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

F. A. Megalopoulos*, M.T. Ochsenkuehn-Petropoulou*

* School of Chemical Engineering, National Technical University of Athens, 9Iroon Polytechneiou Str., 157 80 Athens, Greece (E-mail: *fmegalopoulos@texne.gr*; *oxenki@central.ntua.gr)*

Abstract

Bromate is one of bromination's most toxic by-products, resulting from hypobromous decomposition. Bromination is a common disinfection method for higher pH cooling waters due to chlorine's diminishing capability. Both the US EPA and the European Union have regulated bromate's maximum concentration in drinking water at 10 μg/L. Hypobromous is generally produced in situ by mixing chlorine and sodium bromide solutions and its decomposition is favored in cooling circuit bodies due to the presence of residual free bromine, heavy metal species and sunlight. Cooling water containing residual free bromine leaked to end recipients could cause bromate formation away from the cooling circuit. Granular activated carbon (GAC) is an adsorbent used widely in industry with proven capabilities in toxic substances removal.

In this work GAC's ability to remove bromate from disinfected cooling water body is investigated The adsorption/reduction process is challenged by the presence of high organic content, residual bromine, heavy metals and elevated pH. It was found that the adsorption/reduction process is best expressed by the Freundlich adsorption model. The quality of the adsorption (as express by the K_F constant of the Freundlich equation) is most gravely affected by cooling water's pH. All the parameters under study proved to hinder GAC's bromate removal apart from increasing organic load concentrations. It was found that cooling water bodies less concentrated, frequently and mildly disinfected, containing few corrosion by-products are easier to be bromate-stripped with the help of GAC.

Keywords

Disinfection; cooling water treatment; bromate removal; granular activated carbon adsorbent; Freundlich isotherm

INTRODUCTION

Disinfection is one of the most important treatments that cooling water undergoes within a cooling circuit to protect equipment form corrosion occurring under microbial colonies and keep clean surfaces for optimum heat exchanging. Due to operators' goal to maintain cooling water pH at values greater than 8, chlorination looses effectiveness and therefore bromination is applied instead. Bromine is produced in-situ by mixing chlorine and sodium bromide to produce hypobromous/ hypobromite. Hypobromous decay which is promoted within a cooling circuit by sunlight (Chon 2015), residual free bromine presence and circuit's metallurgy, leads to bromate formation which is a known carcinogen and its maximum concentration in drinking water is regulated by the US EPA as well as the EU to less than 10μg/L (US EPA 2005).

In this work, cooling water was sampled from multiple circuits and bromate was detected in a number of samples at concentrations from 0-50 μg/l. Granular activated carbon (GAC) was tested with respect to its bromate removal abilities under conditions prevailing within a cooling circuit, e.g. high pH, high concentration of organic load, presence of residual free bromine and presence of copper, a common corrosion by-product.

MATERIALS AND METHODS

All materials were of reagent grade supplied by Aldrich (www.sigmaaldrich.com) and for all dilutions ultra pure water (18,2 MΩ electrical resistance) was used. For bromate measurement the EPA Method 300.1 was applied using a Bio-LC ion chromatography system equipped with a

Dionex AS9-HC/AG9-HC set of columns.

Cooling water without having undergone any prior disinfection, was sampled from an industrial cooling circuit and was spiked with 2mg/L bromate. Synthetic matrices were constructed using the sampled water as base by varying the pH as well as the organic load, copper and residual bromine content by 1:1, 2:1 and 3:1 ratios with respect to the bromate content. Isotherm curves were constructed by preparing 100ml aliquots containing 0,05g, 0,1g, 0,2g, 0,5g, 1,0g, 2,0g and 5,0g GAC. The aliquots underwent 1hr intense stirring and were kept away from sunlight for 48h.

RESULTS AND DISCUSSION

Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm equations were tested with respect to their data fit. It was proven that the Freundlich equation provides the best fit (Figure 1) with an R^2 of 0,97.

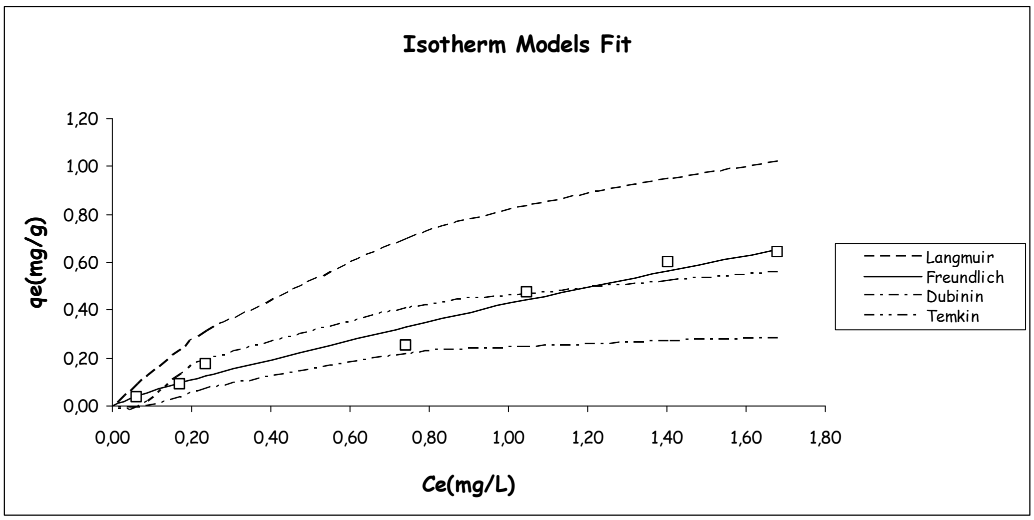

Figure 1. Isotherm models fit, after spiking the sampled water with 2mg/L BrO_3^-, 2mg/L organics (humic acid sodium salt), 2mg/L residual bromine and 2mg/L Cu^{2+}.(Ce (mg/L) is the amount of BrO_3^- remaining in solution after 48h and qe (mg/g) the amount of BrO_3^- adsorbed per g GAC).

Calculating the Freundlich K_F constants of all the synthetic matrices, it was found that pH is the strongest determinant of BrO_3^- removal efficiency followed by copper and bromine content. Organic load was found to promote bromate removal since humic acid acts as BrO_3^- reducer further to GAC.

CONCLUSIONS

It is concluded that frequently disinfected cooling water containing low amounts of residual bromine and organic load, well protected against corrosion, featuring as low pH as possible, are stripped easier from their bromate load with the help of GAC.

REFERENCES

United States Environmental Protection Agency Risk Assessment Forum (2005) Guidelines for carcinogen risk assessment

Chon, K., Salhi,E. and Von Gunten, U. (2015) Combination of UV absorbance and electron donating capacity to assess degradation of micropollutants and formation of bromate during ozonation of wastewater effluents. *Water Research* , **81**, 388-397