Overview on the Separation and Removal of Haloaceticacid`S in Drinking Water

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ABSTRACT

The increase of pollution and the expansion of industrial, agricultural wastewater and urban runoff discharges in water sources have intensified the concentration of water pollutants. Considering that in Iran as in other countries the major part of drinking water is obtained from surface waters and due to the importance of disinfection, chlorination is doubtlessly the optimum and most common water treatment method used. However this method produces chlorination by-products (CBPs).Trihalomethanes(THMs) and Haloaceticacids (HAAs) are the main and most important groups of disinfection by-products (DBPs). Separation of THMs has gained a lot of breakthroughs since a lot of time elapses from its discovery. One of these breakthroughs is the separation of THMs with nanofiltration membranes, carried out by Koyuncu et al.(2007) in Technical University, Istanbul. They were able to reach the required standards (80-1oo µg/l).This research will go through the historic and the studies made on the separation of HAAs.

INTRODUCTION

Chlorination is the most common water disinfection method all over the world due to the fact that it's effective even in low concentration, accessible, cost-effective and has residual. Secondary reactions and the formation of organic chlorinated and pathogenic compounds have intensified the need of removing DBPs and also have raised the importance of world wide researches to be carried out on this issue. Disinfection by-products (DBPs) such as THMs and HAAs, which are the most important, are considered carcinogenic and pathogenic[1]. According to the researches made by U.S. Environmental Protection Agency (EPA), people exposed to dichloroacetic acid for six to seven days at 43 mg/kg/day of, will show reduced blood sugar, reduced cholesterol and triglyceride levels. This causes malignant tumors[37]. In addition, exposure for 60 to 70 years at 2 liters of water containing more than the standards amount of HAAs, will increase the risk of cancer. In 2007, Luben et al. studied the impact of disinfection by-products from THMs and HAAs groups on the sperm concentration during one year, and showed that the amount of sperms had abnormally increased form 90-114 million/ml to 270-360 million/ml and this posed a reproductive risk to men [3]. According to the latest standards of US.EPA in spring 2007, the regulatory limit of HAAs is lower than 60 µg/l [38]. Even in cities such as London which have high health related standards, according to the studies made by Malliarou et al., the average amount of HAAs, in some points of London's water network, with more than 30 sampling, was 95-35 µg/l and in other points it even reached 244µg/l[2] .

What is Haloacetic acid and how is it produced

The Haloacetic acids are one of the most important by-products of chlorination treatment. They are formed when organic matters (Humic acid) in the water react with the chlorine used to treat the water. HAA has 3 hydrogen atoms attached to the functional group carboxylique acid (COOH). The hydrogen atom of acid acetic is replaced by one of the halogens atoms[10]. The amount of THMs and HAAs, depending on the lower level of water's PH, advances the secondary reactions producing HAA [38]. In summer, in comparison with winter, the concentration of HAA in water is very considerable, because in summer the primary material needed for secondary reactions, Humic acid, is more abundant in nature[39]. The structure of three main HAAs groups is as it is shown in table 1[7].
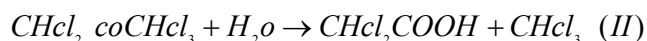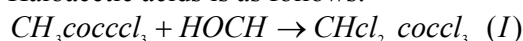
Table 1

Structures of the three groups of HAAs [7]

Monohaloacetic acid	Dihaloacetic acid	Trihaloacetic acid
$\begin{array}{c} H \quad O \\ | \quad || \\ X-C-C-OH \\ | \\ H \\ X = Cl \text{ or } Br \end{array}$	$\begin{array}{c} X \quad O \\ | \quad || \\ X-C-C-OH \\ | \\ H \\ X = Cl \text{ or } Br \end{array}$	$\begin{array}{c} X \quad O \\ | \quad || \\ X-C-C-OH \\ | \\ X \\ X = Cl \text{ or } Br \end{array}$

The physical and chemical characteristics of HAAs are shown in table 2 [41].

Table 2

Physico-chemical properties of HAA5 compounds[36]

Property	MCAA	DCAA	TCAA	MBAA	DBAA
Formula	ClCH2COOH	Cl2CHCOOH	Cl3CCOOH	BrCH2COOH	Br2CHCOOH
Molecular weight	94.50	128.94	163.39	138.95	217.84
Boiling pt (oC)	189.1	193-194	196-197	208.0	195.0
Density (g/cm3)	1.40 at 25° C	1.56 at 25° C	1.62 at 25° C	1.93	n/a
Vapour pressure (mmHg)	0.065 at 25° C	0.179 at 25° C	0.160 at 25° C	0.549 at 25° C	n/a
Dissociation constsnt (pKa) at 25oC	2.87	1.26	0.70	2.69	n/a
Water solubility (g/ml)	1.09 at 25° C	Miscible	1.50 at 25° C	1.75 at25°C	2.11 at 25° C

The reaction mechanism producing one of the Haloacetic acids is as follows:

$$CH_3 cocccl_3 + HOCH \rightarrow CHcl_2\ coccl_3\ (I)$$

$$CHcl_2\ coCHcl_3 + H_2o \rightarrow CHcl_2COOH + CHcl_3\ (II)$$

As it is shown when the hydrolysis of reaction (I) products is carried out, mono, di and tri chloroacetic acid are created (II)[7].

The secondary reactions producing HAAs have been analyzed in two forms:

A) Chlorine and chlorine-based disinfectants react with the organic materials in water which means that the chlorine atom is replaced by the hydrogen atom

of the organic material and by-products are produced during this halogenation[10].

In an oxidation reaction, chlorine oxidizes the natural organic materials in water and produces by-products. The amount of DBPS depends on the temperature, water's PH level, the length of the disinfection process and the characteristics of the water source[10].

Methods used to alleviate DBPs

The studies made on reducing disinfection by-products until now, have lead to four approaches:

A) Minimize precursors and secondary reactions:

Keeping organic matter away from water is one way of preventing DBPs. Absorption with the granular activated carbon can reduce organic matter levels. During their researches, Hossain et al. from the chemistry department of Auckland University, employed UF membranes to remove humic acid. Although they were able to remove a large amount of organic materials, but they still suggested the chlorine disinfection method due to cities distribution system problems[5]. In 2007, Mehmet et al. worked on XAD-8 resins to absorb DBPs and then removing them with ultrafiltration. They first radiated water with a specific ultraviolet absorbance at 254 nm (SUVA 254), then treated water and observed that by-products, especially bromide derivatives,had considerably decreased. The impact of molecular mass on the amount of DBPs absorbed in XAD-8 resins was also examined [6].

B) Reducing disinfectants dosage :

In 2005, Singer et al. studied DBPs reducing methods and came to this conclusion that dividing the overall disinfection process into several sequences and lowering the dosage of disinfectants used in each time, reduces the DBPs [21]. In order to reach higher results, feeding granular activated carbon before each new disinfection stages can considerably minimize natural organic matters. Chlorination can then be performed later.

C) Using alternative disinfectants :

Disinfectants which can substitute chlorine are UV light,potassium permanganate,ozone and chloramines or chlorine dioxide compounds. All of these disinfectants option have their own benefits and disadvantages which are mentioned below:

1) UV light and ozone do not produce any by-products, useful due to their effectiveness at killing bacteria, viruses and fungi. However they do not have residual, can not assure the complete removal of harmful matters in water networks, are ineffective

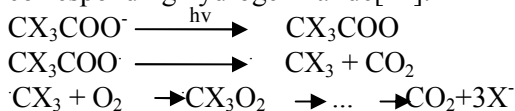for turbid water and are more expensive than chlorine [4].

2) Chloramines, chlorine dioxide and potassium permanganate create other harmful by-products. They are expensive, influence the water's transparency. Of course these disinfectants have great performance in the disinfection process. After the traditional chlorine treatment, a small amount of dissolved chlorine remains in the purified water which continues the disinfection process in the entire water distribution network. On the other hand none of the other disinfectants are as economical as chlorine [8].Therefore the problem of removing HAAs still remains. The increase of world health standards has complicated the process of separating HAAs, in such way that in 2002, the American standard institute, announced the permitted limit of HAA at 80ppb which decreased to 60ppb in 2006 [9].

D) Removing and separating DBPs :

This is one of the best methods because firstly the disinfection process is safely done and in the second place the DBPs removal process takes place with highest performance.

1- Photodegradation of HAAs

Experiments carried out on HAAs in the presence of light and titanium dioxide (TiO2) as a catalyst have shown the degradation of all the chlorinated and brominated HAA species. The rate of photodegradation was found to be directly proportional to the number of halogen atoms in the HAA molecules[11]. The HAAs are considered to undergo photochemical degradation via the photo-Kolbe reaction mechanism to form CO2 and the corresponding hydrogen halide[12].

$$CX_3COO^- \xrightarrow{hv} CX_3COO$$
$$CX_3COO^{.} \longrightarrow {.}CX_3 + CO_2$$
$$^{.}CX_3 + O_2 \rightarrow CX_3O_2 \rightarrow ... \rightarrow CO_2 + 3X^-$$

Where X=Cl or Br

The haloacetic acids have been found to degrade at temperatures as low as 15° C, with the rate of the reaction depending on the electronegativity of the halogen atom and hence, the strength of the C-X bond [11]. The following trend, TCAA>DCAA>MCAA, has been observed for the catalytic photodegradation of the chloroacetic acids, with TCAA degrading most readily. A similar trend, TBAA>DBAA>MBAA, has been observed for the brominated HAA species. Photodegradation of BCAA was also observed with the formation of CO2, Br- and Cl- as final products. But, Br- ions were present at higher concentration than Cl- ions. The catalytic photodegradation reaction of the HAAs has been found to be independent of pH and

temperature. But, the presence of co-dissolved ions like Na+ will affect the catalytic reactivity. It has also been mentioned that the photodegradation reactions of HAAs in surface waters will depend on the light intensity penetrating into the water. Thus, removal of HAAs by photodegradation will be possible for certain water distribution systems only.

2- Electrochemical reduction of HAAs

The electrochemical reduction of HAAs has not been widely studied, except for the experiments carried out by Korshin and Jensen on the electrochemical reduction of the chloro and bromo acetic acids in the presence of copper and gold electrodes. All HAAs, except MCAA, showed positive results[13]. The electrochemical reduction of the brominated HAA species followed different trends for copper and gold electrodes. The rate of the reaction was found to increase with the number of halogen atoms and the reaction proceeded faster with copper electrodes. The final products of the electrochemical reduction reaction were found to depend on the electrode potential and the nature of the HAA species involved. The electrochemical treatment of the brominated compounds led to complete mineralisation with the release of free bromide and acetate. In case of the chlorinated acetic acids, MCAA, acetate and other HAA species, like DCAA, were the end products. At an electrode potential of -0.8 V, TCAA was reduced to form DCAA as the major end product and negligible amounts of MCAA and acetate as well. At the same potential, DCAA was reduced to form 80 % of MCAA and 20 % of acetate. MCAA has been found to exhibit little electroactivity at both gold and copper electrodes at -1.3 V. This explains its inability to be further reduced to acetate and chloride ion. Mass transfer was also a limiting factor in the electrochemical reduction reactions carried out with the haloacetic acids[13].

3- Reductive dehalogenation of HAAs

The HAAs have been found to undergo biological as well as chemical reductive dehalogenation reactions. Two bacterial genera, Rhodospirillum and Rhodopseudomonas have been found to cause the release of the halide ion and the non-halogenated acid upon their reaction with either bromoacetic or chloroacetic acids[14]. It was postulated that these bacteria use the non-halogenated acids produced for growth. The isolation of another bacterium, Trichlorobacter thiogenes, which grows via the reductive dehalogenation of TCAA,further supports the role played by microorganisms in the reductive dehalogenation of HAAs [15]. During the experiment, the bacterial strain transformed TCAA

into DCAA and the increase in DCAA concentration was equal to the decrease in the amount of TCAA. But, no dehalogenation was observed for DCAA or MCAA in the presence of this bacterium. Chemical dehalogenation of the HAAs has been reported in the presence of Fe(0) [16]. The effect of Fe(0) on HAAs is considered to be significant due to the fact that some water distribution systems incorporate mainly cast iron piping. Among the HAAs investigated by Hozalski et al., TBAA was found to degrade completely in the presence of Fe(0) to form acetate and bromide ions via sequential hydrogenolysis. The other acetic acids (TCAA, DBCAA and BDCAA) produced MCAA as the final product. In another study, MCAA was found to undergo degradation within months to form acetate[17]. The mechanistic pathways involved in the degradation of TBAA and the other trihalogenated acetic acids are illustrated below:
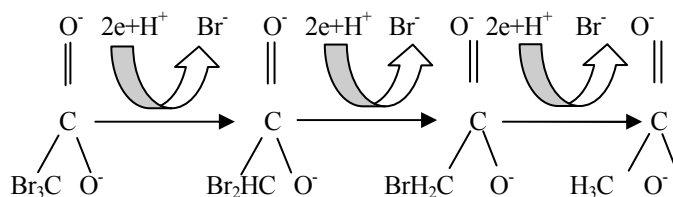

Figure 1
Degradation of TBAA in the presence of Fe(0)

The haloacetic acids undergo pseudo- first order dehalogenation reactions according to the following trend [16,17]:
BDCAA > DBCAA TBAA >> TCAA > MBAA > DCAA. It is also hypothesised that reactions between HAAs and the compounds from the corroded iron pipes could lead to a decrease in HAAs along the water distribution systems [17].

4- Removal of HAAs by BAC and GAC adsorption
It has long been assumed that granular activated carbon (GAC) could not remove HAAs effectively due to the hydrophilic nature of the haloacetic acids and their high ionization in aquatic systems [18]. But research carried out by Singer et al. and Babi et al. has shown the possibility of the removal of HAAs by GAC[19,20]. Speth and Miltner have also observed high GAC adsorption capacities for DCAA and TCAA[22]. Biological degradation is considered to be responsible for the observed decrease in HAA concentration in GAC filter beds. From the pilot-plant study, the decrease in the chlorine residual due to the catalytic activity of the activated carbon surface was found to cause an increase in HAA

removal[20]. The researchers suggested that adsorption of HAAs on the carbon surface is not to be neglected[18]. According to them, the GAC adsorption capacities for the HAA5 compounds follow the trend:
TCAA>DBAA>DCAA>MBAA>MCAA. As such, MCAA will undergo a faster degradation rate. In fact, the greater the number of halogen atoms on the HAA molecule, the greater is the adsorption capacity. They have found Freundlich values of 1630 µg/g and 11,700 µg/g for DCAA and TCAA respectively. The incorporation of bromine atoms on the haloacetic acids also contributed to an increase in their adsorption capacities.These researchers investigated the removal of HAAs within a 76 day period and they found removal of MCAA within 35 days. No MBAA was detected after 45 days. The removal patterns of MCAA and MBAA followed the same trend. The adsorption mechanism is said to predominate over the biological mechanism until the GAC adsorption capacity is exhausted[18].Degradation of HAAs in biologically active carbon (BAC) has also been reported by Xie and Zhou[18]. They studied the removal of MCAA, DCAA, TCAA and DBAA in the presence of BAC. Complete removal of the four HAAs was observed within 196 h. The removal rate of TCAA was found to be in close proximity with that of MCAA or DCAA. This finding supports the fact that other than biodegradation, carbon adsorption is also involved in the removal of HAAs in BAC. Increases in the empty bed contact time (EBCT) and water te mperature cause an increase in HAA removal in BAC columns [23]. The reaction was found to proceed via a first order mechanism at 10° C but at a temperature as low as 4^oC, a zero order reaction mechanism was observed. The lack of biological activity was the explanation for the reaction mechanism at 4^oC. An EBCT of 6-8 min was enough to cause a 50% reduction in MCAA and DCAA at 10^oC and the same reduction in TCAA was achieved within an EBCT of 17.3 min [23]. The analyses performed during the whole operation period (638 days) showed that the GAC breakthrough capacity for DOC was much higher than the capacity for total HAAs, which was higher than that for total THMs. The removal of THMs and the most part of the removal of HAAs and DOC should be attributed to adsorption by GAC, while that of a smaller part of HAAs and DOC may be attributed to biodegradation in the adsorber bed, where dechlorination, caused catalytically by the carbon surface, favoured

microbial growth. Additionally, the GAC postfilter-adsorber showed a much higher adsorption efficiency than a GAC filter-adsorber, due to the smaller size of the carbon and the lower hydraulic loading rate[24].

5- Biodegradation of HAAs

The role of microorganisms on the degradation of haloacetic acids has been well cited in the literature. The fact that low concentrations of HAAs have been observed in the presence of low levels of chlorine or chloramine confirms the involvement of microorganisms in the degradation of HAAs [21]. Several other studies have reported the biodegradation of HAAs in the absence of a disinfectant residual[19,25]. The presence of low concentrations of HAAs at the end of the distribution system, where the disinfectant residual is low and the heterotrophic plate counts (HPC) are high, are yet another indication of the biological degradation of HAAs [26,27]. Baribeau et al. demonstrated the biodegradation of HAAs in annular reactors at both cold and warm water conditions and in the presence and absence of chlorine and chloramine residual. Degradation was observed for the dihalogenated HAA species under warm water conditions.The trihalogenated species, in turn, showed no degradation in the absence of the disinfectant residual. It was suggested that longer retention times are required for degradation of the trihalogenated species to occur. A much greater decrease of DCAA at high temperature than at low temperature is evidence of biologically mediated degradation of HAAs because at higher temperatures, the growth rate of bacteria is enhanced [28]. The ability of some microorganisms to utilize HAAs as a source of energy and carbon has been reported [29,30,31].Experimental results have shown the exponential growth of a certain bacterium (TCAA degraders belonging to gamma sub-group of Proteobacteria) and the subsequent release of chloride ions at concentrations of 20mM (3.27x106 μg/) of TCAA [31]. MCAA (8.51x104 to 4.57x106 μg/l) has been found to favor the growth of Xanthobacter autotrophicus GJ10 strain [30]. The disappearance of MCAA occurred within 7 hours and the products formed were chloride ions and CO2. It is stipulated that the bacteria responsible for HAA degradation are usually present in treated drinking water [7]. Brazos and O'Connor have found that microorganisms multiply in water just after leaving the water treatment works[32]. According to LeChevallier at al., the multiplication of bacteria may be attributed to the release of certain microorganisms from pipe surfaces, their resistance to disinfection and their transport to other parts of the distribution system[33]. Bacterial survival following chlorination has also been reported [34]. DCAA, with an initial concentration of 88 μg/l, was found to disappear in 256 hours at the expense of a 6000 times increase in HPC. In the case of TCAA, only 25% reduction was noticed for an initial concentration of 81 μg/l. The observed trend for the biodegradation of HAAs is as follows[7]:

MCAA>DCAA>TCAA

The increase in the number of halogen atoms and the incorporation of bromine cause an increase in the biological stability of the HAAs. However, studies carried out in pond waters have shown DCAA to undergo faster degradation with a half-life of 28 h compared to that of MCAA (half-life of 157 h) and TCAA (half-life = 345h). It was suggested that different microbial population is involved in the biodegradation of MCAA, DCAA or TCAA. The mechanism proposed for the biodegradation of HAAs on the basis of Ellis et al. experimental results is enzymatic hydrolysis followed by the production of oxalic, glyoxalic and glycolic acids from TCAA, DCAA and MCAA respectively[35]. McRae et al. found that the biological degradation of MCAA, TCAA and MBAA follow the pseudo-first order reaction kinetics. Complete mineralization of the HAA species was observed during biodegradation[29].Granular activated carbon and coagulation of DBPs have been the common technologies used so far. Of course since they are very expensive, these methods are only used in countries with high health and social standards. Given that we are directly dealing with people's health and considering the medical care costs and social damages imposed, these methods should quickly be employed.

KEYWORDS
HAAs − disinfection − nanofiltration membranes − by-products − THMs

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