

Reducing Humic Acid and Disinfection By-products in Raw Water using a Bio-activated Carbon Filter

Wei-Pin Tseng, Jie-Chung Lou, Ming-Ching Wu, Huang-Ming Fang

Abstract—For stricter drinking water regulations in the future, reducing the humic acid and disinfection byproducts in raw water, namely, trihalomethanes (THMs) and haloacetic acids (HAAs) is worthy for research. To investigate the removal of waterborne organic material using a lab-scale of bio-activated carbon filter under different EBCT, the concentrations of humic acid prepared were 0.01, 0.03, 0.06, 0.12, 0.17, 0.23, and 0.29 mg/L. Then we conducted experiments using a pilot plant with in-field of the serially connected bio-activated carbon filters and hollow fiber membrane processes employed in traditional water purification plants. Results showed under low TOC conditions of humic acid in influent (0.69 to 1.03 mg TOC/L) with an EBCT of 30 min, 40 min, and 50 min, TOC removal rates increases with greater EBCT, attaining about 39 % removal rate. The removal rate of THMs and HAAs by BACF was 54.8 % and 89.0 %, respectively.

Keywords—Bio-activated carbon filter, hollow fiber membrane, humic acid, THMs, HAAs, Water Treatment

I. INTRODUCTION

THE natural organic matter (NOM) in water may affect all the processes of the water treatment plant and the quality of drinking water. If humus is present in the water, a yellow-brown color may result, affecting water appearance and potability. Additionally, organic material from certain chemicals can cause taste and odor issues. When microorganisms are present in the water purification process and the water distribution pipelines, the biodegradable organic carbon in NOM may be used as nutrient substrates, leading to microorganism growth that reduces water quality. [1] NOM undergoes complexation with heavy metal ions such as iron and manganese, creating metal complexes and causing significant chemical contamination of the water, endangering human health. [2] After disinfecting by chlorination, NOMs form carcinogenic disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs). [3] To effectively remove organic material from water, high-level processes involving granular activated carbon or membranes must be used. Stronger flocculating agents may also be employed during the flocculation process to increase the removal rate. [4]

Mechanisms involved in bio-activated carbon filter (BACF) removal include adsorption and biodegradation. Tung et al. [5] used BACF filled with GAC to process HAAs in drinking water. Their study found that BACF may effectively remove HAAs. The main operating parameters include temperature, type and dose of disinfectant, oxygen solubility limit, and EBCT. Tung et al. also noted that if the enriched bio-activated carbon obtained directly from the BACF process is used, BACFs can remove HAAs through biodegradation within 24 hr. Thus, the adsorption effect on the activated carbon surface can be ignored safely. The membrane process technique primarily uses the pore diameter or film surface characteristics to separate water impurities. The uses in potable water processing include softening, lowering the organic and inorganic carbon content in water, removing colloidal solids, removing disinfection byproducts and their potential precursors, and removing viruses. [6]

Numerous studies in recent years have reported good results from using advanced oxygenation or mixing processes on surface water or drinking water (ozone and UF/MF membranes: combination of ozone and activated carbon). [7] However, this method is still limited by raw water quality and ozone dosage, which can increase the toxic material, such as bromates from ozone process byproducts, in processed clear water. Studies are being conducted on processing toxic material in potable water using powder activated carbon to resolve this issue. [8]

Among the current methods, using bio-activated carbon to process waterborne organic material is the most effective. A wider range of application is possible if membrane processing techniques are combined and other processing units are integrated. This study integrates the activated carbon biodegradation procedure with hollow fiber membrane filtration to remove trace organic materials during water purification processes, such as total organic carbon (TOC), THMs, HAAs and DBP formation potential (DBPFP). Besides providing additional operational options for water treatment plants in our country, the feasibility of controlling disinfection by-products and their formation potential using bio-activated carbon filters (BACF) to process organic material presenting in water ; thus, we investigated this possibility.

II. MATERIALS AND METHODS

A. Enrichment of microorganisms for bio-activated carbon filter

Granular activated carbon is used as the vector for enrichment in this study. Effluent from the rapid sand filter in the water treatment plant was injected into activated carbon columns to facilitate the adsorption on granular activated carbon pores to form biofilms. The enrichment of

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microorganisms in bio-activated carbon filter typically requires 2 to 3 months. [9] To avoid experimental errors from physical adsorption on activated carbon, and to ensure full growth of biofilms on activated carbon, granular bio-activated carbon was enriched with prepared substrates. Sodium acetate (CH_3COONa) and oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) were used as the main carbon sources. Inorganic nutrient salts, including dipotassium hydrogen phosphate (K_2HPO_4) and potassium dihydrogen phosphate, were used as sources of phosphorous and potassium for microorganism growth and as a buffer solution to maintain neutral pH values. Ammonium chloride (NH_4Cl), calcium chloride (CaCl_2), and magnesium sulfate (MgSO_4) were used to provide essential the elements nitrogen, calcium, magnesium, chlorine, and sulfur.

Influent of the microorganism enrichment substrate was 15 mL/hr. The dissolved organic carbon (DOC) data in this study were obtained from bio-activated carbon filter after 2 months of enrichment and 50 days of experiment. The experiment duration was extended to 100 days under high granular activated carbon concentration conditions.

B. Preparation of synthetic raw water

To investigate the removal of waterborne organic material using a lab-scale of bio-activated carbon filter under different EBCT, we prepared solutions with different humus acid concentrations from commercially available humic acid reagents to establish the calibration curve. The concentrations of humic acid prepared were 0.01, 0.03, 0.06, 0.12, 0.17, 0.23, and 0.29 mg/L. Total organic carbon (TOC) was used as the indicator. Fig. 1 shows the linear relationship graph between humus acid concentrations and TOC concentrations. The R value in this graph is over 0.99, revealing a correlation between humus acid concentrations and TOC concentrations. Additional raw water was prepared at the TOC concentrations 0.5, 1.0, 2.0, 3.0, and 4.0 mg TOC/L. NaCl was added to provide an ionic strength of 1×10^{-3} M. This is used to explore the various TOC concentrations that result from passing through bio-activated carbon columns under EBCTs of 20 min, 30 min, 40 min, and 50 min.

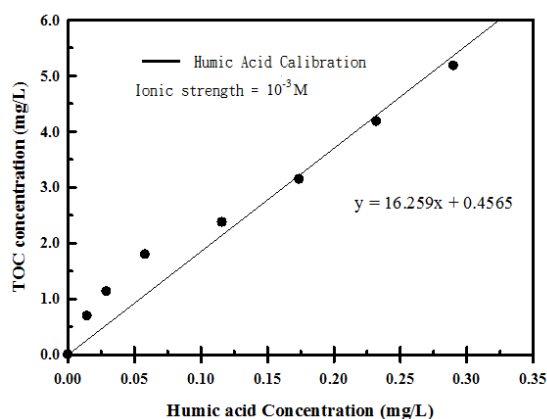


Fig. 1 Linear relationship of TOC Concentration with various humic acid Concentrations

Before beginning the experiment, the flow rate of the bio-activated carbon column was configured to full flow and adjusted to the EBCT required for the day. TOC analysis was conducted when the column effluent exceeded the designated contact time. After completing the experiment, effluent from the rapid sand filter in the Kaohsiung Ping-ding Water Treatment Plant was introduced into the BACT columns to provide the necessary nutrients for organisms.

C. Experimental analysis methods

i. Trihalomethanes

This study follows the published protocol 5710B from Standard Methods for the Examination of Water and Wastewater twentieth edition to determine the trihalomethane. N-pentene was used to extract trihalomethane from the water sample. The organic layer was then analyzed using GC/ECD.

ii. Conditions for gas chromatography analysis

An Agilent 7890A gas chromatograph equipped with an Agilent 7683A automatic sampler, an electron capture detector (ECD), a 30-m HP-5 capillary column, and computer operating software were the instruments used in this study. The operational parameters we employed for gas chromatography are as follows:

1. Injector: Automatic sampler and syringe were used to inject the sample. The injector temperature was stabilized at 200 °C, with split ratio configured at 1:50.
2. Detector: 280 °C with ECD
3. Column: HP-5, 30 m \times 0.25 mm ID, and with a membrane thickness of 0.25 μm .
4. Carrier gas: Nitrogen, a flow rate of 1.0 mL/min.
5. Auxiliary gas: Nitrogen, a flow rate of 30 mL/min.
6. Column temperature: The initial temperature was maintained at 40 °C for 7 min before being increased at a rate of 10 °C per min to 90 °C (13 min). Then, the temperature was further increased by 40 °C per min to 150 °C and maintained for 1 min (15.5 min).

iii. Haloacetic acids

We determined the haloacetic acids content following the protocol published under NIEA W538.51B. The water sample was first acidified to pH 0.5 and then extracted with methyl-tert-butyl ether (MTBE). Sulfuric acid methanol was added to enable analytes, such as HAA or Dalapon, to form methyl esters. An organic solvent layer containing methyl esters was separated and sampled for analysis using GC/ECD.

iv. Conditions for gas chromatography analysis

This study used an Agilent 7890A gas chromatograph equipped with an Agilent 7683A automatic sampler and ECD for the gas chromatography analysis. The operational parameters for the gas chromatography process were as follows:

1. Column: DB-1701, 30 m × 0.32 mm ID, with a membrane thickness of 0.25 μm .
2. Injector Temperature: 250 $^{\circ}\text{C}$
3. Detector Temperature: 300 $^{\circ}\text{C}$.
4. Temperature increase regimen:
40 $^{\circ}\text{C}$ (maintained for 10 min) \rightarrow 2 $^{\circ}\text{C}/\text{min} \rightarrow$ 80 $^{\circ}\text{C} \rightarrow$ 5 $^{\circ}\text{C}/\text{min} \rightarrow$ 100 $^{\circ}\text{C} \rightarrow$ 20 $^{\circ}\text{C}/\text{min} \rightarrow$ 200 $^{\circ}\text{C}$ (maintained for 2 min)

III. RESULTS AND DISCUSSION

A. Removing TOC from synthetic raw water under different EBCTs

Synthetic raw water with different TOC concentrations (0.5, 1.0, 2.0, 3.0, 4.0 mg TOC/L) were prepared and adjusted to 1×10^{-3} M ionic strength by adding NaCl. The solutions were then passed through batch columns with different EBCTs (20 min, 30 min, 40 min, and 50 min). Fig. 2 shows that the changes in TOC concentrations can be classified into two categories, namely, low carbon concentrations at 0.69 to 1.03 mg TOC/L and high carbon concentrations at 1.79 to 4.18 mg TOC/L.

Fig. 3 shows that the curve eases and the removal rate shows signs of saturation. The current standard for TOC in influent of raw water is 4 mg/L, thus, we may assume that 3.14 to 4.18 mg TOC/L is a high carbon concentration. The removal rate may reach 77 % when the EBCT is 50 min. Under low TOC conditions (0.69 to 1.03 mg TOC/L) with an EBCT of 30 min, 40 min, and 50 min, TOC removal rates are similar. TOC removal increases with greater EBCT, attaining a 39 % removal rate.

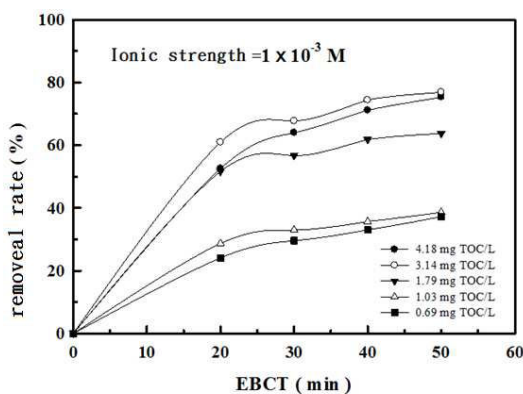


Fig. 2 Removal rate of TOC under different EBCT from synthetic raw water of various influent concentration of TOC

B. Analysis of THM and HAA for bio-activated carbon filter serially connected with hollow fiber membranes

i. Trihalomethane

As shown in Fig. 4, the trihalomethane concentration range for rapid sand filter efflux from a certain water purification plant

is between 0.01090 to 0.03233 mg/L. The current potable water standard set by the Environment Protection Agency (EPA) in Taiwan for trihalomethane concentration is 0.08000 mg/L, whereas the standard set by the U.S. EPA is 0.04000 mg/L. Through experiments using rapid sand filter efflux as raw water, we found that trihalomethane concentrations decreased when water was passed through either BACF or BACF+UF procedures. These results indicate that adding processing systems with bio-activated carbon serially connected to hollow fiber membranes can reduce trihalomethane concentrations in water, maintaining the total trihalomethane concentration between 0.00460 and 0.01130 mg/L, with a removal rate above 45 %.

As shown in fig. 4, trihalomethane removal is most efficient when EBCT is 50 min under BAC and serially linked with UF.

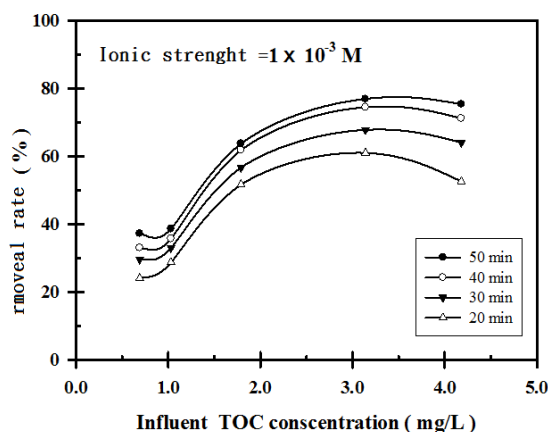


Fig. 3 Removal rate of TOC at various EBCT under different influent concentration of TOC

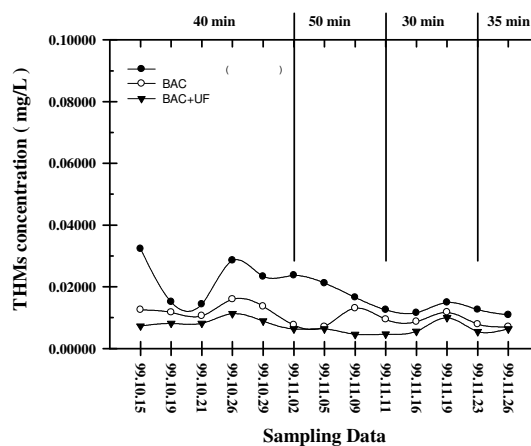


Fig. 4 Change of THMs concentration with various time in a water treatment plant under continuous operation of a pilot plant

ii. Haloacetic acid

As shown in fig. 5, HAA concentrations for rapid sand filter efflux from a certain water purification plant were between 0.04094 to 0.05771 mg/L. Because the EPA in Taiwan currently has no standard for HAA concentration in water, we used the standard established by the U.S. EPA, which is 0.03000 mg/L.

For the raw water from the rapid sand filter efflux used in this experiment, we found that by passing through either BAC or BAC+UF, the water's HAA concentration decreases. This experimentally proves that adding a bio-activated carbon processing system after the rapid sand filter can remove waterborne HAA, controlling HAA concentrations to within 0.00424 to 0.00867 mg/L with a removal rate above 80 %.

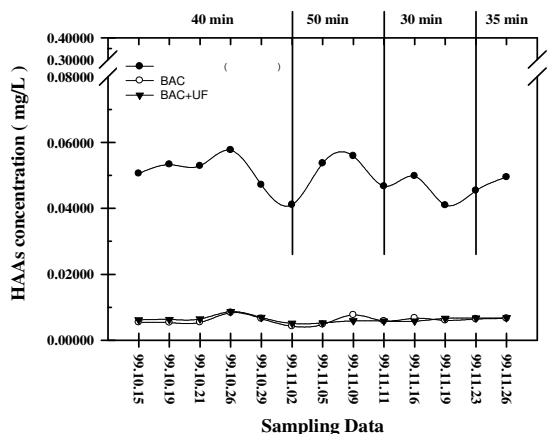


Fig. 5 Change of HAA concentration with various time in a water treatment plant under continuous operation of a pilot plant

IV. CONCLUSION

This study shows that using bio-activated carbon filter in water treatment processes can effectively lower TOC concentrations. When high TOC concentrations of humic acid in influent was between 3.14 to 4.18 mg TOC/L, a 77 % removal rate is achieved with 50 min EBCT. At low TOC concentrations of humic acid was between 0.69 to 1.03 mg TOC/L, the TOC removal rates for an EBCT of 30 min are similar to those for EBCT of 40 min and 50 min, reaching about 39 % removal rate.

This study shows that adding a bio-activated carbon filter system during actual installation of in-field can effectively lower the concentration of disinfectant by-products in raw water (including THMs and HAAs).

Although microorganisms in bio-activated carbon filters may age, the biofilm can also detach. Adding membranes in downstream of BACF process is necessary to prevent the out of detached biofilm.

The most efficient removal rate of THM and HAA is achieved at a EBCT of 50 min for a BACF serially connected with UF.

REFERENCES

- [1] Khan, E., R. W. Babcock, I. H. Suffet and M. K. Stenstrom, "Biodegradable dissolved organic carbon for indicating wastewater reclamation plant performance and treated wastewater quality", *Wat. Environ. Res.*, vol. 7, pp. 1033-1040, 1998.
- [2] Barber, L.B., Leenheer, J.A., Noyes, T.I. and Stiles, E.A., "Nature and transformation of dissolved organic matter in treatment wetlands", *Environ. Sci. Technol.*, vol. 35, pp.4805-4816, 2001.
- [3] Bolto, B., G. Abbt-Braun, D. Dixon, R. Eldridge, F. Frimmel, S. Hesse, King, S. & Toifl, M., "Experimental evaluation of cationic polyelectrolytes for removing natural organic matter from water", *Water Science and Technology*, vol. 40, no. 9, pp. 71-79, 1999.
- [4] Jacangelo, J. G., Aieta, E. M., Carns, K.E., Cummings, E. W., and Mallevialle J., "Assessing hollow-fiber ultrafiltration for particulate removal." *J. AWWA*, vol. 89, 1989.
- [5] Hsin-Hsin Tung, Richard F. Unz and Yuefeng F. Xie, "Evidences of HAAs Biodegradation in GAC Filtration", *J. Environ. Eng. Manage.*, vol. 19, no. 1, pp. 59-66, 2009.
- [6] Pearce, G. K., Heijnen, M. and Reckhouse, J., "Using ultrafiltration membrane technology to meet UK cryptosporidium regulations", *Membrane Technology*, vol. 2002, no. 1, pp. 6-9, 2002.
- [7] Su, D. J. and Gao, N. Y., "A study of removing organic matters in slightly-polluted water by an ozone-active carbon combined process", *Ind. WaterWaste-water*, vol. 32, pp. 26-28, 2005.
- [8] Gai, X. J. and Kim, H. S., "The role of powdered activated carbon in enhancing the performance of membrane systems for water treatment", *Desalination*, vol. 225, pp. 288-300, 2008.
- [9] Servais, P., Laurent, P. and Randon, G., "Comparison of the bacterial dynamics in various french distribution system." *J Water SRT-Aqua.*, vol. 44, no. 1, pp. 10-17, 1995.