NATURAL ORGANIC MATTER (NOM) IN SOUTH AFRICAN WATERS: CHARACTERIZATION, TREATABILITY AND METHOD DEVELOPMENT FOR EFFECTIVE NOM REMOVAL FROM WATER

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ABSTRACT

NOM is a heterogeneous mixture of organic compounds that can be of human origin or derived primarily from plant and microbial residues. The inadequate removal of NOM has a bearing on the capacity of the other treatment processes to remove organic micro-pollutants or inorganic species that may be present in the water. Owing to the complexity and structure of NOM, the techniques employed for the characterization of NOM have a limitation in terms of an all inclusive characterization protocol of NOM to molecular level. This study is thus aimed at developing a rapid method of NOM characterization. Water samples will be collected from the five geographic water regions of South Africa to effectively study the nature of the South African water source for its NOM composition. The polarity rapid assessment method (PRAM) will be employed as a rapid NOM characterization tool. The characterization under PRAM is based on preferential adsorption of dissolved organic matter (DOM) fractions onto solid phase extraction (SPE) sorbents. By extension, the study would then develop a rapid NOM removal strategy that would remove NOM from source during pre-treatment and along the treatment train. A rapid NOM removal technique will then be employed, where different sorbents (e.g. cyclodextrin polyurethanes impregnated with nano-particles) will be employed as sorbents for NOM removal.

INTRODUCTION

The removal of natural organic matter (NOM) from water has become increasingly important due to the formation of carcinogenic disinfection by-products (DBPs) if organic carbon is insufficiently removed (1). NOM occurs naturally from the degradation of animal and plant material. Besides the natural sources, there are also anthropogenic effects that contribute to the presence of organic matter in water systems e.g. the use of agricultural chemicals.

During water treatment, NOM reacts with chlorine and other disinfectants to form halogenated DBPs e.g. trihalomethanes (THMs) and haloacetic acids (HAAs).Many of these DBPs are known carcinogens and are reported to be mutagenic or endocrine disrupting compounds (2). Also, NOM present in domestic water causes aesthetic problems like visual repulsion (due to low water clarity), foul taste and bad odour. NOM has the ability to associate with metal ions and organic compounds and exhibits a relatively high persistence in the environment due to a comparably low potential for microbial decomposition (3).

NOM plays an important role in diverse environmental processes including fate and transport of contaminants, heavy metal speciation and the global carbon cycle (4). During water treatment, NOM affects coagulation and membrane filtration and also serves as the main substrate for the formation of DBPs (5). As NOM is generated by physical, chemical and biological activities in the watershed surrounding a water source itself, (1) this therefore implies that the NOM composition of any water source varies from region to region, based on the kind of plant and animal material present.

In order to comprehend the mechanism of NOM removal from water, the composition of NOM in the local source water must be grasped since the types of NOM are not universal (6). Accordingly; NOM in source water needs to be characterized in order to craft the best removal strategy. Owing to the complexity and structure of NOM, the techniques employed for the characterization of NOM have a limitation in terms of an all inclusive characterization of NOM to molecular level.

Common NOM characterization techniques include: Dissolved organic Carbon (DOC) measurement, Ultraviolet (UV) absorbance analysis at a wavelength of 254 nm, specific ultraviolet absorbance (SUVA) analysis, size exclusion chromatography (SEC) and the use of ion exchange chromatography. A combination of these techniques assists in underpinning the characteristic properties of NOM. However, none of these methods is rapid enough to give characterization results within a short period of time.

The complexity of NOM is attributed to the differences in geographical areas and seasons. This leads to the difficulty in NOM characterization, which provides limited information pertaining to its character and behaviour. Due to this limitation, research efforts to characterize NOM in water supplies and to reduce its levels in drinking water supplies are currently underway. The presence of NOM in drinking water sources has a bearing on its treatability particularly with respect to its removal. Among different NOM removal processes, the following are the most commonly used: enhanced ozonation, advanced oxidation process, ozonation in combination with bio-filtration, adsorption and membrane filtration. However, the high variability in the levels and composition of NOM in South-African water sources in different regions means that no single treatment process can be prescribed for the entire country. Further, the treatability of NOM varies along the water treatment train and there are varying effects of NOM on the efficiency of these processes.

This project is thus aimed at developing a rapid method of NOM characterization. Understanding the character of NOM within a short period of time would help inform water treatment engineers and necessary adjustments to be carried out within the water treatment plant since the composition of NOM changes during the water treatment process. By extension, the study would remove NOM from source, during pre-treatment and along the treatment train.

METHODOLOGY

Sample collection and preservation

Water samples were collected from the a water treatment plant (Gauteng province), which uses ozonation as part of its standard treatment protocol. Samples were taken before and after the ozonation process and the sampling was repeated after one month. All water samples were filtered through a 0.45 μm cellulose filter paper and stored in the refrigerator at 4°C for not more than 48 hrs. Two litres of each sample were then fractionated to observe the variation of the organic species.

Conditioning of resin columns

Three types of ion exchange resins, namely; XAD-7HP, Dowex ® 88 and Diaion-WA-10, were filled into three separate glass columns (inner diameter: 2.5 cm) up to a height of 20 cm. Each resin was cleaned thoroughly before the isolation of the different NOM fractions to significantly reduce the level of dissolved organic carbon (DOC) bleeding from the resins as described below.

The XAD-7HP resin was sequentially extracted using Soxhlet for 24 h with acetone and hexane. Methanol was pumped through the resin until the effluent was free of hexane. Following methanol, distilled water was pumped through the resin until the DOC of the effluent was less than 1 mg/L. Finally the resin was rinsed with 0.1 N NaOH and 0.1 N HCl to remove any remaining impurities.

The Dowex ® 88 resin was subjected to Soxhlet extraction with methanol for 24 h, after which 3 N NH_4OH was pumped through the resin. The resin was then protonated to saturation with 300 ml of 2 N HCl. Distilled water was finally passed through the resin to remove any remaining impurities.

The Diaion-WA-10 resin was first subjected to Soxhlet extraction with acetone for 24 h. Following the Soxhlet extraction, 1 N HCl was pumped through the resin until the DOC of the effluent was less than 1 mg/L. An excess of 3 N NH$_4$OH was pumped through the resin until the resin changed its off white colour to a yellowish colour (indicating that resin was in its free base form). Finally, distilled water was passed through the resin until the DOC of the effluent was less than 1 mg/L.

Fractionation procedure

Fractionation of the NOM was performed through adsorption using three types of ion exchange resins namely; XAD-7HP, Diaion-WA-10 and Dowex ® 88, as described in the procedure by Marhaba *et.al Al.* (2003) (7). According to this technique, the organic matter was divided into six fractions namely; hydrophobic acid (HpoA), hydrophobic base (HpoB), hydrophobic neutral (HpoN), hydrophilic acid (HpiA), hydrophilic base (HpiB) and hydrophilic neutral (HpiN). The fractionation procedure is illustrated in Figure 1.
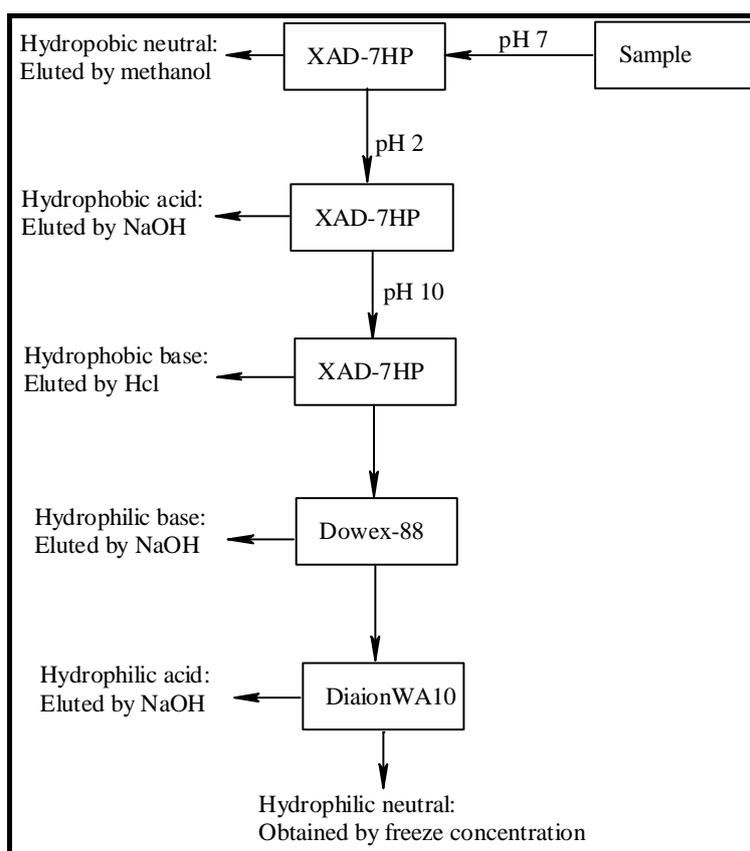

Figure 1: Fractionation method

Organic Carbon Analysis

The dissolved organic carbon (DOC) was used as an indicator of the organic content in the water samples. DOC is the organic constituent that can pass through the 0.45μm filter paper. The DOC of each NOM fraction was measured with a total organic carbon (TOC) analyzer (Tekmar Dormann Apollo 9000). Standards of 0, 1, 2, 5, and 10 mg/L C were prepared with potassium hydrogen phthalate (KHP), using ultra pure water for all dilutions. At least three replicates of each measurement were carried out and more replicates were performed where the variation between each measurement exceeded 5%.

Ultra Violet-Visible (UV-Vis) Spectroscopy analysis

The water samples were also analyzed on a UV-vis spectrophotometer at a wavelength of 254 nm. The absorption at this wavelength has been reported to represent the "aromatic character" of the organic species. UV-254 was measured with a Cary-50 UV spectrophotometer with a 1-cm quartz cell.

Passage of each NOM fraction through polymer

The CD polyurethane was synthesized as per procedure described by Li and Ma (2000) (8). The polymer was washed first to remove un-reacted cyclodextrin and other pollutants that may interfere with TOC measurements. This was done by first heating the polymer for an hour in an oil bath at 156°C to displace any trapped moisture and solvents. It was then allowed to cool to room temperature. The polymer (300 mg) was then loaded into empty SPE cartridges and washed with de-ionized water while taking TOC readings at intervals of 30 minutes until the TOC was less than 0.5 mg/L. The isolated NOM fractions were then treated with the polymer by passing 30 cm^3 of each organic fraction through the polymer at a filtration rate of 10 cm^3/min. The polymer-treated water was then analyzed for its carbon content using the TOC analyzer to determine how much of the percent carbon had been absorbed onto the polymer.

RESULTS AND DISCUSSION

Characterization of samples before fractionation

The samples exhibit a relatively high TOC content as shown by the TOC values in Table 1.The Specific Ultra Violet Absorbance (SUVA) was used as an indicator for the aromaticity of the NOM in the water samples. SUVA gives an indication of the amount of humic substances relative to non-humic substances in the water samples (Kiwa, 2006: Chen *et.al*. 2002) (9,10). Since the SUVA for both samples (Table 1)

was low, this suggested that the NOM in the samples was not highly aromatic in nature.

Table 1: Characterization of samples obtained after 1st and 2nd sampling

Sample 1	TOC (mg/L)	SUVA [l/(mg.m)]	pH	Conductivity (µS)	Turbidity (NTU)
Before ozonation	12.0	1.1	7.0	602	1.3
After ozonation	10.5	0.9	6.6	611	0.3
Sample 2					
Before ozonation	14.6	1.5	7.6	599	0.4
After ozonation	12.8	0.7	7.0	620	0.4

The TOC of the water samples decreased by approximately 12% after ozonation (from 12.0 to 10.5 mg/L in sample 1 and from 14.6 to 12.8 mg/L in sample 2). The ozone dosage at this particular plant was set as 3.5 mg/L. This slight decrease was expected since ozonation as reported by Bose *et.al.* (2007) (11) tends to convert biodegradable organic matter to biodegradable organic carbon. In other words higher molecular weight compounds are converted to lower molecular weight compounds.

The effect of ozonation on the NOM was also confirmed by the slight decrease in pH (see Table 1). There is a slight decrease in the pH values for both samples after ozonation, confirming the oxidation effect of ozone on NOM.

Figure 3 shows an IR spectrum displaying the different functional groups that are present in water samples for both samples 1 and 2. As can be seen the ozone treatment caused an increase in the oxidised and more acidic functional groups such as OH. Zhang *et.al.* (2008) (12) also reported that oxidation of NOM results to an

increase of the more acidic functional groups hence a slight decrease in pH values after ozonation.
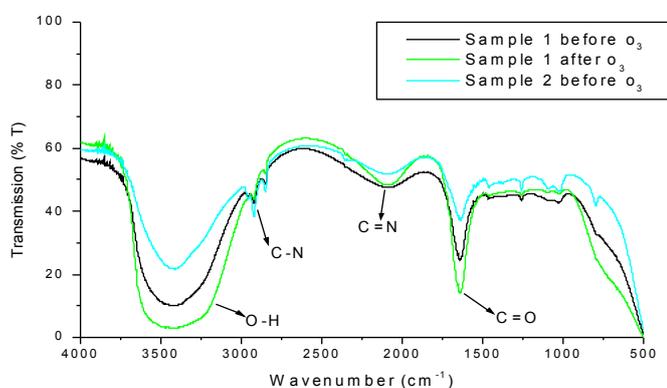

Figure 2: An IR spectrum displaying the functional groups mainly associated with the NOM in raw water

Fractionation of organic matter

The mass balance of the different organic fractions is summarized in Table 2 for both samples 1 and 2. The negative percentage surplus meant that the quantity of the six organic fractions was less than the total amount of the initial TOC. This was due to organic fractions being trapped in the resins and some organics lost during elution. Notably the losses were greater after ozonation- an effect which is still being investigated. In fact, Kiwa (2006) (9) reports that all resins remove NOM fractions but with significant differences.

Table 2: Mass balance of organic species for sample 1 and sample 2

Sample 1	TOC (mg/L)	HpoB (mg/L)	HpoA (mg/L)	HpoN (mg/L)	HpiB (mg/L)	HpiA (mg/L)	HpiN (mg/L)	% Surplus
Before ozonation	12.0	1.5	2.5	1.7	3.1	1.0	1.5	-5.8
After Ozonation	10.5	0.8	2.6	2.2	1.4	0.9	1.5	-10.5
Sample 2								

Before ozonation	14.6	1.4	3.0	2.2	4.1	0.7	1.7	-10.3
After ozonation	12.8	1.1	3.5	2.5	1.8	0.3	1.6	-16.4

According to Table 2, the distribution of the hydrophobic fraction was 50.4% and 59.6% for sample 1, before and after ozonation respectively. The distribution of the hydrophobic fraction was 50.4% and 65.7% for sample 2, before and after ozonation respectively. This indicates that the water samples were mainly composed of the hydrophobic NOM fractions hence implying that the NOM consisted mainly of humic substances. This result supports the general assertion that hydrophobic substances constitute a larger fraction than the hydrophilic fraction in natural waters (Yavich *et.al*, 2004) (13).

Ozonation led to a decrease of the TOC of the hydrophobic basic and the hydrophilic basic fractions, with the hydrophilic basic fractions being the most reduced fraction by this process. The hydrophilic basic (HpiB) TOC was reduced by 55% and 56% for both samples 1 and 2 respectively by ozonation. The high reduction of this fraction was due to the fact that the hydrophilic base fraction is not aromatic and the ozone reacts readily with the base functional group, hence the significant decrease in the TOC. The hydrophobic basic (HpoB) TOC was also slightly reduced by ozonation but not as significantly as the HpiB's. This was due to the aromaticity of the hydrophobic fraction. The neutral fraction's TOC (both hydrophobic and hydrophilic) was generally not affected by ozonation. However, the TOC of the hydrophobic acid fraction for both samples increased after ozonation. This may be attributed to the carbon that was lost as carbon dioxide during the ozonation of the NOM.

Treatment of the organic fractions with β-CD HMDI polymer

The isolated NOM fractions were then passed through β-CD HMDI (hexamethylene diisocynate) polyurethane to determine the extent with which each organic fraction can be removed by the polymer. Table 3 gives the percentage removal of each NOM fraction by the polymer. In general the polymer exhibited a low capability at removing the NOM fractions as shown by the values in Table 3. The acidic fractions (HpoA and HpiA) were the best absorbed by the polymer at 27% and 29% removal efficiency for HpoA and HpiA respectively. The acidic fractions are more ionic and have a high charge density, thus their greater affinity to the cavity of the CD polyurethanes. The neutral fractions were the least absorbed fractions by the polymer, with an absorbance of 9% and 6% for HpoN and HpiN respectively. The low absorbance of the neutral fractions was due to the fact that these fractions are

less ionic with a low charge density; hence they cannot be easily absorbed onto the cavity of the CD polyurethane.

Table 3: The percentage absorbance of each NOM fraction by the CD polymer

NOM fraction	TOC before polymer (mg/L)	TOC after polymer (mg/L)	% Absorbed
HpoB	1.4	1.2	14
HpoA	3.0	2.2	27
HpoN	2.2	2.0	9
HpiB	4.1	3.5	15
HpiA	0.7	0.5	29
HpiN	1.7	1.6	6

Table 4 demonstrates the success of the combination of ozone treatment and CD polymers in removing the NOM fractions from water.

Process	HpoB	HpoA	HpoN	HpiB	HpiA	HpiN
Ozonation	-21%	+17%	+10%	-56%	-57%	-6%
CD polymer	-14%	-27%	-9%	-15%	-29%	-6%
Overall reduction	-35%	-10%	~0%	-71%	-86%	-12%

Noteworthy, if the combined effects of ozonation and treatment with the CD polyurethanes are evaluated, the results obtained show a great success of this combination method in removing the NOM fractions from water. Results from Table 4

indicate an up to 86% removal of the hydrophilic acid (HpiA) fraction from the water source, which were not attained by either process alone.

CONCLUSION

Characterization results (SUVA and mass balance of fractions) indicated that the water samples mainly consists of humic substances in the form of hydrophobic NOM. Ozonation, at this particular dosage of 3.5 mg/L, was less effective in removing NOM since it only resulted in a 12% overall decrease of the TOC of the water samples. However, ozonation reduced the TOC of the hydrophilic basic fractions by over 50% and that of the hydrophobic basic by approximately 35%. The acidic fractions (HpoA and HpiA) were the best absorbed fractions by the polymer (27% and 29% respectively). However, the effect of the combination treatment (i.e. ozonation and treatment with CD polyurethanes) in removing NOM resulted in the polymer exhibiting a relatively good capability to remove NOM from water as evidenced by an up to 86% reduction of the HpiA fraction. Work on testing each of the NOM fractions for their DBP formation potential is currently being done in our laboratories.

FUTURE WORK

More work on investigating the nature of NOM occurring in source water in the relevant parts of the country is underway. Treatability studies on the removal of NOM by different treatment technologies/strategies are also being currently investigated in the laboratory and various treatment plants around South-Africa. The study is also currently investigating the use of suitable existing and novel techniques and processes which could be employed to remove the problematic NOM fractions. The main focus will be on three technologies namely, enhanced coagulation, activated carbon and nano-porous polymers.

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