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Cross Relationship between Chlorine and Bromine in Drinking Water

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Abstract

The research addressed the competitive relationship between chlorine and bromine as halogens and oxidized elements, where these properties were used to study health implications when this competition occurs during the process of sterilizing water for safe and safe drinking water through the formation of dangerous and carcinogenic By product compounds such as Chloroform, one of the compound of the(TriHalo methane) Group (THM), Dichloroacetic acid and TriChloroacetic acid, two compounds located within the dangerous Haloacetic acid group as well as bromates, where it was found that there was replacement occurring Between chlorine and bromine depending on temperature, acid function(PH) as well as total organic carbon(TOC) and bromide ion(Br^-) concentration.

Keywords: Bromate, Chloroform, Halogen , Halo acetic acid , sterilizing ,Tri Halo Methane, , Total Organic Carbon.

Introduction

The research dealt with a very important topic, which is the formation of dangerous by product chemical compounds during the process of sterilizing water with chlorine.It consists of a group of trihalomethane, a group of haloacetic acid and a group of chloroamines and other compounds.

Researches, studies and practical experiments have proven have a dangerous and carcinogenic effect on humans[1]. It is necessary to control the amount of chlorine that added to sterilize water in order to avoid the formation of these dangerous compounds formed as a result of the reaction between chlorine (used for the sterilization) with bromide salts and organic substances present in surface waters [2]. Since water pollution is an eternal problem because of which a large number of people died, so the research, investigation and hard work began to provide a substance that sterilizes water and oxidizes compounds and elements with harmful environmental and health effects.

The discovery of chlorine is considered one of the most important discoveries of the twentieth century, it was used as a sterilizer and oxidizer for contaminated water, and it was used on a large scale. Indeed, many diseases resulting from drinking contaminated water were eliminated, such as cholera, typhoid, dysentery and other diseases as well as eliminating pathogens such as bacteria, viruses and germs [3].

During the water sterilization process to get rid of the above, a new problem has emerged, which is the formation of chemical compounds with a very dangerous effect due to chlorine reactions and factors surrounding the sterilization process such as temperature, acidity and others[4].

Recent scientific studies have proven that reducing the percentage of chlorinated compounds (which are compounds resulting from the interaction of chlorine with organic substances in source water) does not keep us away from the danger circle because there may be a displacement towards the formation of brominated carcinogenic compounds (which are compounds resulting from the interaction of bromine with organic compounds) [5].The presence of a high percentage of bromide salts in the surface water before performing the sterilization process is the main reason for the formation of the bromide ion, which in turn reacts to form compounds that are not

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less dangerous than the compounds that resulted from the reaction of chlorine[6].Therefore, water free of bromide salts must be used.The important evidence between chlorine and bromine during chlorine process is that the bromine substitution factor(BSF), is defined the ratio of(bromine combined with total organic compounds) to (total concentration of chlorine and bromine in the disinfection by product [7].

BSF=(DBP-Br)/(DBP-(Cl-Br))------(1)

Where:

DBP=Disinfection by products

DBP-Br =Concentration of total organic compound combined with bromine

DBP-(CL-Br)= Concentration of chlorine and bromine in the disinfection by product

Calculating the bromine substitution factor (BSF) is very important as it determines the type of side compounds, reaction time, acidity function and the temperature at which these compounds are formed [8].

Trihalomethane (THM_s) group is considered one of the groups containing carcinogenic side compounds (Chloroform, Dichloromethane, Dibromochloromethane). The Environment Agency of Amereica (EPA) has set maximum limits for Trihalomethane pollution (0.15 mg/l) [9]. Chloroform is considered the most effective , and its advantages are that it does not ignite in the air and is used as a solvent in many industries such as the manufacture of medicines, dyes and pesticides, and it was previously used as a surgical anesthetic. Many countries have worked to ban its use as a solvent in the food, drug and cosmetics industry after confirming that it causes many cancerous diseases [10].The Haloacetic acid group contains two dangerous chemical compounds (Dichloroacetic acid and Trichloroacetic acid), and this group is classified among the carcinogenic side groups resulting from water sterilization with chlorine [11]. Several researches have proven that high temperature and reaction time leads to a decrease in the concentration of Trihalomethane. and Haloacetic acid with a high substitution potential towards brominated compounds [12].Another problem in this field is the formation of the carcinogenic bromate ion. The bromate ion(BrO_3^-) is produced from the oxidation of chlorine to the bromide ion originally present in surface water during the chlorination process [13].Both chlorine and bromine are considered halogens and effective oxidants that react strongly with natural organic compounds (NOM) to form halogenated side compounds. To determine the ratio of bromine to replace chlorine in the THM group [14] (Bromine Incorporation Factor)(BIF)

BIF=DBP-Br/DBP……..(2)

Where:

BIF=(Bromine Incorporation Factor)

DBP= Disinfection By Product

DBP-Br = The Bromine in the molar concentration combined with the group of THM

The aim of this research:

lies in highlighting a very important point: the absence of sterile water from chlorinated by product compounds does not necessarily to give the green light to the validity of these water because there may have been a replacement or Incorporation of bromine, so it is necessary to thoroughly analyze and evaluate both types of compounds (chlorinated and brominated).

Experimental

1.Collection of the Sample

1.1Collecting samples of raw surface water from (Tigris River) before entering it into sterilization with chlorine. One sample was taken monthly and over a period of six months of the year (February, April, June, Augest , October, December).

1.2. Evaluation of Total Organic Compounds present in the raw water (TOC)

The total organic compounds of the water samples were measured using a UV device. We determine the absorbance at a wavelength of 254 nm, which is the wavelength at which the organic compounds are absorbed, and using equation (3) to calculate the amount of TOC in units of mg/l [15].

$TOC(mg/l)=33\times UV_{245}+0.6736\pm0.085$------(3)

Where:

TOC=Total Organic Compounds

UV_{245}= absorbance at wavelength (245) nm

1.3. Evaluation of Bromide ion

Using an ion selective device (ISE 1199060 WTW). The bromide ion concentrations in surface waters were evaluated[16], as this device senses very small concentrations with high accuracy.the table (1) show the data for TOC and Ion Bromide.Figure(1) shows the concentrations of TOC and Br^- during the six months of the year.

2. Collection of drinking water samples from residential areas in Baghdad governorate.

Drinking water samples were collected from different areas in Baghdad governorate (Sidia, Assadar City, Jadiriyah, Zayoun, Karrada and Zafraniya) identified on the map of baghdad.

The by product compounds resulting from the chlorine sterilization process were evaluated for these samples over a period of six months of the year (February, April, June, August , October, December).

3. Evaluation of Chloroform Concentration.

The samples were collected in clean and dried glass containers and then used **GC** technology to determine the concentration of chloroform where we start making measurements immediately after taking the samples because a legacy of up to a few days gives completely different results than in the first period of time [17-19].

Using the Hexan solvent and then injecting the Gas Chromotography device with an high sensitivity electronic detector for halogen compounds (ECD) and using very pure nitrogen gas as a transport gas and column (DN-1) and we bring several chloroform concentrations to make the standard curve[24]. The acid function (PH) is measured by a (pH meter) .The table (2) shows the concentration of Chloroform in the six samples over six months of the year.Figure 2 shows the concentrations of chloroform during the six months of the year.

4. Evaluation of Dichloroacetic acid Concentration.

It is one of the chlorinated compounds of the halloacetic acid group, a dangerous halogen derivative resulting from the process of water Chlorination, and the di Chloro acitc acid compound has been evaluated for six residential areas in Baghdad (Sidia, Assadar City, Jadiriyah, Zayoun, Karrada and Zafraniya) and over six months of the year(February, April, June, August , October and December).

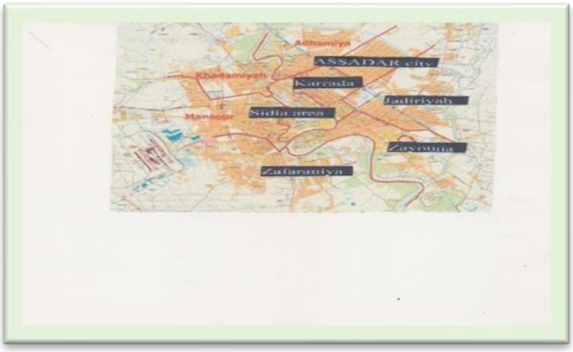
table (3) illustrate these data over the specified months. This determinant was assessed by the gas chromatography device [25-26]and we compare the value obtained with the last Iraqi specification (417) and with the values installed in the approved international specifications. Figure (3) shows the concentrations of Dichloroacetic acid during the six months of the year.

2.5 Evaluation the Concentration of bromate ion (BrO_3^-)

The proportion of this ion was determined using ion chromatography approved in (method 3001-determination of USEPA) [27]. The main reason for the formation of the bromate ion is the presence of the bromide ion in the source water in a high percentage. According to recent research and studies, the bromide ion concentration in river water is less than that in sea water. Table (4) shows bromate ion concentrations in residential areas over a period of six months. Figure (4) shows the concentrations of bromate ion during the six months of the year.

2.6. Evaluation the Concentration of Free Bromine .

An assessment of the important drinking water factor was carried out for the six residential areas and for the previously limited month of the year, where these determinants were measured using the spectrophotometer in the(Al-Karunji Company for the production of water and juices).the table (5) shows the concectration of Free Bromine in drinking water.



Results and Discussion

Table (1) showes the Concentration of bromide ion and total organic compound of raw water

Table 1: values of bromide ion and total organic compound of raw water in six months.

Con.(Br-) mg/l	Con.(TOC) mg/l	**Months**
0.027	6.43	February
0.035	6.99	April
0.038	8.30	June
0.044	9.1	August
0.060	7.22	October
0.029	6.98	December

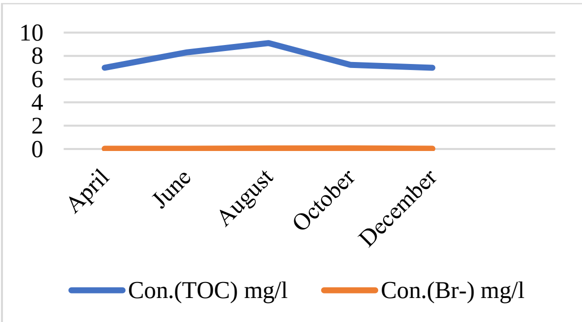


Fig. 1: value of (TOC)and (Br-) and allowable limit in mg/l.

The value of bromide ion (Br^-) is determined by (0.03mg/l) and shows from the table that there is an inverse relationship between bromide ion and total organic compound. The dose of chlorine is directly proportional to the total organic compound.When bromine is replaced with chlorine, this indicates the presence of a high percentage of bromine that exceeds the percentage of chlorine added as a sterilizer, and also indicates the presence of brominated compounds with higher concentrations than chlorinated compounds.

.We also note that as the temperature increases, organic compounds increase and therefore we need a higher percentage of chlorine to eliminate it, but increasing chlorine from the permissible limits leads to the formation of chlorinated carcinogenic side compounds such as Tri hallo methane and others .From Table (1) we notice an increase in the proportion of bromide ion above the permissible limit set by the World Health Organization, which is 0.03mg/l for surface water. The presence of high concentrations of this ion leads to the actual displacement towards the formation of brominated compounds and a high replacement of bromine in place of chlorine.

Table (2) showes the concentration of Chloroform of baghdad's six areas(Sidia, Assadar city, Jadiriyah, Zayouna, Karrada and Zafraniya) and for six months of the year (February, April, June, August , October, December).

The percentage of trihallomethane in drinking water should not exceed (0.15mg/L) and since chloroform is the first compound in this group, which is through the interaction of chlorine used as sterile and oxidized with organic matter in raw water [28]."The highest values in these residential areas were recorded in the eighth month(August), where the temperture in Iraq is very hot and the temperature is as high as 50 degrees Celsius where the TOC value is as high as possible and reaches (9.1mg/l), and this is also reflected in the chloroform concentrations, which were as high as possible in the eighth month. Also to avoid the formation of chlorinated carcinogenic organic compounds we reduce the amount of chlorine added during the sterilization process and this gives an opportunity for bromine to enter these compounds as a strong chlorine competitor and in this case consists of organic compounds concluded at least dangerous chlorinated compounds. The chloroform values recorded in table(2) of the selected areas are mostly higher than the limit allowed in the specifications adopted .the concentration of bromide ion in raw water for eighth month it equal to (0.044mg/l) For the tenth month it was (0.06mg/l) and this makes the possibility of replacement high as bromine is easily introduced into organic compounds in the event of any reduction in chlorine.

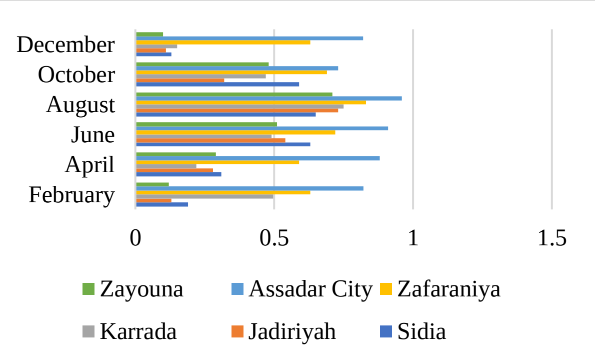


Fig. 2: value of chloroform and allowable limit in mg/l.

Table 2. Chloroform Concentrations in the six regions and six months of the year.

month	($CHCL_3$) mg/l Sidia	($CHCL_3$) mg/l Jadiriyah	($CHCL_3$) mg/l karrada	($CHCL_3$) mg/l zafraniya	($CHCL_3$) mg/l assadar city	($CHCL_3$) mg/l Zayouna
February	0.19	0.13	0.496	0.63	0.821	0.12
April	0.31	0.28	0.22	0.59	0.88	0.29
June	0.63	0.54	0.49	0.72	0.91	0.51
August	0.65	0.73	0.75	0.83	0.96	0.71
October	0.59	0.32	0.47	0.69	0.73	0.48
December	0.13	0.11	0.15	0.63	0.82	0.1

Table (3) showes the concentration of the dichloro acitic acid in(Sidia, Assadar city, Jadiriyah, Zayoun, Karrada and Zafraniya) and for six months of the year (February, April, June, August , October, December). The value of this carcinogenic chemical compound in Iraqi specifications has been determined at (0.05mg/l) and table (3) shows that most areas did not record a significant rise in this compound where the values were accepted with a slight rise in Assadar city as well as Zafraniya which may be due to the inefficiency of sterilization plants or refractions in the water distribution network, which led to the emergence of these concentrations near the limit allowed doing it.

Table(4) and Table (5) showes the bromate ion and free bromine in drinking water for six area (Sidia, Assadar city, Jadiriyah, Zayoun, Karrada and Zafraniya) and for six months of the year (February, April, June, August , October, December).

Table 3. Dichloroacetic acid concentration in drinking water for the six areas of Baghdad and of six months of the year.

month	con.(mg/l) Sidia	con.(mg/l) Jadiriyah	con.(mg/l) Karrada	con.(mg/l) Zafraniya	con.(mg/l) Assadar city	con.(mg/l) Zayouna
February	0.025	0.011	0.022	0.039	0.051	0.02
April	0.022	0.019	0.021	0.037	0.042	0.031
June	0.03	0.021	0.033	0.058	0.044	0.022
August	0.038	0.025	0.03	0.048	0.053	0.042
October	0.04	0.031	0.024	0.062	0.051	0.042
December	0.031	0.038	0.034	0.042	0.029	0.019

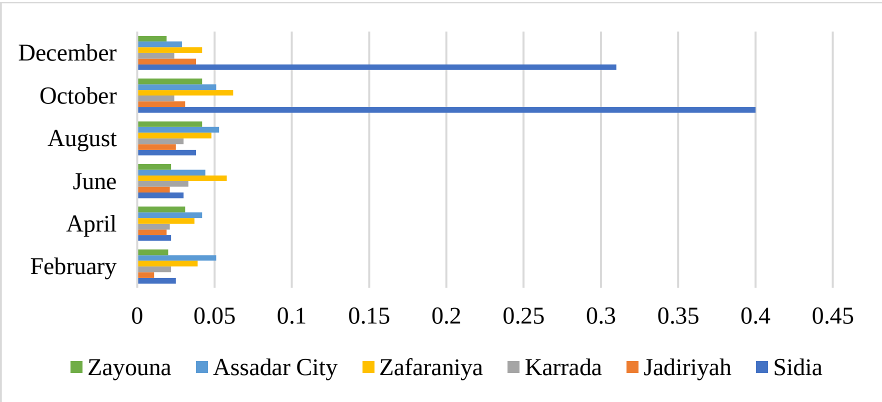


Fig. 3: value of dichloroacetic acide and allowable limit in mg/l.

Table 4. Ion Bromat Concentrations for the six areas in Baghdad and six months in the year.

Month	con.(mg/l) Sidia	con.(mg/l) Jadiriyah	con.(mg/l) Karrada	con.(mg/l) Zafraniya	con.(mg/l) Assadar city	con.(mg/l) Zayouna
February	0.011	0.029	0.002	0.002	0.002	0.015
April	0.009	0.021	0.00	0.00	0.001	0.009
June	0.002	0.005	0.001	0.002	0.001	0.005
August	0.004	0.0053	0.009	0.009	0.002	0.003
October	0.002	0.003	0.002	0.005	0.005	0.002
December	0.01	0.024	0.003	0.005	0.0019	0.013

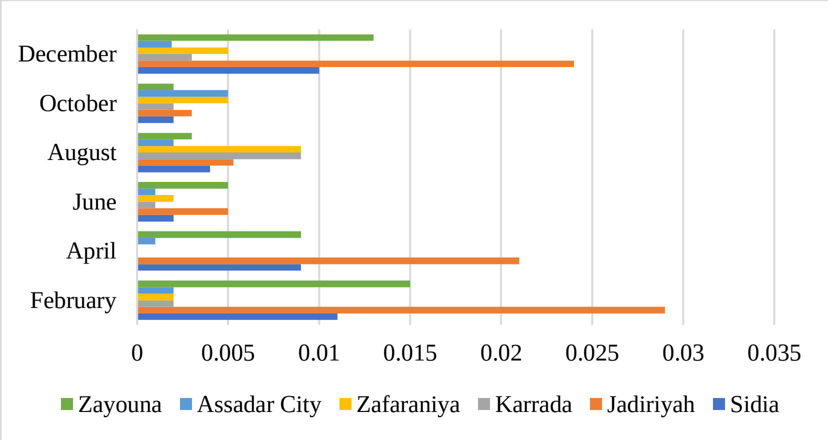


Fig. 4: value of bromate ion and allowable limit in mg/l.

Table 5. free bromine values for the six regions over the six months of the year (February, April, June, August, October and December).

month	con.(mg/l) Sidia	con.(mg/l) Jadiriyah	con.(mg/l) Karrada	con.(mg/l) Zafraniya	con.(mg/l) Assadar city	con.(mg/l) Zayouna
February	0.17	0.16	0.11	0.27	0.31	0.12
April	0.18	0.16	0.1	0.31	0.33	0.10
June	0.26	0.21	0.18	0.25	0.29	0.15
August	0.25	0.13	0.11	0.35	0.30	0.10
October	0.18	0.11	0.15	0.20	0.25	0.13
December	0.11	0.10	0.10	0.26	0.29	0.11

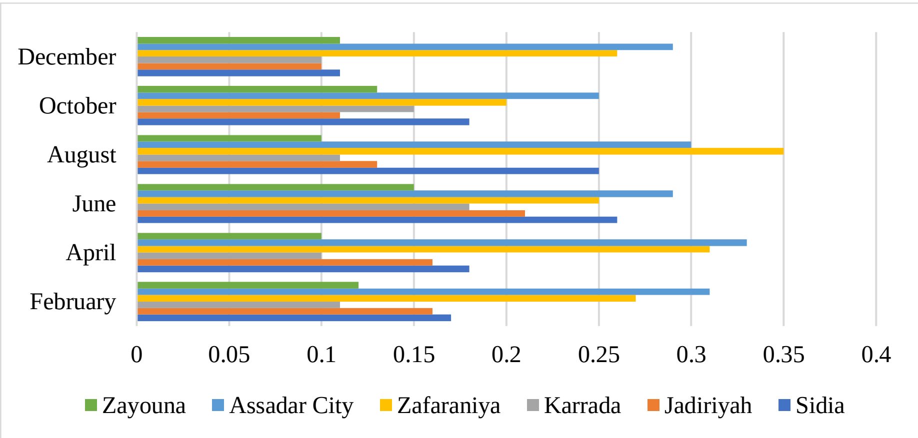


Fig. 5: value of free bromine and allowable limit in mg/l

The value of bromate ion (BrO_3^-)has been determined by (0.1mg/L) in the last Iraqi specification and the rate of bromide ion in surface water by (0.03mg/l). (when decreases the value of pH Leads to the formation of brominated organic compounds and((not bromine)). where the more bromide ion in the source water, the more promatogenic it is expected to be because chlorine oxidized the bromide ion and convert it into bromine Br_2 and this turns into bromate if it is oxedized [25-27]. The degree of acidity as well as bromide ion and the proportion of organic compounds are factors that lead to the formation of this ion and here the replacement towards bromine is easy and certain.

From the table, we note that there is a rise in the month (February) and (December) and for the following areas (Sayedia, Jadriya, Ziona) which did not have high concentrations for chloroform, which is a sure sign of strong displacement towards the brominated compounds and a high replacement between chlorine and bromine. We note from table 1 that the ratio of ion bromine was not low in these months (February and December) as it recorded (0.027mg/l) and (0.029mg/l) respectively and is very close to the highest allowed limit of (0.03mg/l). As for the bromine group represented by of free bromine which is the remainder of it after all oxidation and operations have ended and the union with existing organic materials must be (non-existent) In drinking water is an indication of the presence of a high percentage of bromine, part of which is interaction with organic compounds and another converted to bromine and the remaining section is called (free bromine) so it must be stressed to make the concentration of bromide ion in surface water non-existent or very low and below the limit allowed to avoid the formation of all these side compounds and prevent replacements between chlorine and bromine.

Conclusions

1- Through the results we have obtained, it is certain that drinking water is not free of chlorinated compounds such as carcinogenic tri halo methane, which means the validity of this water because there may be a replacement process with bromine.

2. From investigation and research it has been concluded that bromine compounds have no less harmful impact on human health than chlorine compounds.

3- The need to conduct intensive laboratory tests of raw water before being introduced into the sterilization process and the tests include both the acid function, total organic carbon, and the ratio of bromide ion because of its direct and significant impact on the formation of dangerous side compounds of both chlorinated and brominated types.

4- Temperature is a major and important factor where the higher the temperature the more organic compounds in the source water decompose and the greater the likelihood that the totals classified as dangerous and carcinogenic.

5- Spreading awareness and establishing workshops on the need to conduct laboratory tests before, during and after the sterilization process to make the picture complete and to know most of the chemical compounds formed.

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References

[1] Deng, Y. L., Luo, Q., Yuan, X. Q., Liu, C., Lu, T. T., Shi, T., ... & Zeng, Q. (2022). Associations between drinking water disinfection byproducts and menstrual cycle characteristics: A cross-sectional study among women attending an infertility clinic. *International Journal of Hygiene and Environmental Health*, *241*, 113931.

[2] Cao, G., Huang, K., Whelton, A. J., & Shah, A. D. (2020). Formation and sorption of trihalomethanes from cross-linked polyethylene pipes following chlorinated water exposure. *Environmental Science: Water Research & Technology*, *6*(9), 2479-2491.

[3] Sathasivan, A., Kastl, G., Korotta-Gamage, S., & Gunasekera, V. (2020). Trihalomethane species model for drinking water supply systems. *Water Research*, *184*, 116189.

[4] Ding, S., Chu, W., Krasner, S. W., Yu, Y., Fang, C., Xu, B., & Gao, N. (2018). The stability of chlorinated, brominated, and iodinated haloacetamides in drinking water. *Water research*, *142*, 490-500.

[5] Zhang, H., Xue, J., Wang, Q., Yuan, L., & Wu, H. (2022). Formation of halogenated disinfection by-products during ballast water chlorination. *Environmental Science: Water Research & Technology*, *8*(3), 648-656.

[6] Zhang, X. Y., Du, Y., Lu, Y., Wang, W. L., & Wu, Q. Y. (2022). Characteristics of the formation and toxicity index of nine newly identified brominated disinfection byproducts during wastewater ozonation. *Science of The Total Environment*, *824*, 153924.

[7] Han, J., Zhang, X., Jiang, J., & Li, W. (2021). How much of the total organic halogen and developmental toxicity of chlorinated drinking water might be attributed to aromatic halogenated DBPs?. *Environmental science & technology*, *55*(9), 5906-5916.

[8] Kim, D., Kanan, A., Sharma, N., Westerhoff, P., & Karanfil, T. (2020). Total organic halogen (TOX) species formation at different locations in drinking water distribution

systems. *Environmental Science: Water Research & Technology*, *6*(9), 2542-2552.

[9] Ackerson, N. O. B., Liberatore, H. K., Plewa, M. J., Richardson, S. D., Ternes, T. A., & Duirk, S. E. (2020). Disinfection byproducts and halogen-specific total organic halogen speciation in chlorinated source waters–The impact of iopamidol and bromide. *Journal of Environmental Sciences*, *89*, 90-101.

[10] Chen, B., Bu, Y., Yang, J., Nian, W., & Hao, S. (2020). Methods for total organic halogen (TOX) analysis in water: past, present, and future. *Chemical Engineering Journal*, *399*, 125675.

[11] Frimmel, F. H., & Jahnel, J. B. (2003). Formation of haloforms in drinking water. *Haloforms and Related Compounds in Drinking Water*, 1-19.

[12] Winid, B. (2015). Bromine and water quality–Selected aspects and future perspectives. *Applied Geochemistry*, *63*, 413-435.

[13] Abusallout, I., Rahman, S., & Hua, G. (2017). Effect of temperature and pH on dehalogenation of total organic chlorine, bromine and iodine in drinking water. *Chemosphere*, *187*, 11-18.

[14] Wang, L., Niu, R., Chen, B., Wang, L., & Zhang, G. (2017). A comparison of photodegradation kinetics, mechanisms, and products between chlorinated and brominated/iodinated haloacetic acids in water. *Chemical Engineering Journal*, *330*, 1326-1333.

[15] Criquet, J., Rodriguez, E. M., Allard, S., Wellauer, S., Salhi, E., Joll, C. A., & Von Gunten, U. (2015). Reaction of bromine and chlorine with phenolic compounds and natural organic matter extracts–Electrophilic aromatic substitution and oxidation. *Water Research*, *85*, 476-486.

[16] Tan, J., Allard, S., Gruchlik, Y., McDonald, S., Joll, C. A., & Heitz, A. (2016). Impact of bromide on halogen incorporation into organic moieties in chlorinated drinking water treatment and distribution systems. *Science of The Total Environment*, *541*, 1572-1580.

[17] Alomirah, H. F., Al-Zenki, S. F., Alaswad, M. C., Alruwaih, N. A., Wu, Q., & Kannan, K. (2020). Elevated concentrations of bromate in drinking water and groundwater from Kuwait and associated exposure and health risks. *Environmental research*, *181*, 108885.

[18] Ayoob, A., Sadeek, G., Saleh, M. (2022). Synthesis and Biologically Activity of Novel 2-Chloro -3-Formyl -1,5-Naphthyridine Chalcone Derivatives. *Journal of Chemical Health Risks*, 12(1), 73-79. doi: 10.22034/jchr.2022.688560

[19] salih, W., Saied, S., Natheer, R., Saleh, M. (2021). Removal of Pb(II) ions from Tigris river wastewater in Mosul city by using modified commercial activated carbon. *Egyptian Journal of Chemistry*, 64(12), 7309-7314. doi: 10.21608/ejchem.2021.77656.3790

[20] Yang, J., Ma, H., Wang, C., & Liu, H. (2022). Bromate formation during oxidation of bromide-containing water by the CuO catalyzed peroxymonosulfate process. *Chinese Chemical Letters*.

[21] Liu, Y., & Mou, S. (2004). Determination of bromate and chlorinated haloacetic acids in bottled drinking water with chromatographic methods. *Chemosphere*, *55*(9), 1253-1258.

[22] Saied, S., Mohammed, S., Khaleel, B., Saleh, M. (2021). Comparative Studies between Conventional Techniques and Green Chemistry to Synthesis of Novel Piperidinium Salts Ionic Liquids (PBSILs). *Journal of Chemical Health Risks*, 11(4), 451-456. doi: 10.22034/jchr.2021.686640

[23] Echigo, S., Itoh, S., Natsui, T., Araki, T., & Ando, R. (2004). Contribution of brominated organic disinfection by-products to the mutagenicity of drinking water. *Water Science and Technology*, *50*(5), 321-328.

[24] Al-Thakafy, N., Al-Enizzi, M., Saleh, M. (2022). Synthesis of new Organic reagent by Vilsmeier – Haack reaction and estimation of pharmaceutical compounds (Mesalazine) containing aromatic amine groups. *Egyptian Journal of Chemistry*, 65(6), 685-697. doi: 10.21608/ejchem.2021.101851.4729

[25] Wang, Y., Small, M. J., & VanBriesen, J. M. (2017). Assessing the risk associated with increasing bromide in drinking water sources in the Monongahela River, Pennsylvania. *Journal of Environmental Engineering*, *143*(3), 04016089.

[26] Abdullah, J. A., Yhya, R. K., & AL-Sayd Toohi, H. T. (2021). Synthesis of some Imidazolidinone compounds under phase transfer conditions and photo cleavages studies of molecular for these compounds. Egyptian Journal of Chemistry, 64(12), 2-3.

[27] Toohi, H. T. A. S., Rabeea, M. A., Abdullah, J.

A., & Muslim, R. F. (2021). Synthesis and characterization activated carbon using a mix (asphalt-polypropylene waste) for novel azo dye (HNDA) adsorption. *Carbon Letters*, *31*(5), 837-849.

[28] Hamdoon, A., salih, W., Ahmed, S., Saleh, M. (2022). Modifying The Rheological Properties Of Asphalt Using Waste Additives and Air Blowing and Studying The Effect Of Time Aging On The Modified Samples. *Egyptian Journal of Chemistry*, 65(5), 447-453. doi: 10.21608/ejchem.2021.94414.4439