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Study of THMFP in Karun River Water, Iran

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Abstract. Organic matters in raw water have a potential to generate harmful disinfection by-products such as trihalomethanes (THMs) during the chlorination process. The objectives of this study were to investigate the trihalomethane formation potential (THMFP) in Karun River water and to determine the effect of several factors including total organic carbon (TOC), pH, chlorine dosage, water temperature and seasonal variation. The results showed that, among all factors, TOC and water temperature have a remarkable effect on THMFP. The experimental results from batch studies indicated that increasing of pH value yielded a greater THMFP concentration for Karun River water. THMFP levels of Karun River water in summer times, when water temperature exceeded 26°C, were 1.2-1.6 times higher than in the spring and fall seasons, when water temperature was below 15°C. It was found that the measured THMFP at Karun River water in the spring and fall seasons were very rarely higher than100 μg/L.

Keywords: THMFP, Karun River, Seasonal variation, pH, Chlorine, Water.

1. Introduction

Surface water has been reported to contain organic matter derived from natural degradation of some organic substances within the ecological systems and also from human activities. Organic contaminants in surface water are different from location to location due to the differences in the ecosystems and the human activities in each specific location. This organic matter cannot easily be captured using normal water treatment techniques such as coagulation, and therefore it can enter the municipal water treatment system and then distributed through the water supply network. Moreover, during the disinfection process with chlorine, which is a common treatment technique in municipal water supply facilities, the organic matter could potentially be converted to potentially harmful disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs)[1]. Some epidemiologic studies [1,2, 3] have shown an association between long-term exposure to disinfection by-products and increased risk of cancer and potential adverse reproductive effect. The general reaction of organic matter with chlorine can be expressed as follows [4]:

$$\text{Organic matter} + \text{free chlorine} \rightarrow \text{THMs} + \text{HAAs} + \text{HANs} + \text{cyanogen-halides} + \text{other DBPs} \quad (1)$$

The government of Iran has been prepared to set a MCL for THMs to 100 μg/L in order to comply with World Health Organization (WHO) and USEPA (ISIRI 1997) [2,5,6]. It was reported that THM occurrence in chlorinated water may vary significantly based on season and geographical location of water resources [7, 8]. These variations are due to changes in raw and treated water quality as well as in operational parameters related to chlorination [9]. The operational parameters that influence THM formation in the treatment systems are chlorine dose, water temperature, pH and travel time of water within the system. Several laboratory and field research studies have indicated that the higher values for these parameters, the higher

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concentrations of THMs caused [10,11,12]. Due to the fact that very little research has been performed to investigate THM concentrations in drinking water resources, information about the concentrations of THMs and its potential formation in Iranian waters is lacking. Therefore, the main purpose of this study was to assess the effects of some water quality and operational parameters on trihalomethanes formation potential (THMFP) in major river water in Iran (i.e. Karun River). The results of this water resource will be useful in the future management of water treatment plants which services millions of people living in around of this river.

2. Materials and Methods

2.1. Sampling Strategy

The Karun River is the longest river in Iran. It lies in the west of Iran and flows from north to south until it impounds into the Persian Gulf. Karun River water provides the drinking water source for many cities and Mahshahr petrochemical complex zone. Samples were collected from Karun River at the point of Koot-Amir where water pumped to water treatment plant of Mahshahr petrochemical complex zone. 1). To investigate the occurrence of THMFP within the raw water of Karun River, an intensive average of 13-week sampling program was under taken during some seasons of the year 2008 and 2009. The study period was 1-year from October 2008 to September 2009. Therefore, we collected 4 samples for each month or about 12-13 samples during the seasons. For purpose of validation, a total of 52 samples were collected from the raw water of Karun River. It was ensured that the sampling point was accessible for all over the year.

2.2. Experimental Design and Analysis

All experiments (including determination the effect of parameters such as pH, seasonal variation, water temperature, chlorine dosage and TOC concentration on THMFP) were performed in batch mode in 150-mL bottles. Specifically, 10 mg/L chlorine were added to raw water containing original natural organic matter and then mixed at 125 rpm using a rotary shaker (Glas-col) under anaerobic conditions and various initial pH values. The pH of the solution was adjusted to 4.5, 8 and 10 by adding 0.1 N HCl or 0.1 N NaOH. In another experiment, the water temperature was varied from 8 to 30 oC in a water bath. Thirty mL aliquots of the samples were then collected from the bottles by pipette at various time intervals (10- 100 h) for analysis of TTHMs. All experiments were conducted in triplicate and the average values are presented. All tests were measured according with the standard methods for examination of water and wastewater [13].

3. Results and Discussion

3.1. Effect of pH

Fig. 1 shows the effect of initial solution pH (4.5, 8 and 10) on THMFP in the raw water of Karun River. After reaction time of 100 h the values of THMFP for the initial pH of 4.5, 8 and 10 were raised to 21.65± 6.18, 113.57± 10.51 and 143.25±9.31 µg/L, respectively. Higher THMFP rate (143.25 µg/L) was observed in higher pH. In the other word, increasing pH from 4.5 to 10 has significant effect on the THMFP, and THMFP content increases with rising of pH. This is due to the fact that initial attack is dependent on HClO concentration, which is related to pH. The lower pH the higher HClO concentration resulting in a shift to higher concentration of humics. The formation of THMs depends mainly on the last step of THM reaction pathway, which is based- catalysis as with the haloform reaction. Another probable reason is the humic acids have many functional groups (especially acetyl group) that active in high pH and reacted with chlorine. This is similar to the results of other research [8,14]. However, as Platikanov and coworkers (2010) have mentioned pH would affect the equilibrium of the reaction and the effects of pH on chlorination process must be explained simultaneously by the deprotonation of hypochlorite and/or the organic compound which may change the reaction kinetic.

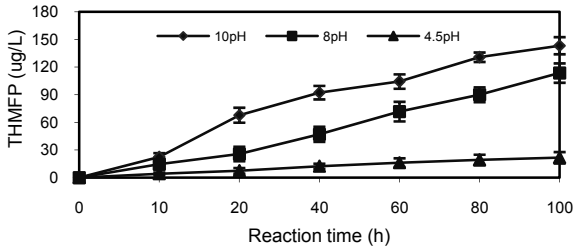

Fig. 1: Effect of initial water pH on THMFP (pH 7.32, chlorine dosage 10 mg/L)

3.2. Effect of TOC Content

Many types of organic compounds are found in natural waters. They are of natural origin, referred to as natural organic matter (NOM). The THMs are formed when the disinfectant reacts with NOM. TOC is one of the most widely used measures for quantifying the amount of NOM in water [15]. Therefore, during the experiments the effect of TOC on THMFP was monitored for 80 h (Fig. 2). The initial TOC concentration and the chlorine dosage were maintained at 3, 5 and 7 mg/L and 10 mg/L, respectively. The THMFP in the presence of 3, 5 and 7 mg/L TOC without any pH control were 50.04± 5.53, 101.14± 5.30 and 164.14±9.19 µg/L, respectively after 80 h. In the other hand, THMFP was increased with increasing of TOC content of raw water samples. As reported by other researchers [16] THMs formation rises with increasing soluble humic material content in natural occurring water. The rate of THMs formation is equal to that of the TOC consumption. These results also show that a higher available TOC will provide more THMFP. However, from Fig. 3 a first order reaction was implied with respect to TOC concentration. Indeed, a higher available TOC will provide more THMs if enough residue chlorine is available. As reported in literature, the characteristic and type of organic matters may be responsible for the chlorination reactivity differences [17]. Fulvic acid account over 90% of the aquatic humic in many water sources. Babcock and Singer found that relative contributions to THM production came from humic fraction than fulvic fraction since the former reacts more readily with chlorine [18].

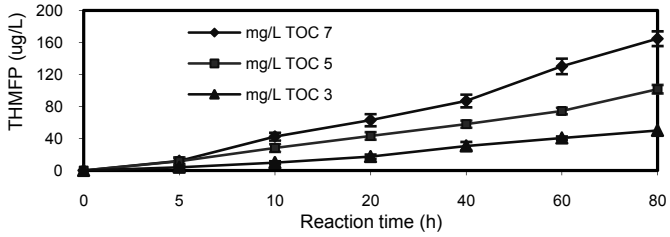

Fig. 2: Effect of TOC content on THMFP of Karun River (pH 7.13, chlorine dosage 10 mg/L)

3.3. Seasonal Variations of THMFP

As shown in Fig. 3, THMFP of Karun River water was varied during the period of study (the year of 2008 and 2009). As expected, levels of THMFP were especially high during summer and low in spring and fall. Indeed, the average levels of THMFP measured in the summer months in the raw water of Karun River were 1.61 times higher than the average levels measured in the spring months. In the other word, during spring and fall seasons the measured THMFP were very rarely higher than 100 µg/L, MCL for THMs in drinking water according to EC and Iran regulations. These seasonal THMFP variations can be explained by a number of different factors. First, the average water temperature of raw waters was low in the beginning of spring (12.3°C), and this factor resulted in lower chlorine demand. Finally, it was observed that water quality variations were also appreciable within seasons. For example, as mentioned by Uyak and Toroz [19,20], during the spring time, THMs levels measured in distribution system varied from 55 to 75 µg/L in Buyukcekmece, 64 to 81 µg/L in Beylikduzu, from 74 to 96 µg/L in Avcilar, and from 83 to 99 µg/L in Esenyurt; during the summer period, THM levels measured in the distribution system varied from 96 to 116 µg/L in Buyukcekmece, 100 to 130 µg/L in Beylikduzu, from 116 to 145 µg/L in Avcilar, and from 128 to 154 µg/L in Esenyurt. These THMFP variations are largely due to water temperature and mainly to variations of THMs precursor concentrations, in accordance with the Rodriguez and Serodes modeling study

[21]. The reason probably is the high level of THMs precursor and bromide concentrations during summer in Karun River water. As stated by other researcher, THMs precursor concentrations and the salinity content (chloride and bromide) of water were increased with a temperature rise in the summer [20].

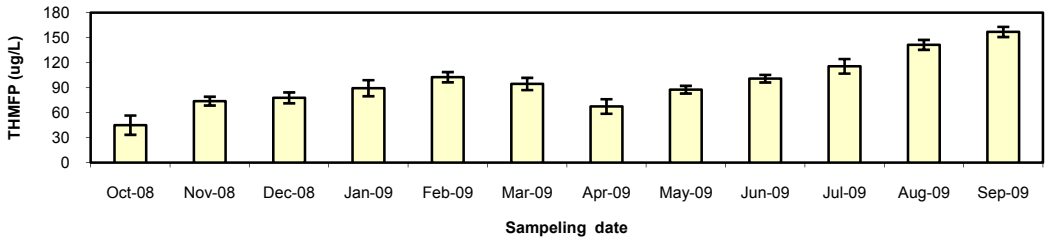

Fig. 3: Average monthly variation of THMFP at sampling point of Koot-Amir (chlorine dosage 10 mg/L)

4. Conclusions

This study elucidated that the THMFP were influenced by many water quality parameters including TOC, pH, water temperature, content of chlorine and seasonal variations. The correlations between THMFP and TOC were significant positive correlation. In designed pH (4.5, 8 and 10) of Karun River water, a high pH had a remarkable effect on THMFP. The content of THMFP was increased with the increasing of pH. The chlorine dose has a functional relationship with the formation potential of THM, and the concentration of THMFP displays a seasonal variation with the variation of water temperature.

The results of this investigation demonstrate that seasonal variations of THMFP were considerable in Karun River. Such variations were mainly related to the significant changes in water quality and temperature that occur throughout the year in Karun River water. The study results showed that THMFP levels vary significantly from one season to another. When water temperature exceeds 26 °C in summer, the THMFP levels are particularly 1.2 to 1.6 times higher than spring season, while when water temperature is below 15 °C, and in the spring and fall the measured THMFP were very rarely higher than100 µg/L.

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