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SCHOOL OF CHEMICAL ENGINEERING

LABORATORY of INORGANIC and ANALYTICAL CHEMISTRY

Bromate detection in bromine disinfected cooling water and removal with the use of Granular Activated Carbon

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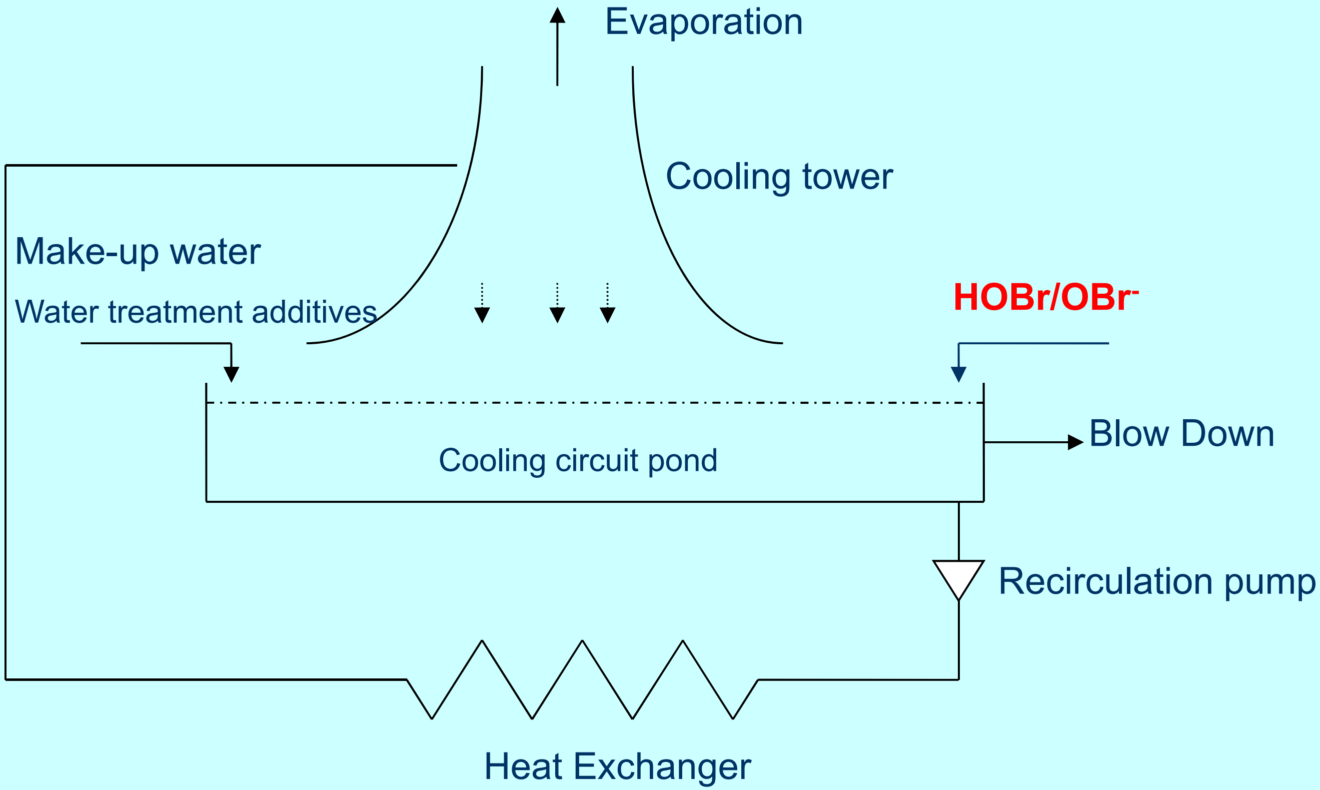

Cooling circuit depiction

- Bio-fouling is one of the most important challenges as it inhibits heat exchanging and destroys equipment
- pH value is adjusted to >8,0 to render cooling water less corrosive
- Chlorine's (the most common disinfectant) biocidal capability is deteriorating at pH>7,5
- Bromine in the form of hypobromous acid/hypobromite is employed instead
- In most cases bromine is produced in-situ

$$NaOCl + NaBr \rightarrow NaOBr + NaCl$$

$$Br_2 + H_2O \rightleftarrows HOBr + HBr$$

- Bromate (BrO_3^-) is formed due the decay of hypobromite

$$3HOBr \rightarrow BrO_3^- + 2Br^- + 3H^+$$

- Bromate is a strong carcinogen. Max. concentration allowed in drinking water is 10μg/L
- Conditions prevailing in a cooling circuit favor bromate formation
  - ✓Sunlight
  - ✓Presence of CuO
  - ✓Presence of residual free chlorine

Sampling for bromate is usually a challenge since its presence is depending on:

- Bromination pattern (continuous or shock application)
- Weather conditions / Time of bromination
- Time of sampling (after application)

Bromate can be detected even away (downstream) from the circuit, if the circuit operates under low cycles of concentration.

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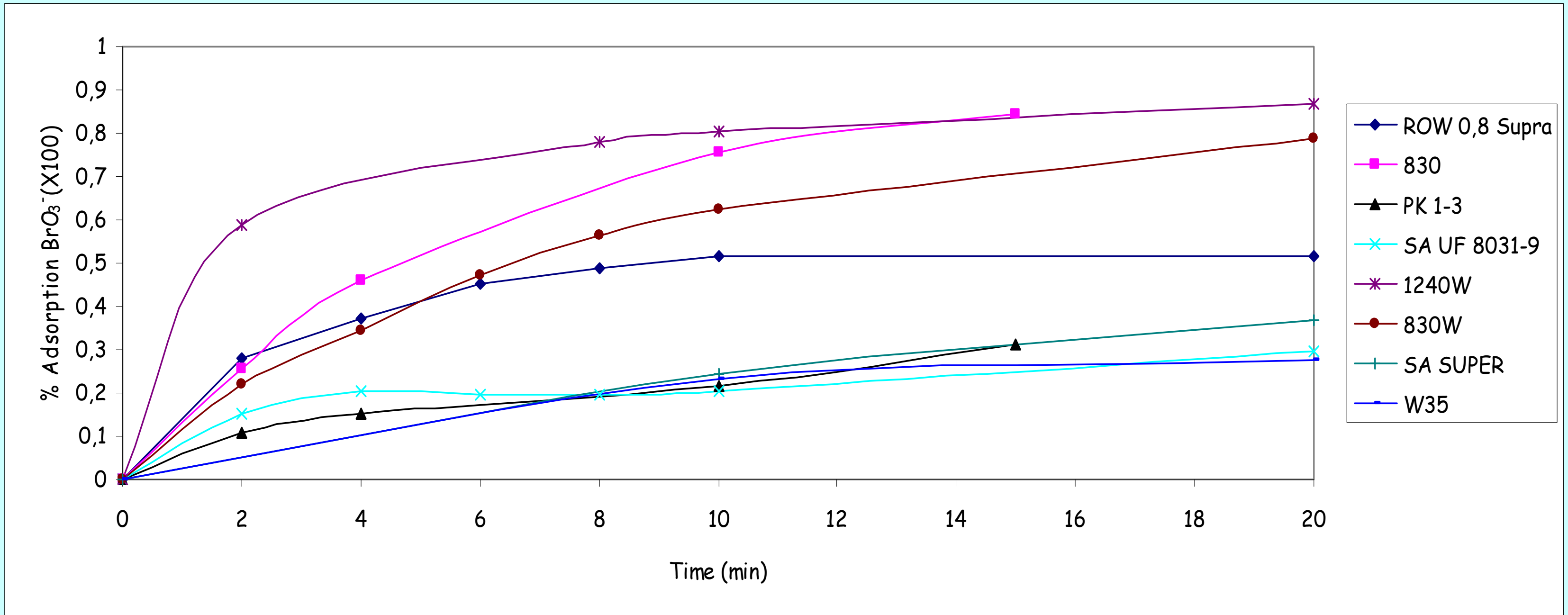
Experimental Conditions:

A number of Activated Carbons was tested with respect to their BrO_3^- removal efficiency



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GOAL

Evaluation of the manner that cooling water specific conditions affect GAC's ability to remove bromate

Cooling water poses further challenges to GAC with respect to its ability to remove BrO_3^-, in comparison to drinking water such as

- Higher pH
- Higher conductivity
- Strong organic matter presence
- Strong residual oxidant presence
- Strong presence of additives to control corrosion and/or scale such as polycrylate and phsphonate salts

Experimental Conditions:

Cooling water was sampled from an industrial metal processing unit

PARAMETER	SAMPLE VALUE	ATHENS DRINKING WATER
Electric Conductivity (μS/cm)	1864,0	270,0
pH	7,9	7,5
M alkalinity (as mg/L $CaCO_3$)	370,0	112,0
Total Hardness (as mg/L $CaCO_3$)	515,0	130,0
Cl^- (mg/L)	187,0	5,0
SO_4^{2-} (mg/L)	140,6	20,0
Mg^{2+} (mg/L)	48,2	5,0
Ca^{2+} (mg/L)	131,4	45,0

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Experimental Conditions:

The type of activated carbon used was type 1240W by Cabot Norit

Physical-Chemical parameter	1240W
Activated Carbon's nature	GAC
Surface (BET)	1100 m^2/gr
Apparent Density	485 kg/m^3
Effective size D_{10}	0,6-0,7mm
% BrO_3^- adsorption after 20min contact time	84

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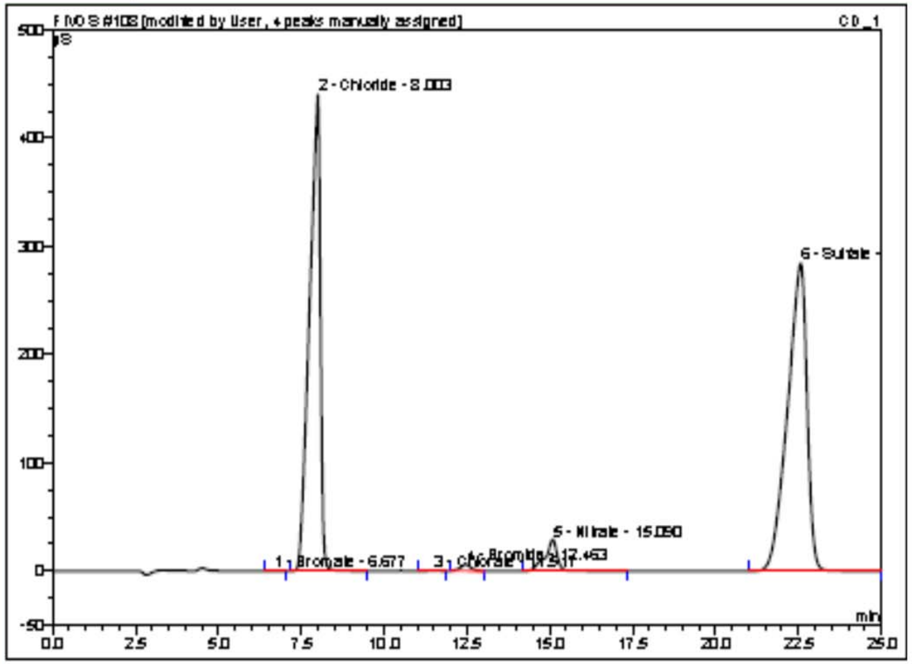
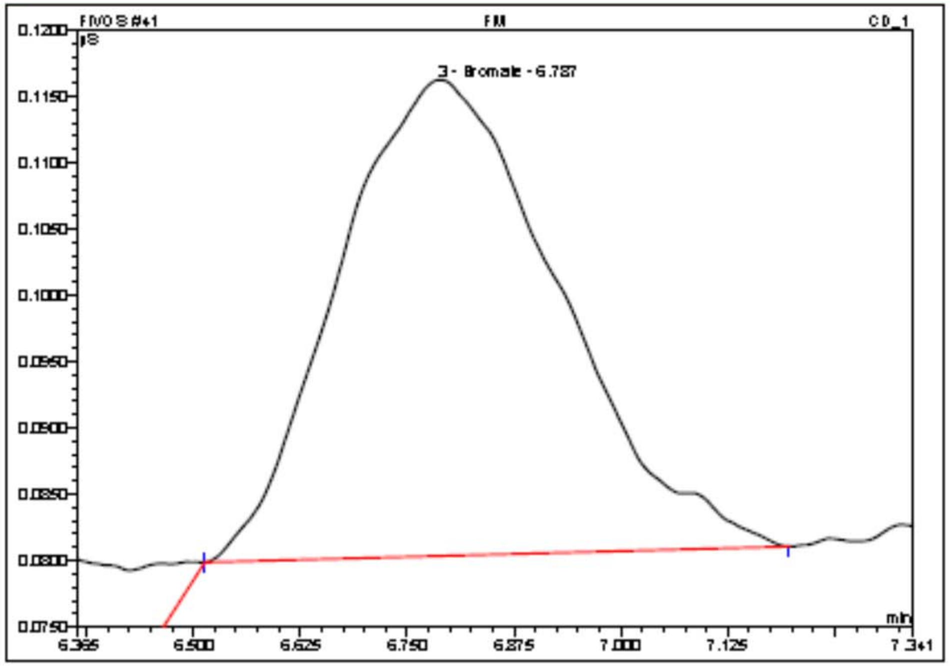
Experimental Conditions:

Analytical Method used to measure BrO_3^-

Ion Chromatography (EPA Method 300.1) for concentrations <1,0mg/L





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•Bromate has been detected in a number of samples of bromine disinfected waters coming from power plants, metal processing units etc.

•Chlorite is usually an issue when measuring bromate with IC (Ion chromatography). It occurs when bromine is produced under chlorine-affinity conditions

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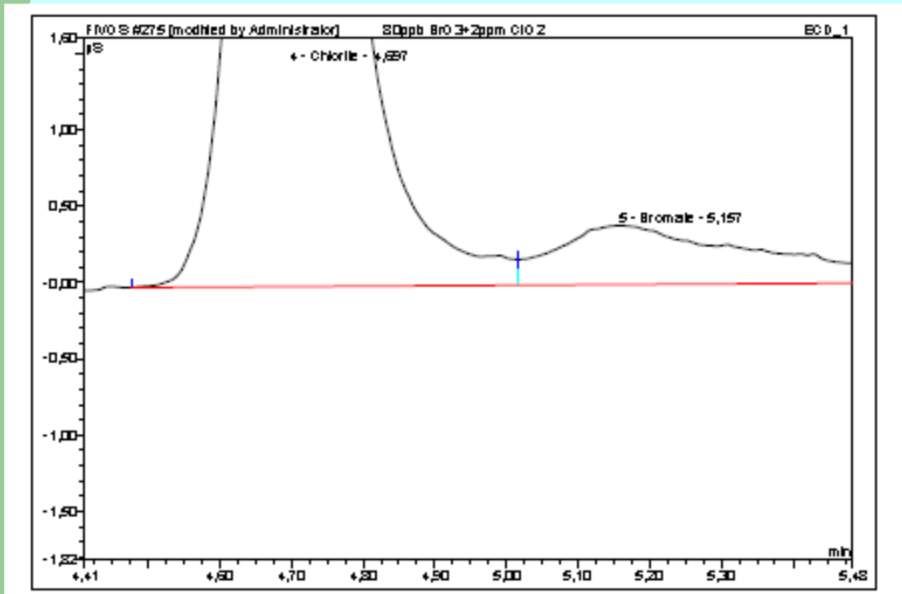

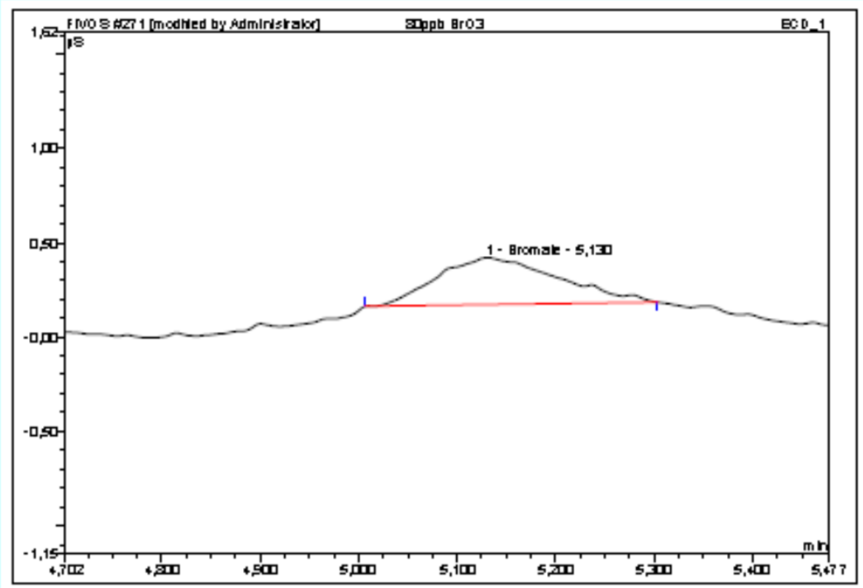

Experimental Conditions:

- Isotherm curves were constructed using 0,05, 0,1, 0,2, 0,5, 1,0, 2,0 and 5,0 gr of GAC in 100mL aliquots
- The initial bromate concentration was 2mg/L
- Varying conditions were applied with respect to
    - pH
    - Organic load
    - Cu^{2+}
    - Residual Bromine

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Matrices under study

	Matrix 1 (base case)	Matrix 2	Matrix 3	Matrix 4	Matrix 5	Matrix 6	Matrix 7	Matrix 8	Matrix 9
Bromate (mg/L)	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0
pH	8,0	9,0	10,0	8,0	8,0	8,0	2,0	8,0	8,0
Organic Load (mg/L)	2,0	2,0	2,0	4,0	6,0	2,0	2,0	2,0	2,0
Cu^{2+} (mg/L)	2,0	2,0	2,0	2,0	2,0	4,0	6,0	2,0	2,0
Residual Bromine (mg/L)	0,0	0,0	0,0	0,0	0,0	0,0	0,0	4,0	4,0

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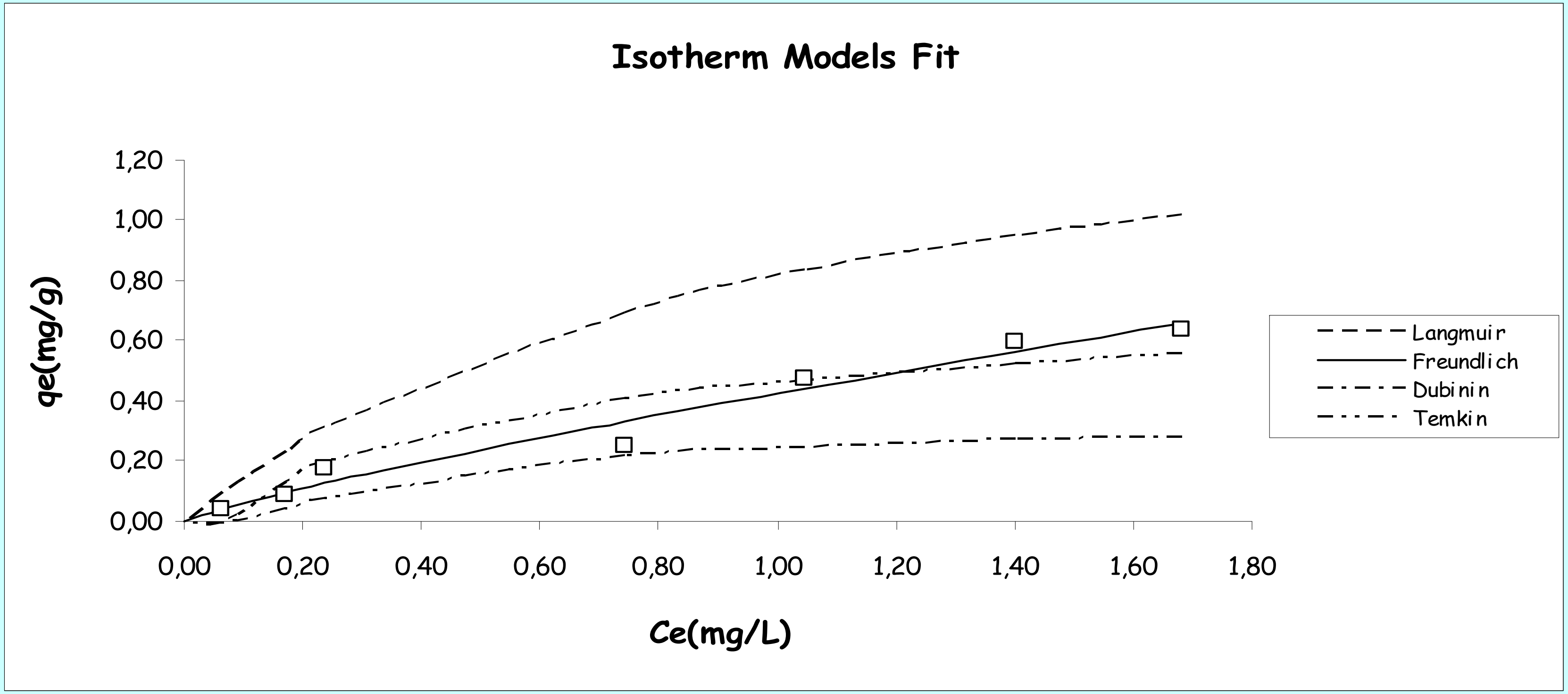
Results:

The isotherm curves seem to fit the Freundlich model (**$q_e = K_f C_e^{1/n}$**) best



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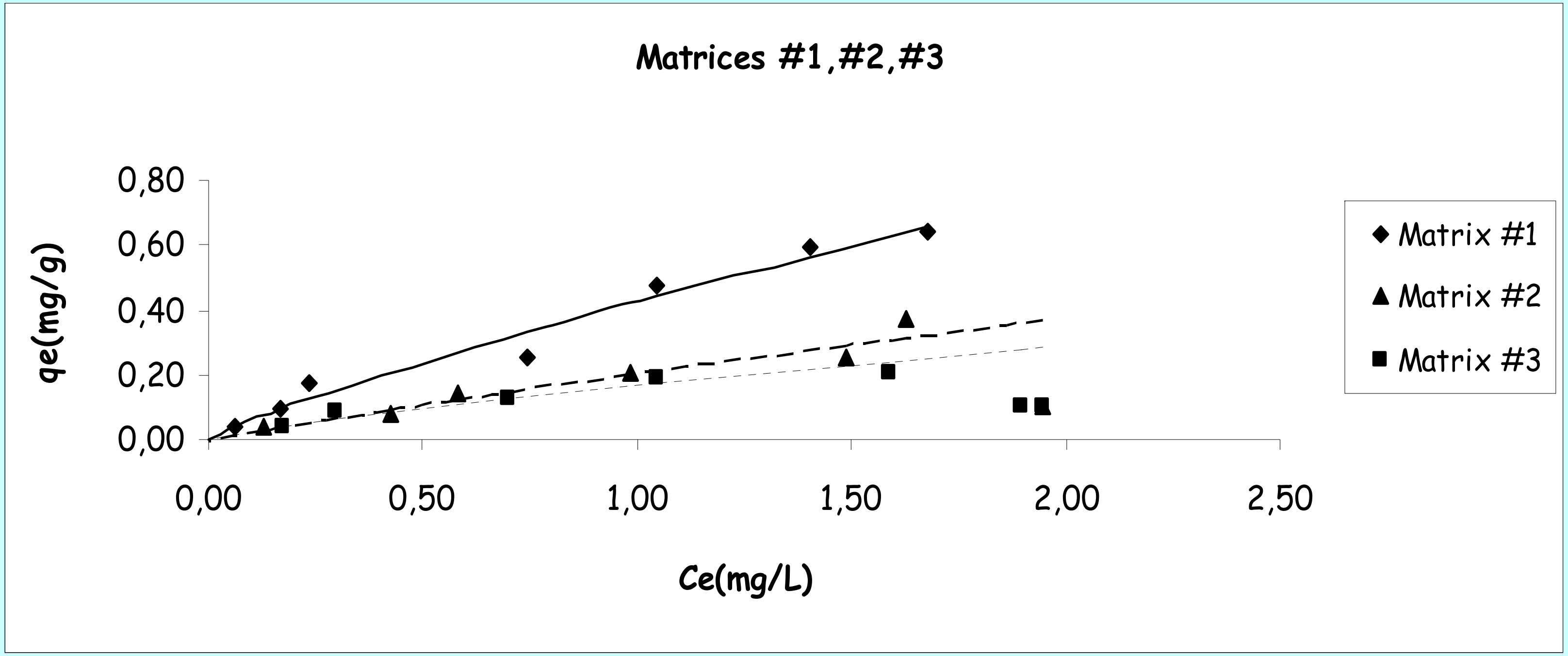
Results:

Freundlich curves for matrices #1, #2 and #3



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Results:

	Freundlich's K_f	Qmax* (mg BrO^{3-}/g GAC)
Matrix 1	0,43	0,70
Matrix 2	0,21	0,64
Matrix 3	0,16	0,61
Matrix 4	0,46	0,54
Matrix 5	0,52	0,67
Matrix 6	0,36	0,52
Matrix 7	0,29	0,46
Matrix 8	0,38	0,62
Matrix 9	0,35	0,57

Conclusions:

•pH seems to be the most important factor in removing bromate from cooling water. Higher pH means poorer bromate removal as it is the case in drinking water

•The organic load is found in different form in the presence/absence of Residual free bromine

•Organic load in the form of humic acid promotes bromate removal due do its reducing action

•Copper Ion (a common corrosion by-product) as well as residual bromine also inhibit bromate removal by GAC

•In practice, due to cooling water's extremely variable profile from circuit to circuit, the generalization of the results is challenging

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Thank you for your attention

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