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NDMA, N-Nitrosomethylethylamine [NMEA], NDEA, Nnitrosodi-N-Propylamine [NDPA] and N-Nitrosodi-N-Butylamine [NDBA] Nitrosamine (NA) Removals in Drinking Water Surface Waters

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1. Abstract

Some N-nitrosamines (NAs) have been identified as emerging disinfection by-products during water treatment. In this study, the levels of NAs namely (NDMA, N-nitrosomethylethylamine [NMEA], NDEA, Nnitrosodi-n-propylamine [NDPA] and N-nitrosodi-n-butylamine [NDBA] were measured. With coagulation/sedmentation 29% removals were detected for the N as mentioned above. Activated Carbon (AC) adsorption removed over 40% of the non-polar NDMA and NDEA fractions. Bio-treatment removed 97-999% of the cationic fraction NAs studied. With aerobic biological treatment 99% NDMA, N-nitrosomethylethylamine [NMEA], NDEA, Nnitrosodi-n-propylamine [NDPA] ana N-nitrosodi-n-butylamine [NDBA] yields were detected from the surface water in İzmir

2. Introduction

Some N-nitrosamines (NAs) have been identified as emerging disinfection by-products during water treatment. Some N-nitrosamines (NAs) have been identified as emerging disinfection by-products (DBPs) in drinking water [13]. NAs present much higher carcinogenicity than the traditional carbonaceous DBPs, such as trihalomethanes (THMs) and haloacetic acids (HAAs) [1, 3, 11]. The studies showed that N-nitrosamines (NAs) have various sources, including secondary amines [2, 6, 8, 10], certain water treatment polymers [13, 15], certain pharmaceutical and personal care products (PPCPs) [4, 5], certain pesticides or their degradation products [15, 16], wastewater treatment plant effluent organic matter (EfOM) (Mitch and Sedlak, 2004; Wang et al., 2014), certain industrial chemicals [12, 14], algal organic matter [19] and natural organic matter (NOM) [3, 10]. A general conclusion can be drawn from these investigations that N-nitrosamines (NAs) generally have the dialkyamine, tertiary amine or quaternary amine functional groups [7, 13].

The objective of this study was to compare tree N-nitrosamines (NAs) removals from drinking water treatment processes, including coagulation and sedimentation, activated carbon (AC) adsorption, and aerobic bological treatment.

3. Materials and Methods

3.1. Raw Surface Water Characterisation

Water samples were taken from one surface water located in İzmir. The water quality of the raw water for this investigation is shown in Table 1. RSDs were determined by triplicate tests of the samples. The specific UV absorbance (SUVA) was low, which indicated that the water was low in humic substances.

Table 1: Pollutant characteristics of surface water

Parameter	Unit	Concentration
pH	unitless	7,5
DOC	mg/l	19
SUVA	mg/l.m	6,45
BOD5	Mg/l	39
TOC	mg/l	29
COD	mg/l	67
TN	mg/l	2,6
TP	mg/l	1,2
TSS	mg/l	80
NDMA, N-nitrosomethylethylamine [NMEA]	µg/l	18
NDEA, Nnitrosodi-n-propylamine [NDPA]	µg/l	20
N-nitrosodi-n-butylamine [NDBA]	µg/l	32

3.2. PRAM Method

The PRAM procedure included a syringe pump (Longer Pump Corp.), glass syringes, SPE cartridges, connecting tips, and 40-mL vials as filtrate collectors. Two SPE cartridges types were used for PRAM measurements; the C18 and SCX cartridges. The cartridges (Extract Clean SPE kit catalog #210100) were purchased from All-tech Associates (U.S.A.). The matrix of the C18 cartridge was octadecyl-silyl. The organic matter adsorbed by the C18 cartridge was defined as the non-polar fraction and the filtrate was defined as the polar fraction. The matrix of the SCX cartridge was benzenesulfonic acid-silyl. The organic matter adsorbed by the SCX cartridge was defined as the cationic fraction and the filtrate was defined as the non-cationic fraction. In PRAM, the quantitative difference in organic matter concentrations between the influent and effluent of the cartridges was determined. More details of the PRAM operation were presented by Chen [7]. A UV/Vis photometer was used to monitor the UV absorbance of the filtrate in real time as a quality assurance procedure.

3.3. Configuration of the Reactors

3.3.1. Coagulation and sedimentation: A jar tester was used for the coagulation and sedimentation test. An alum coagulant (20 mg/L as Al2O3) was used. The jar tester was set at the speed of 200 rpm for 1 min (rapid mix); 60 rpm for 6 min, 45 rpm for 6 min, and 20 rpm for 6 min (three stages of flocculation), Then, the jar tester was stopped and sedimentation was allowed to occur for 20 min. The supernatant was further filtered with a 0.45- mm membrane filter to remove the tiny flocs and particles. The residual concentration of NAFP and other water quality parameters were determined.

3.3.2. AC adsorption: For adsorption tests, a powdered activated carbon (PAC)was used in a column with a volume of 500ml The water was pumped to this column.

3.3.3. Biological reactor: A stainless steel reactor with a volume of 3 liters was used containing 2500 mg/l bacteria. It was aerated with an air pump during a HRT of 50 hours

3.4. Analitical Procedure

Tree NAs namely (NDMA, N-nitrosomethylethylamine [NMEA], NDEA, Nnitrosodi-n-propylamine [NDPA] ana N-nitrosodi-n-butylamine [NDBA] were analyzed with the SPE pretreatment and ultra-performance liquid chromatography (UPLC)-(MS) method. The SPE pretreatment was conducted in accordance with EPA Method 521 (Munch and Bassett, 2004). An Agilent UPLC coupled to a tandem quadrupole MS with electrospray ionization (Model 6460, Agilent, USA) was used to identify and quantify the NAs. Multiple Reaction Monitoring (MRM) transitions in the positive-ion mode were used for each NA. A C-8 BEH column (2.1 100 mm, 1.7 mm) (Waters, MA, USA) was employed for separation. The mobile phase was composed of acetonitrile (ACN) and 0.05% formic acid. The solvent gradient was from 5 to 10% ACN in 1 min, and from 10 to 90% ACN over 5 min. Equilibration with 5% ACN was carried out between sample injections. The total run time was 8 min. The flow rate was 3 mL/min, and the sample injection volume was 10 mL.

3.5. Conventional pollutant analysis

DOC and Total Dissolved Nitrogen (TDN) were measured with a Shimadzu TOC-VCPH analyzer (Kyoto, Japan) with total nitrogen measurement apparatus. DON was determined by subtracting nitrate, nitrite, and ammonia concentrations from TDN. Ammonia was analyzed using the colorimetric phenolate method, nitrate was measured by the UV spectrophotometric method, and nitrite was measured using colorimetric method [2]. UV254 was measured with an UVeVis spectrophotometer.

Characterisation of raw surface water is given in Table 1.

4. Results and Discussion

Treatment of characterization of three NA organics (NDMA, N-nitrosomethylethylamine [NMEA], NDEA, Nnitrosodi-n-propylamine [NDPA] and N-nitrosodi-n-butylamine [NDBA] nitrosamine (NA) by sequential coagulation /sedimentation, AC adsorption, and bio-treatment

The coagulation-sedimentation process has low (about 23 -28%) removal of the tree NA compounds, TOC, DOC and for the other pollutant parameters (Table 2).

The cationic or polar fraction of NDMAFP and DOC was even recalcitrant to coagulation because the ferric or alum coagulants are also cationic-rich. AC adsorption effectively removed all fractions of the NDMA 80% of the cationic fraction, 60% of the non-cationic, 90% of the non-polar and 40% of the polar fraction (Table

3). Its performance on NDEA precursors was similar to that of the NDMA, except for the polar fraction (9% removal). The high removal of NDBA matches the previous studies [11, 20] (Table 3). However, AC did not remove much of the DOC in total (about 20%) and none of the cationic fraction. This is in contrast to other studies with PAC [11]. NA pollutants were most likely removed by a non-polar adsorption mechanism. The positively charged di-alkylamine functional group did not influence greatly the AC adsorption of the nonpolar part of the NA compounds.

Bio-treatment under the tested condition presented a high removal of the NA pollutants in total (90-95%) (Table 4). There was a higher removal of the cationic fractions of NDMA precursors (92%) and

NDEA precursors (80%) than the non-cationic fractions (42% and 55%), respectively. The removal of polar or non-polar fractions of NAs was quite similar. It has been shown that dimethylamine, a NDMA pollutant, could be metabolized by certain microorganism as the carbon and nitrogen source [22, 23]. Bio-treatment remove the DOC in total, but it appeared to remove cationic (54%) and non-polar (73%) fractions of DOC. This suggests that bio-treatment transformed the DOC (decreased the concentrations of some fractions, increased the concentration of the polar fraction). Bacteria can present a negative charge on their surface. These results suggested that the NA pollutants were removed by the static attraction or the bio-sorption between the negatively charged bacteria.

Table 2: Removal efficiencies with coagulation-sedimentation

Parameter	Removal efficiencies with
DOC	25
SUVA	26
BOD5	23
TOC	27
COD	25
TN	26
TP	23
TSS	26
NDMA, N-nitrosomethylethylamine [NMEA]	28
NDEA, Nnitrosodi-n-propylamine [NDPA]	26
N-nitrosodi-n-butylamine [NDBA]	27

Table 3: Removal efficiencies with adsorption

Parameter	Removal efficiencies with
DOC	29
SUVA	28
BOD5	26
TOC	27
COD	28
TN	24
TP	25
TSS	38
NDMA, N-nitrosomethylethylamine [NMEA]	80
NDEA, Nnitrosodi-n-propylamine [NDPA]	70
N-nitrosodi-n-butylamine [NDBA]	67

Table 4: Removal efficiencies of   NDMA, N-nitrosomethylethylamine [NMEA], NDEA, Nnitrosodi-n-propylamine [NDPA], N-nitrosodi-n-butylamine [NDBA] nitrosamine (NA) in biological treatment

Parameter	Removal efficiencies with
DOC	99
SUVA	98
BOD5	96
TOC	97
COD	96
TN	99
TP	99
TSS	99
NDMA, N-nitrosomethylethylamine [NMEA]	99
NDEA, Nnitrosodi-n-propylamine [NDPA]	99
N-nitrosodi-n-butylamine [NDBA]	99

5. Conclusions

With the sequential utilization of coagulation/sedimentation, adsortion and biological treatment NAs namely (NDMA, N-nitrosomethylethylamine [NMEA], NDEA, Nnitrosodi-n-propylamine [NDPA] ana N-nitrosodi-n-butylamine [NDBA] were removed with high yields from the surface water which this will be used as tap water.

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