A Study of Removing SUVA and Trihalomethanes by Biological Activated Carbon

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Abstract—SUVA (equivalent to UV_{254}/DOC) value in raw water is a precursor for the formation of trihalomethane during chlorination at a water treatment plant. This study collected rapidly filtered water from an advanced water treatment plant for use in experiments on raw water. The removal rate of treating the trihalomethanes formation potential (THMFP) was conducted by using a biological activated carbon. The hydraulic retention time and SUVA loading were major factors in biological degradation tests. The results showed that biological powder-activated carbon (BPAC) lowered the average concentration of UV_{254} and value of SUVA in raw water. A removal efficiency of THMFP was present in the treatment of the three primary organic carbon items. These results highlighted the importance of the BPAC had an excellent treatment efficiency on THMFP.

Keywords—Water treatment, BPAC, THMFP, SUVA, correlation analysis.

I. INTRODUCTION

THE hydrophobic organic matter has become hydrophilic in this scenario, coagulant removal is not beneficial [1], [2] and causes the added chlorine disinfectant to derive a large number of disinfection by-products (DBPs), such as trihalomethanes [3].

In southern Taiwan, most water purification processes use pre-chlorination for disinfection. Combination of pre-chlorination and the organic matter in raw water results in formation of disinfection by-products [4]. Therefore, excessive amounts of disinfection by-products are often discovered when inspecting water in this region [5]. Workers at water purification plants in southern Taiwan wish to resolve this problem.

Many disinfection by-products are carcinogenic, teratogenic, and mutagenic to humans [6]. The primary disinfection by-product is trihalomethane [7]. Current methods for decreasing the production of disinfection by-products include reducing the amount of chlorine or removing as many organic precursors as possible prior to the chlorination process [8].

Biological activated carbon (BAC) can remove the organic matter in water [9]. BAC systems use the motion of microorganisms on the activated carbon surface to decompose pollutants, increase biological stability, and decrease the amount of chlorine in the pipelines after treatment. These features make the method of BAC one of the best available

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technologies for controlling drinking water quality in water treatment plant.

This research investigates the use of a BPAC to remove SUVA and THMFP in raw water. It is hoped that the result will provide water treatment plants with an additional choice for the advanced treatment process that would also aid in conserving land.

II. MATERIALS AND METHODS

A. Raw Water Samples Collection and Analytical Procedure

The raw water samples came from the Fengshan Water Treatment Plant (FSWTP) in Southern Taiwan. Most of the raw water was taken from the surface water of the Gaoping River. After treatment, raw water becomes drinking water for the people of Kaohsiung City. The FSWTP is comprised of advanced water purification systems with the ability to provide 30,000 CMD of clean water. The primary process includes the use of distribution wells, flocculation and sedimentation, pellet softening, rapid filtering, ozone disinfection, and biological activated carbon filtration.

The raw water was used to cultivate microorganisms in the laboratory. This allowed the microorganisms to grow on the powder-activated carbon (PAC), forming biofilm. Samples were taken from the outflowing water in the BPAC to perform water quality analysis, with items tested including DOC, UV_{254}, SUVA and THMFP.

B. Analytical Procedure

1. Dissolved Organic Carbon (DOC)

An appropriate concentration of potassium hydrogen phthalate ($KHC_8H_4O_4$, KHP, Nacalai Tesque, Japan) was mixed to prepare a standard calibration. The solution was then passed through a filter membrane of 0.45 μm for analysis. A 1030 W wet oxidation TOC analyzer (OIA) was used. The water sample was acidified and had its inorganic carbon purged. The sample was then oxidized at a temperature between 116 and 130°C in an autoclave with peroxodisulfate.

The organic carbon in the water sample was oxidized into carbon dioxide, and then immediately brought by the carrier gas into a non-dispersive infrared analyzer that can absorb carbon dioxide of a specific wavelength to detect the peak area of this carbon dioxide. After the peak area of the blank test solution is eliminated, the concentration of non-purgeable organic carbon (NPOC) could be obtained through calibration. The concentration of the dissolved organic carbon in the water sample could thus be measured.

2. UV$_{254}$ and SUVA

The absorbance of UV$_{254}$ was determined according to Standard Method 5910 B Ultraviolet Absorption Spectrophotometry for American water and wastewater. First, the pH value of the analyzed water samples was adjusted to 7 ± 0.5 with 0.1 N NaOH or HCl. During the sample absorbance determination, the detecting wavelength was set to 254 nm and inorganic pure water was used for the calibration of the apparatus. Following this setup, an excessive amount of the water sample was placed into a quartz sample cell with a light path of one cm, where its absorbance was read. This value was the UV$_{254}$ value.

Previously, Singer [10] indicates that the analysis data of absorbance ratio SUVA (UV$_{254}$/DOC) are easier to obtain because the analysis method is simpler and easier. Therefore, this is a good substitution parameter for judging the content of unsaturated bonds and aromatic compounds in water.

3. Formation Potential of Trihalomethane

A 120mL brown sample bottle was filled with the sample water until it was almost entirely full and without air bubbles. A microneedle was used to inject a suitable amount of NaOCl. After sealing the sample bottle, it was capped immediately. The vial was shaken for at least 15s, allowing the sample to mix evenly before it was placed in a dark environment at room temperature to react for 3 days. The dosage of NaOCl was based on the formula suggested by Krasner, with slight adjustments [11]:

$$Cl_2\,(mg/L) = 3 \times DOC + 7.6 \times NH_3 - N + 1 - 10\ mg/L$$

After 3 days of reaction time, the residual chlorine was measured in a portion of the water sample. 1 to 5 mg/L of free residual chlorine were required in the sample. NH$_4$Cl was added to the rest of the water sample to inhibit the residual chlorine and stop the reaction within the water sample. This sample was analyzed following the THM method, in which, and the THMFP was determined.

The analysis of trihalomethane is based on an improved version of the USEPA Method 501.2. After using pentane to extract the disinfection by-products in the water sample, the organic layer was removed and analyzed four types of THM and disinfection by-products with the GC/ECD method: chloroform, bromodichloromethane, dibromochloromethane, and bromoform.

4. 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, 30m × 0.25mm ID, and with a membrane thickness of 0.25μm.
4. Carrier gas: Nitrogen, a flow rate of 1.0mL/min.
5. Auxiliary gas: Nitrogen, a flow rate of 30mL/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 1min (15.5min).

TABLE I
WATER QUALITY PARAMETERS OF TESTED RAW WATER

Parameters	Unit	concentration
pH	-	8.25±0.30
Temperature	°C	23.76±2.47
Conductivity	μmho/cm	538.26±15.14
TDS	mg/L	335.96±69.96
DOC	μg/L	0.68±0.14
UV$_{254}$	1/m	0.92±0.36
SUVA	L/mg-m	1.34±0.29
NH$_3$-N	mg/L	0.03±0.02
NO$_3^-$-N	mg/L	0.89±0.35
THMFP	μg/L	20.54±6.48

III. RESULTS AND DISCUSSION

A. Quality Parameters of Raw Water

Table I is the summary of water quality parameters of tested raw water. The results showed the range of concentration of DOC, UV$_{254}$, SUVA and THMFP are 0.68 ± 0.14mg/L, 0.92 ± 0.36 1/m, 1.34 ± 0.29 L/-mg-m and 20.54 ± 6.48 μg/L respectively.

B. Removal Rate of SUVA

Hydrophobic matter is generally considered to be richer in aromatic compounds. This type of organic matter is also the primary precursor of disinfection by-products. Korshin et al. [12] indicated that as the SUVA value increased, the formation potential of trihalomethanes also increased. Calculations indicated that the average SUVA value of the inflowing water was 1.06 ± 0.27 L/mg-m, whereas that of the outflowing water was 0.82 ± 0.27 L/mg-m. The average SUVA value decreased to 22% from 23% between retention times from 1 to 6 hrs, indicating that the BPAC can decrease the double bond structures of the organic matter within the water, preventing unsaturated conjugated double bonds from forming the precursors of chlorination by-products.

C. Removal Rate of THMFP

Trihalomethane potential before and after BPAC treatment was 24.64 ± 6.74 μg/L and 14.75 ± 4.04 μg/L, respectively. The removal fractions fell between 36% and 46% and its trend was stable, as shown in Fig. 1.

Each component's concentration and percentage (shown in Fig. 2) indicate that TCM accounts for 56% of THMFP. Prior research in experimental epizootiology has proven that TCM can cause liver and kidney tumors. Therefore, the discovery of the removal effect of BACS on THM is especially important. The removal fraction of this system on TCM and BDCM was
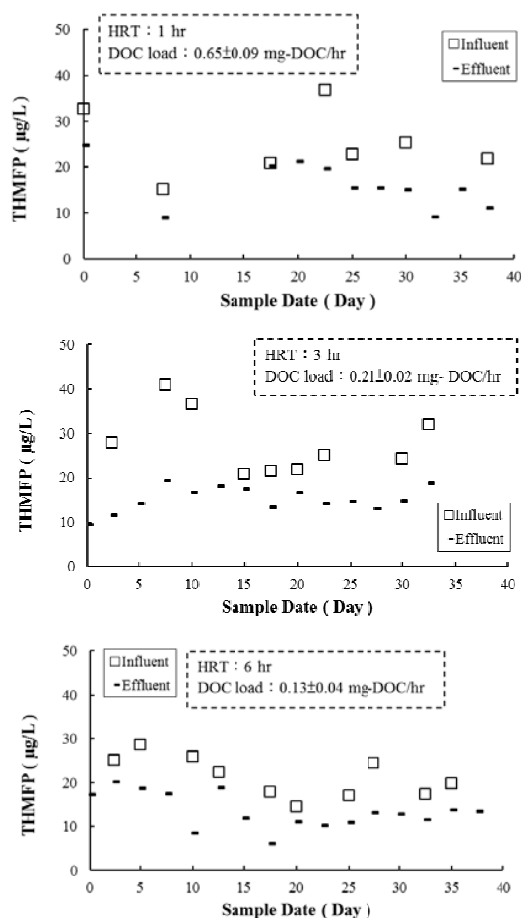
50% and 31%, respectively.

Fig. 1 Variation in THMFP over time at different HRT during the use of a BPAC. The solid dots represent inflowing water and the hollow dots represent outflowing water

When using the BPAC to decrease trihalomethane formation potential, the removal fractions at three different hydraulic retention times fell between approximately 36% and 46%. This result was similar to that of SUVA, indicating that an excellent removal fractions was found in the outflowing water treated by the biological activated carbon system. The system decreased the double bond structure of the organic matter in the water, preventing unsaturated conjugated double bonds from forming the precursors of chlorination by-products.
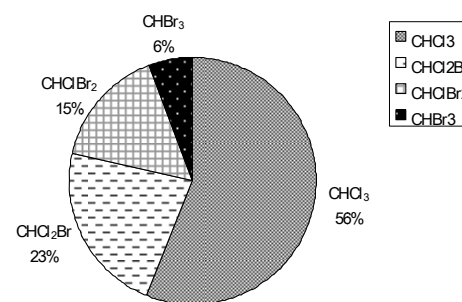

Fig. 2 Proportional graph of four types of THMFP in the outflowing water of the BPAC

D. Equations Relating to SUVA and THMFP

This study used SUVA as a surrogate index for the potential for disinfection by-products. Because the study revealed that testing methods for disinfection by-products can be complicated and time-consuming, establishing a prediction model would reduce the time needed to estimate disinfection by-product potential.

This paper divided SUVA into concentration of THMFP to perform correlation analysis. Graph of regression results was obtained (Fig. 3). The R^2 values in these regressions is 0.82. The R^2 correlation results indicate that is highly negatively correlated. Equation (1) is the prediction equation of SUVA on THMFP.

Using ozone oxidation can decrease the SUVA value because the organic matter of small molecular mass increases. After then passing through the biological filter bed, the small molecules can be decomposed and used by the organisms. This allows the DOC removal rate to increase, and the ozone oxidation process also increases disinfection products such as BrO^{3-}. Therefore, it can be conjectured that before the raw water has gone through the purification process, the direct correlation between its DOC and THMFP is comparatively clear.

However, after the water sample has gone through the purification process, most of the organic matter in the water has been removed, and the DOC concentration of the water sample could have already greatly decreased. Therefore, the concentration of DOC and DBP in the purified water sample has no clear direct relationship. If the SUVA concentration were to be used as a basis for ascertaining DBP formation potential, a better result would be obtained if compared with the formation potential concentration.

The real relationship between SUVA and THMFP might not be truly reflected in this study due to the limited data collected. Long-term monitoring and analysis may therefore be required to more confidently understand the true degree of the relationship between SUVA and DBP. These actions would establish a complete database to serve as the next step for controlling and predicting THMFP in water treatment plants according (1).

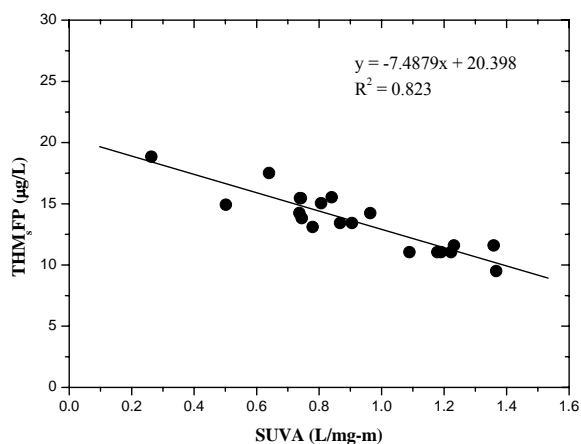$$THMFP (\mu g/L) = -7.5(SUVA) + 20.4, \ (R^2 = 0.82) \quad (1)$$

Fig. 3 Relationship between THMFP values and SUVA

IV. CONCLUSION

1) BPAC was found to have removal effect on the organic carbon in raw water. The SUVA value dropped to 15% from 18% and 22% from 23% in the experiments, indicating that this treatment system decreases organic matter and the concentration of THMFP in raw water.

2) This method was clearly removing THMFP. Their average concentrations in out flowing water were lower than the legal standard of 80μg/L in Taiwan. This improvement could lower risk from carcinogens.

3) Correlation analysis of SUVA on the water quality concentration of THMFP resulted in R^2 values of 0.82. These values indicate a high level of negative correlation.

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