

HYDROPHOBICITY CHARACTERISTICS OF NATURAL ORGANIC MATTER AND THE FORMATION OF THM

(Pencirian Kehidrofobikan Sebatian Organik Semulajadi dan Pembentukan THM)

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Abstract

This study investigated the relationship between the characteristics of natural organic matter (NOM) and the formation of trihalomethanes (THMs). NOM from Semenyih river was isolated using resin adsorption method into six fractions based on hydrophobicity and acidity. Hydrophobic acid (40 %) and hydrophilic neutral (22 %) were the major component in the water sample. All the six classes of NOM were evaluated for their trihalomethane formation potential (THMFP) and related parameters. The result shows that the major fractions (hydrophobic acid and hydrophilic neutral) were not the reactive organic fractions in the formation of THMs. Hydrophobic base and hydrophilic base were found to be the most reactive fractions of concern with respect to the formation of THMs. Hydrophobic contents in NOM favoured the formation of THMs. In addition, increasing pH from 6 to 9 increased THM formation. The results from the present study indicated that the identification and specific removal of NOM fractions in raw water would minimize the formation of THMs during chlorination process.

Keywords: Natural organic matter, trihalomethanes, chlorination

Abstrak

Kajian telah dijalankan untuk mengkaji hubungan antara ciri-ciri sebatian organik semulajadi (NOM) dan pembentukan trihalometana (THM). NOM daripada Sungai Semenyih telah diasingkan kepada enam pecahan berdasarkan kehidrofobikan dan keasidan dengan menggunakan kaedah penjerapan resin. Asid hidrofobik (20%) dan neutral hidrofilik (22%) merupakan komponen utama dalam sampel air yang dikaji. Potensi pembentukan trihalometana dan parameter berkaitan lain dinilai terhadap kesemua fraksi NOM.. Keputusan menunjukkan fraksi utama (asid hidrofobik dan neutral hidrofilik) merupakan spesis yang tidak aktif dalam pembentukan THM. Bes hidrofobik dan bes hidrofilik didapati merupakan spesis yang paling reaktif dalam pembentukan THM. Kandungan hidrofobik dalam NOM didapati lebih cenderung untuk membentuk THM. Peningkatan pH daripada 6 ke 9 meningkatkan keupayaan pembentukan THM. Hasil kajian ini menunjukkan bahawa pengenalpastian dan penyingkiran NOM yang spesifik boleh meminimumkan pembentukan THM semasa proses pengklorinan.

Kata kunci: Sebatian organik semulajadi, trihalometana, penklorinan

Introduction

Natural organic matter (NOM) in drinking water source is of primary concern because it acts as precursor in the formation of potentially harmful disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) [1,2]. NOM reacts with disinfectants (chlorine and chloramines) during water treatment process to form DBPs. To understand the character and role of NOM in the formation of DBPs, it is necessary to investigate the chemistry of each fractions of NOM. For this reason, a number of studies were conducted to characterize and quantify NOM in water source [3-5]. NOM is a complex mixture of hydrophilic and hydrophobic organic materials which varying in size, functional groups and reactivity. The formation of DBPs depends on the source water quality characteristics and the operational parameters during the treatment processes. Generally, nature and concentration of NOM, pH, water temperature, contact time and disinfectant dose are the main parameters influence the formation of type and amount of DBPs [6,7]. Reactions between chlorine and NOM has shown that DBP formation increases with the aromatic content of NOM [8].

Traditionally, characterization of NOM in water source has focused on the surrogate parameters such as dissolved organic carbon (DOC). Nonetheless, over the last two decades, the importance of size, structure, functionality,

hydrophobicity of NOM were recognized [9,10]. Moreover, the ratio of UV and DOC – specific UV absorbance (SUVA) is a good indicator of aromatic content in NOM and has been correlated with the formation of DBPs [11-13]. In addition, fluorescence spectroscopy, size exclusion chromatography, polar fractionation have been utilized to provide insight into a better understanding of NOM characteristic and its tendency to form DBPs [14]. Because of different components of NOM from different sources may form distinct level of DBPs, the understanding of the role of the NOM fraction is crucial in controlling DBPs in drinking water.

Considerable works had been done by previous researchers to compare the role of hydrophobic and hydrophilic of NOM in the formation of DBPs [15]. Imai et al. [16] obtained a significant relationship between the formation of THMs and HAAs and the content of hydrophilic acids ($R^2=0.63$, $P<0.01$). Liang and Singer [6] found that hydrophilic NOM is a more important source of the formation of THMs and HAAs than the corresponding hydrophobic NOM. This shows that NOM characteristics vary from different water sources. It is influenced by the natural photosynthetic activities of terrestrial and aquatic plants, algae and photosynthetic bacteria. The trophic status of the sampling environment also influences the concentration and composition of NOM. Further investigation is needed to understand the behaviours of NOM in the water source. Knowledge of the reaction between NOM fractions with chlorine is useful in identifying potential precursors of DBP and the treatment strategies. The primary objective of this study is to access the impact of NOM characteristics on the formation of THMs. The fractionation of NOM was conducted based on the separation of hydrophilic-hydrophobic and acidic-base breaks to evaluate the characteristics of NOM in Semenyih river. In addition, relationship between formation of THMs and characteristic of NOM were also investigated.

Materials and methods

Collection of water sample

In this study, water samples were collected from Semenyih river which is the source of raw water for a water treatment plant, the Semenyih River Water Treatment plant. This plant produces about 145 MGD of treated water and is source of drinking water for more than 1 million people. Samples were collected from one monitoring station in Semenyih river, transferred to the laboratory in an ice cooler to minimize changes in the constituents. Samples were prepared by filtering through a 0.45 μ m membrane filter and were ready for fractionation and analysis.

Fractionation Procedure

The fractionation of NOM was performed based on the resin adsorption procedure (Marhaba et al. 2003; Thurman & Malcolm 1981). Briefly, NOM was fractionated into hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB) and hydrophilic neutral (HPIN). The filtered raw water sample was passed through DAX-8 resin column. HPON was then extracted out with methanol. The sample was then adjusted to pH 10 and passed through second DAX-8 column and the HPOB fraction was eluted with HCl. The effluent was then passed through DAX-8 column. HPOA was eluted with NaOH. The remaining hydrophilic acid fractions were extracted by AG-MP-50 and WA-10 resin and were eluted with NaOH. The final fraction retained in the sample was HPIN.

Trihalomethanes formation potential

THM was analyzed by purge and trap coupled with capillary column gas chromatograph with electron capture detector. Hewlett-Packard HP 5690 series II gas chromatograph with HP chemstation was used to generate THM data. THMFP test were performed in accordance with standard methods 5710-B (APHA 1998). Chlorine solution was prepared in the form of concentrated sodium hypochlorite (100 mg/l). Residual chlorine was measured at the end of 7-day reaction period. Only the samples with residual chlorine of 3-5 mg/l were analyzed for THM. Residual chlorine was quenched with 0.1 mL of 100g/L sodium sulfite. The change in THM concentration for 7-day period was determined as the THMFP.

Results and Discussion

Characteristics of Water Sample NOM

Fig. 1 shows the percentage distribution of the organic fractions in Semenyih river. HPOA was the most dominant fraction in the water sample (40 %) whilst HPIN was the second (22 %). Two basic fractions, HPIB and HPOB approximated 14 % in the sample analyzed. Fig. 1 clearly shows that HPOA which usually contains fulvic and

humic acids is the major contributor of the total DOC in Semenyih river. HPOB and HPON constituted on average of 8 and 11 % of the NOM (as DOC). Hydrophilic fractions generally make up a smaller fraction of DOC compared to hydrophobic fractions. HPIN contributed 22 %, while HPIA and HPIB contributed 13 % and 6 %, respectively, of the total NOM.

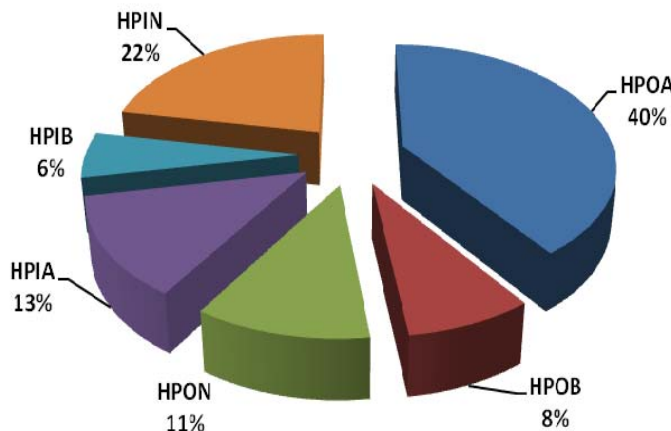


Fig. 1. NOM fractions distribution of samples from Semenyih river

Trihalomethanes Formation Potential

In an effort to understand the reaction between NOM and chlorine on a more fundamental level, the relationships between NOM fractions and the THM formed was investigated. Trihalomethanes formation (THMFP) test is a measure of the potential of the water samples to form THM after the addition of chlorine. In this study, THMFP tests were conducted using the organic isolates from the fractionation of NOM. Fig. 2 shows the total THMFP for each organic fraction. The greatest THMFP was associated with the HPOA and HPIN. This is because both HPOA and HPIN were the most dominant constituent among the six organic fractions in the water sample. HPOB and HPIB contributed the least to the total THMFP because both of the fractions only accounted for 14 % of the total NOM in the water source.

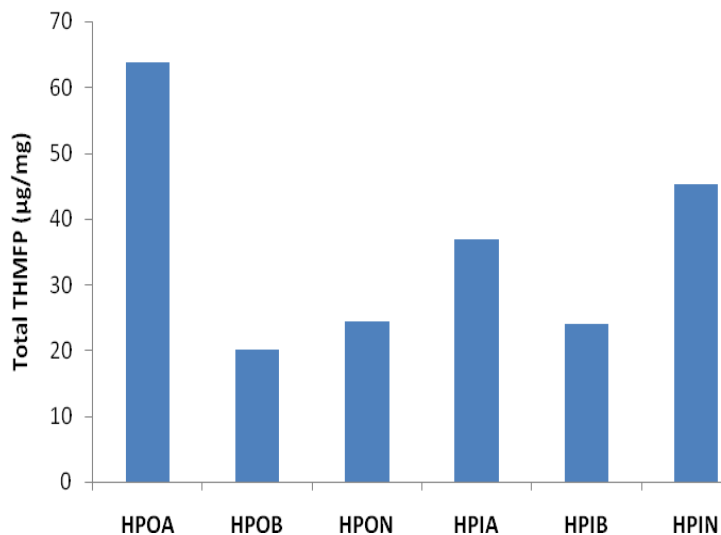


Fig. 2. Total THMFP for each organic fraction

Fig. 3 shows the specific THMFP for all the six organic fractions. In order to investigate the reactivity of the THMFP of each organic fractions, all the THMFP data was normalized to the ratio between THMs formed and DOC content of each organic fraction to obtain specific THMFP yield. It was found that HPOB and HPIB gave the highest specific THMFP indicating both fractions were highly reactive in the reaction with chlorine to form THMs. Basic fractions (HPIB and HPOB) tend to form more THM than acid and neutral fractions. This may be due to the higher aromatic content in the basic fractions [17]. Specific THMFP of the six organic fractions, from high to low, were HPOB, HPIB, HPON, HPIA, HPOA and HPIN, respectively. The most active organic fractions in forming THMs was not the organic fraction which exist in large quantity.

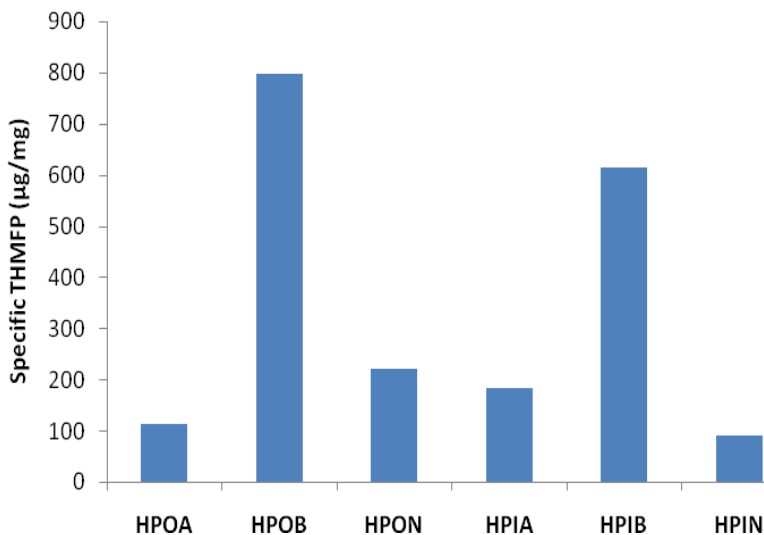


Fig. 3. Specific THMFP for each organic fraction

The results from Fig 2 and Fig. 3 revealed that the main precursors of THMs (HPOA and HPIN) were the most inactive organic fractions to form THMs during chlorination. The organic fractions which exist in slight quantity (HPOB and HPIB) were observed to be the most active THM precursors.

Effect of pH on THMFP

The organic fractions were chlorinated at chlorine dosage of 10 mg/l at different pH from 6 to 9 and the THMs formed were measured. Reckhow et al. [18] found that the distribution and the formation of THMs strongly depend on the chlorination pH. Fig. 4 demonstrates the effect of pH on the THMs formations. Increasing pH from 6 to 9 significantly increased the formation of THMs. As shown in Fig. 4, pH adjustment (increasing of pH) enhanced the formation of THMs for both hydrophobic and hydrophilic fractions. Based on the mechanism suggested by Reckhow and Singer [18], transient β -diketone groups are formed from the oxidation of fulvic acids. Under alkaline conditions, base-catalyzed enhances the formation of THMs. The THMs formed from the hydrophobic fractions were consistently higher than the hydrophilic fractions. This may be due to the rich aromatic content, hydroxyl groups and conjugated double bonds in hydrophobic fractions. Jung and Son [19] also reported that the hydrophobic fraction yielded more THMs compared to hydrophilic fractions. Nonetheless, the nature and the distribution of hydrophilic and hydrophobic materials may vary in different water source.

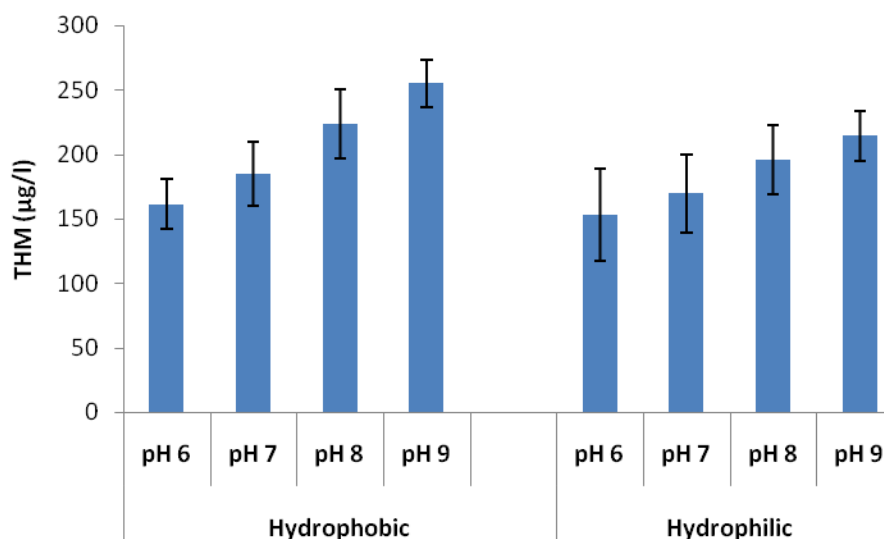


Fig. 4. Effect of pH on THM formation from NOM fractions

Implications for Drinking Water Management

The formation of THMs in treated water depends on the raw water quality, especially the concentration of NOM. The water of Semenyih river is not suitable for drinking water supply without extensive treatment. The characterization of NOM from this study suggested that HPOA and HPIN were the major precursor for the formation of THM. These fractions must be primarily reduced to minimize the formation of THMs and other DBPs. Selective removal of the reactive fractions (HPOB and HPIB) is crucial to minimize the formation of THMs as they are the most active species to form THMs during chlorination. Management strategies to control the THMs level in treated water should be optimized to remove the THM precursors. Coagulation usually remove larger molecular and more hydrophobic NOM. Activated carbon is normally applied to remove the dissolved organic contents in water. Granular activated carbon (GAC) is effective in removing the lower molecular weight and hydrophilic fractions of NOM. Further more, the development of membrane filtrations may be an option for utility to control the formation of THMs in drinking water. This study may be useful for drinking water utility to optimize the treatment process to remove the NOM in raw water thereby reducing the formation of THMs.

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