobilized on the BTS-55 and PVDF Membrane

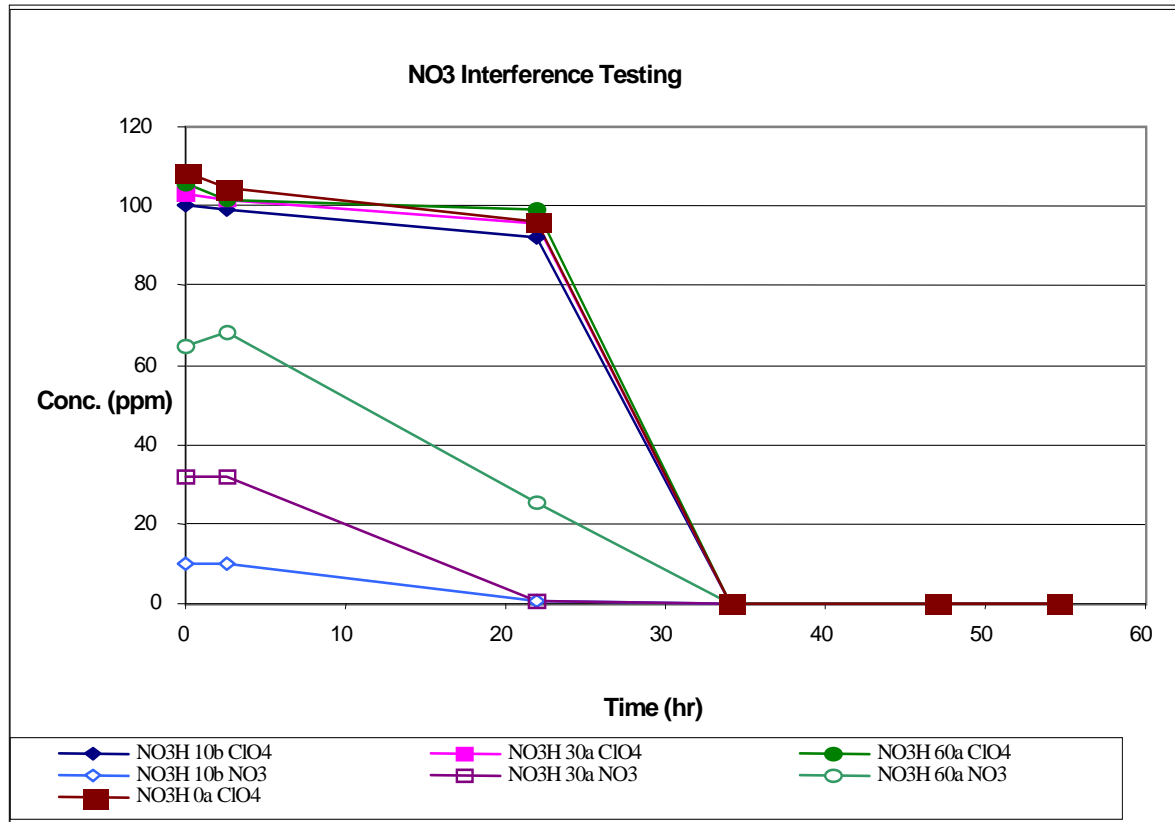
BTS-55	1st Cycle	$\text{ClO}_4^- / \text{Cl}^- : 0.82$	Moles $\text{ClO}_4^-/\text{day} : 1.95$
	2nd Cycle	$\text{ClO}_4^- / \text{Cl}^- : 1.03$	Moles $\text{ClO}_4^-/\text{day} : 0.90$
	3rd Cycle	$\text{ClO}_4^- / \text{Cl}^- : 0.86$	Moles $\text{ClO}_4^-/\text{day} : 1.75$
PVDF	1st Cycle	$\text{ClO}_4^- / \text{Cl}^- : 0.99$	Moles $\text{ClO}_4^-/\text{day} : 0.5$

CONCLUSIONS

- **The reactor set-up separates the perchlorate contaminated water from the microbes, greatly minimizing the presence of microbes in the finished water -An important feature, when removing perchlorate from drinking waters.**
- **The presence of the membrane allows for controlled diffusion and biodegradation of ClO_4^- , so that perchlorate levels in the treated water can be kept at desired levels without fluctuations and sporadic spikes.**

RESULTS

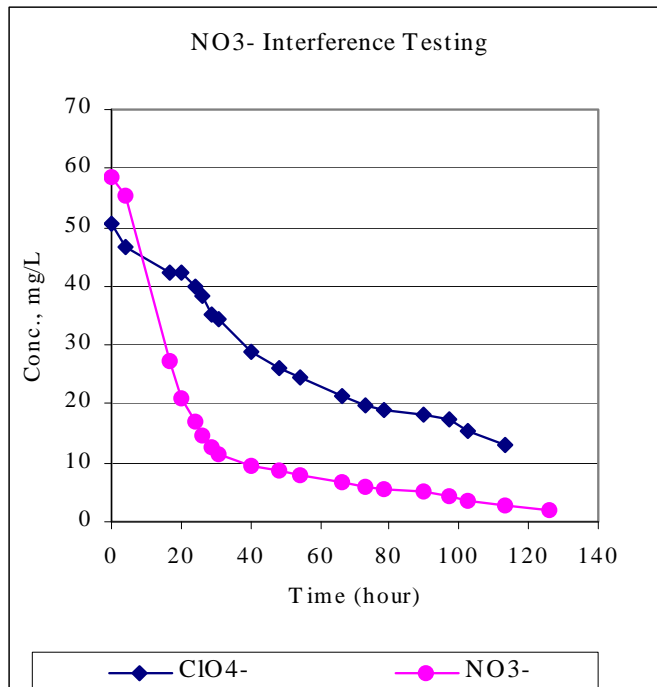
Batch Experiments on the Interference of Nitrate on Perchlorate Biodegradation



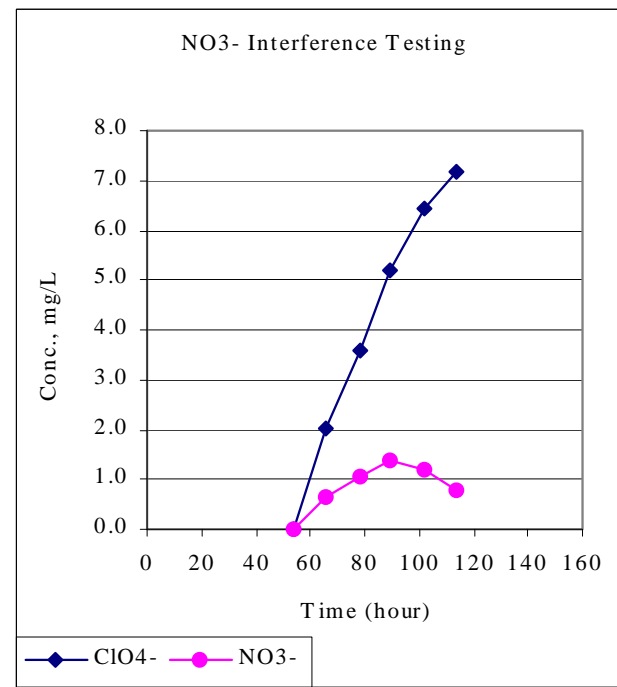
RESULTS

Interference of Nitrate on Perchlorate Biodegradation by BTS-55 Membrane (1)

DR Reactor



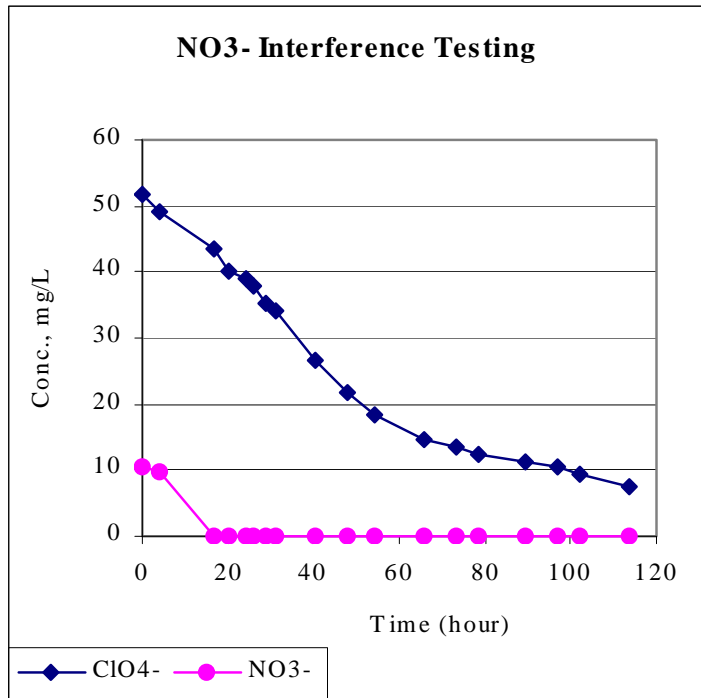
BR Reactor



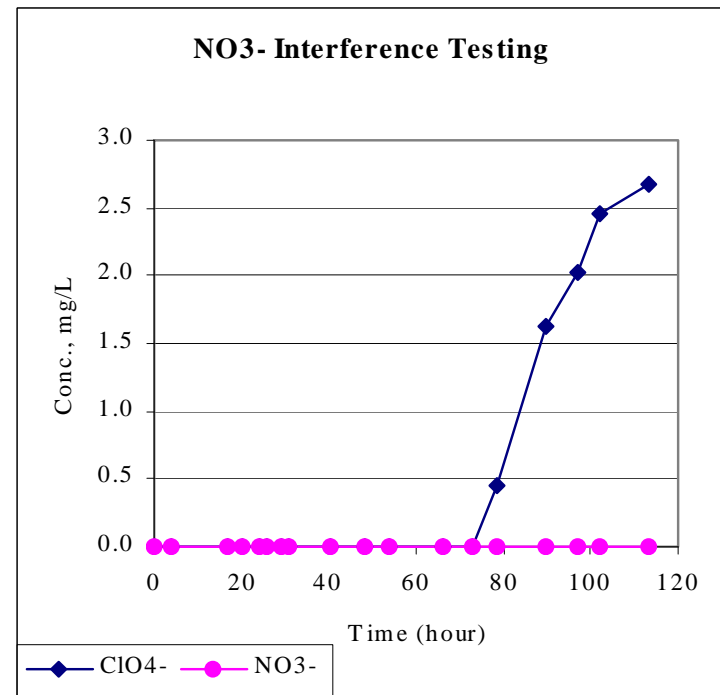
RESULTS

Interference of Nitrate on Perchlorate Biodegradation by BTS-55 Membrane (2)

DR Reactor



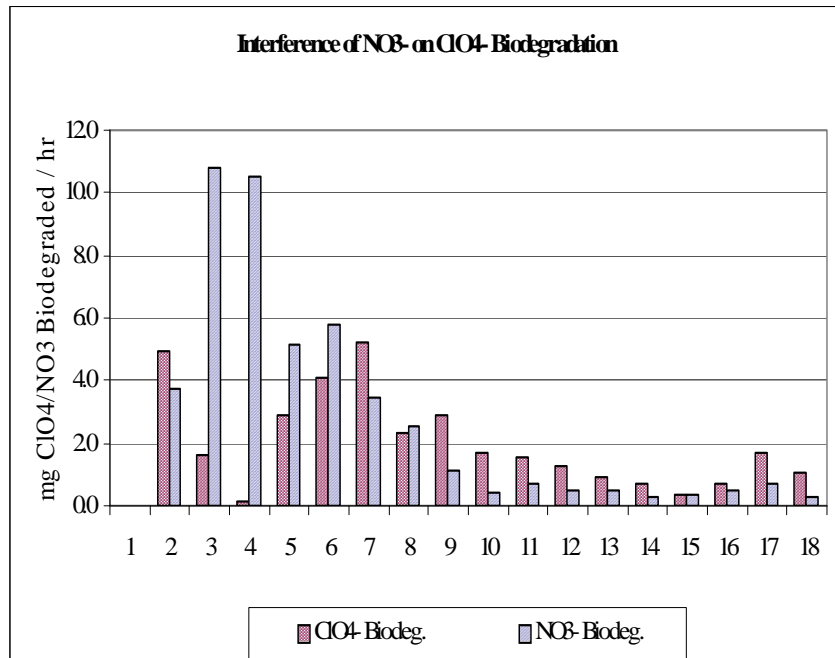
BR Reactor



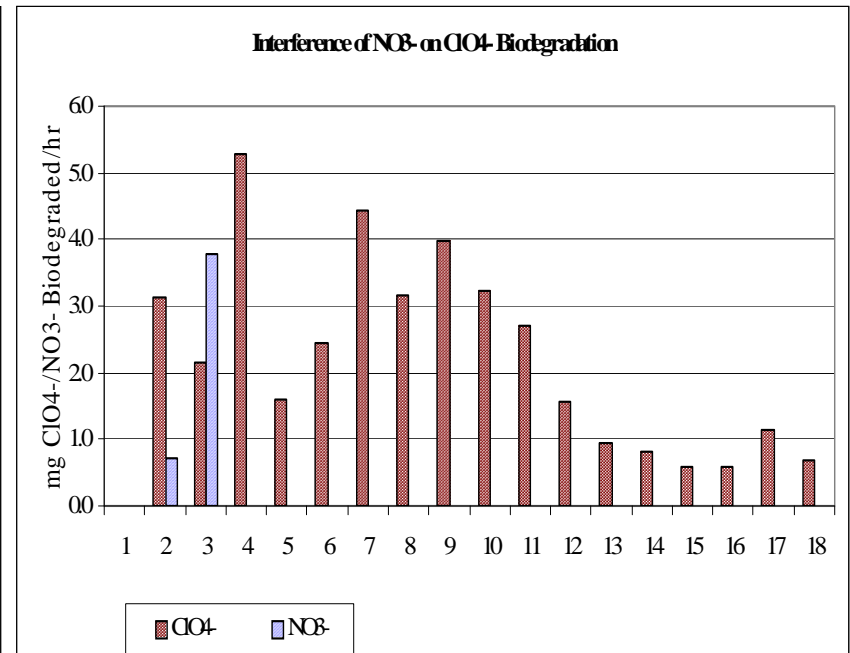
RESULTS

Interference of Nitrate on Perchlorate Biodegradation by BTS-55 Membrane

Testing 1



Testing 2



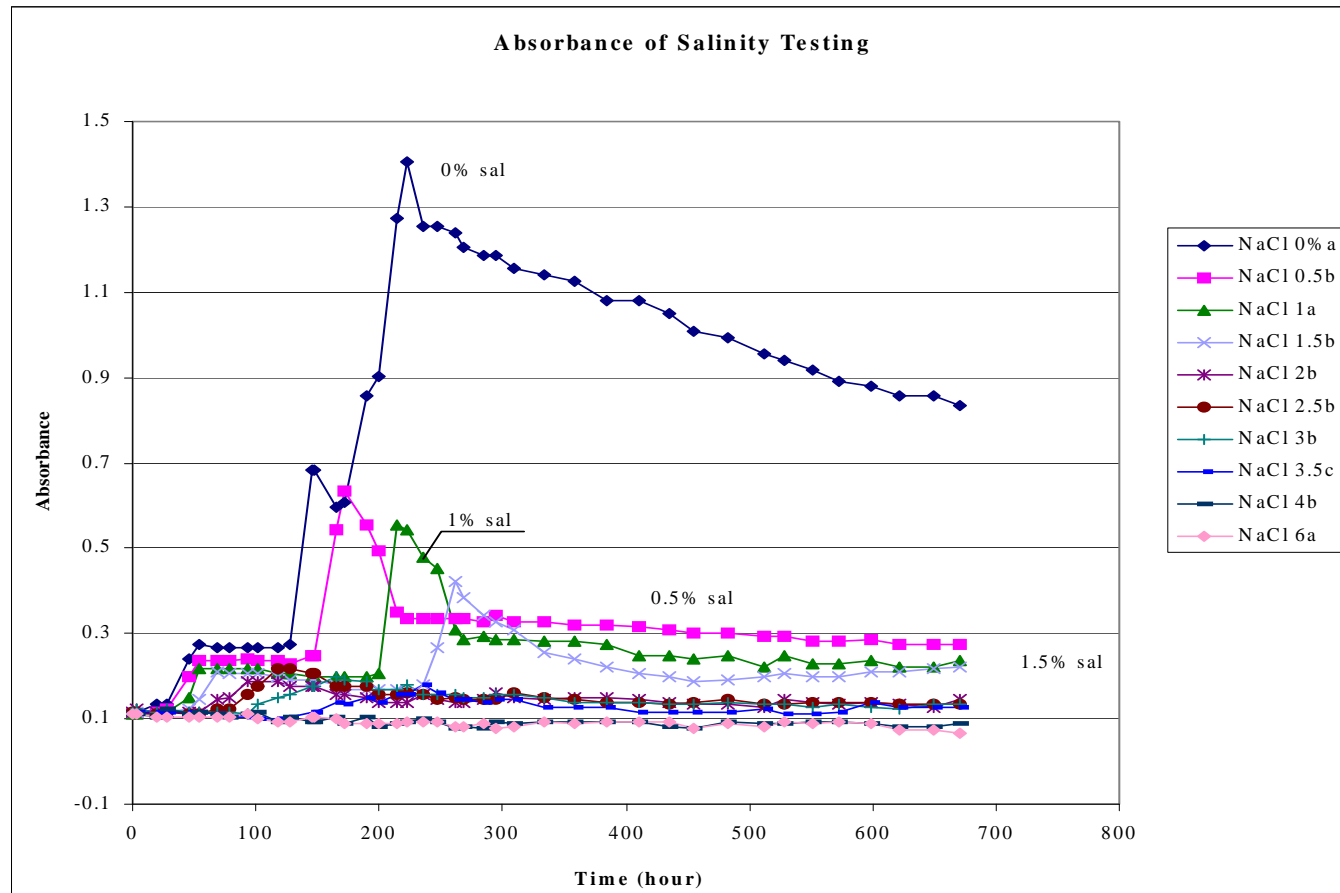
CONCLUSIONS

Nitrate has a negative impact on perchlorate biodegradation.

At first, microbes prefer nitrate to perchlorate as an electron acceptor, however, perchlorate reduction is not totally eliminated in the presence of nitrate.

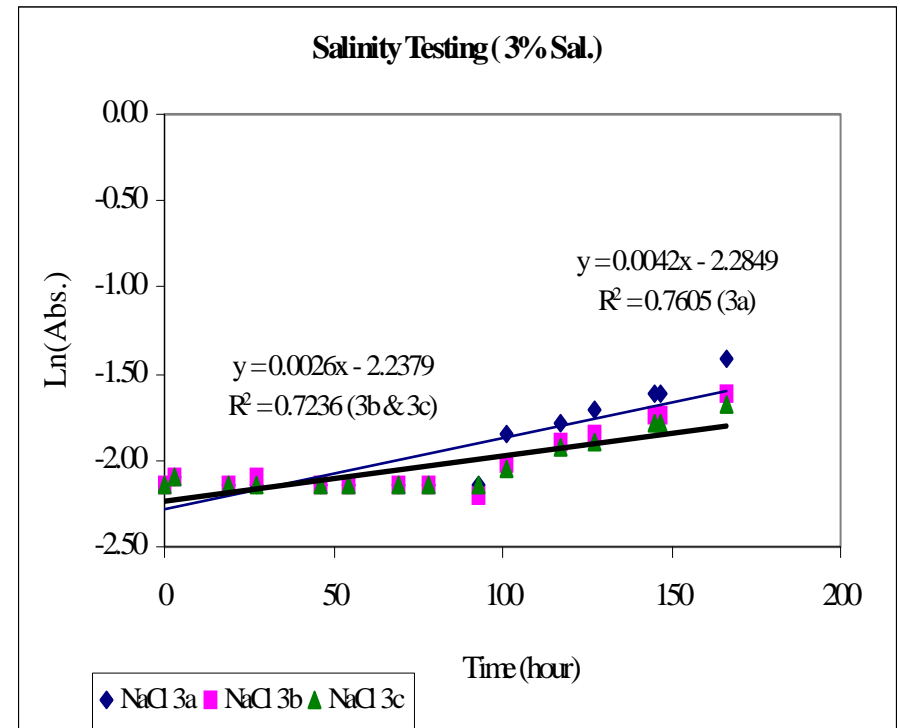
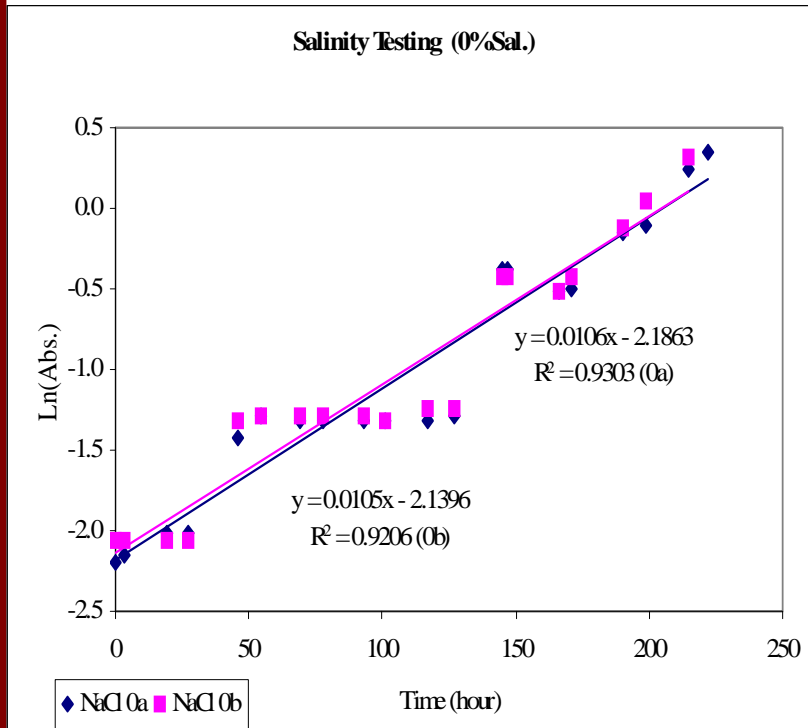
RESULTS

Interference of Salinity on Perchlorate Biodegradation by “BALI Culture”



RESULTS

Interference of Salinity on Perchlorate Biodegradation by “BALI Culture”



RESULTS

Summary of Growth Coeff. For “BALI” Culture at Different Salt Levels

Salinity Conc.	μ , day ⁻¹	R ²	Fraction of 0% Salinity
0 %	0.26	0.93	100 %
0.5 %	0.19	0.78	73 %
1.0 %	0.096	0.61	37 %
1.5 %	0.072	0.544	28 %
2.0 %	0.096	0.69	37 %
2.5 %	0.096	0.70	37 %
3.0 %	0.072	0.72	28 %
3.5%	0.048	0.67	18 %
4.0 %	No growth		
> 5 %	No growth		

CONCLUSIONS

- **Salinity negatively affects the perchlorate biodegradation.**
- **No microbial growth was observed at salinity $\geq 4\%$.**

CONCLUSIONS

- **Hybrid (membrane / biological) system proven feasible for perchlorate removal.**
- **System allows for high quality effluent as compared to fixed/fluidized bed systems.**
- **High nitrate and TDS levels have negative impact on perchlorate biodegradation.**
- **Scale-up configuration for the reactor will involve long sandwiched channels.**