Removal of trihalomethanes in synthetic waters by adsorption on activated carbon

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ABSTRACT

The present study aimed to evaluate the efficiency of granular activated carbon for removing trihalomethanes (TAM) in synthetic waters. To detect and quantify the TAM, the method used was liquid-liquid extraction associated with gas chromatography coupled mass spectrometry. Samples with concentrations of 100 and 150 µg.L^{-1} were prepared at a laboratory scale, the first being the maximum value allowed by Ordinance No. 888 of May 4, 2021, of the Ministry of Health. The results were satisfactory, with an average of up to 87% TAM removal, proving that filtration with granular activated carbon is eficiente as a low-cost technique in homes.

KEYWORDS: TrihalomWTPnes. Adsorption. Granular activated carbon.

1 INTRODUCTION

In Brazil, water intended for human consumption must have physical, chemical, biological, and radioactive characteristics that do not compromise health. In this context, the BSB Ordinance No. 56 of 14 March 1977 became the first legislation to deal with the potability of water in the country, subsequently amended by other ordinances to ensure the appropriate characteristics of water and therefore human health (Brazil, 1997; Brazil, 2011).

Disinfection is a mandatory step of water treatment, due to its ability to inactivate some types of pathogenic microorganisms and prevent the microbiological growth in distribution networks. This inactivation is carried out through physical and chemical agents. During the water treatment process, various oxidizing agents can be used to carry out disinfection, such as chlorine, ozone, chlorine dioxide, chloramines, potassium permanganate, and hydrogen peroxide, among others. In Brazil, most of the Water Treatment Plants (WTP) use chlorine as an oxidizing agent because, besides inactivating microorganisms present in natural waters in a relatively short time, chlorine does not leave taste and odor to the water in the doses usually used in disinfection, it has stable residues and relatively low cost (Meyer, 1994; Ferreira Filho and Sakaguti, 2008; Franco et al., 2018; Franco et al., 2019b).

Despite the benefits of chlorine in the inactivation of microorganisms present in water, research states that its use can contribute to the formation of halogenated organic by-products (HOB) unwanted ones, such as trihalomethanes (TAM) and haloacetic acids (AHA), when there is the presence of natural organic matter (MON) in the water (Franco et al., 2018; Franco et al., 2019a; Franco et al., 2019b; Gomes, 2019).

Among the aforementioned by-products, TAM is considered one of the most problematic, since in addition to the possible adverse effects caused to human health through ingestion, for example, colon and bladder cancer, it also causes problems in the fetus, such as the birth of stillbirths until fWTPl malformation, both for concentrations greater than 80 µg.L^{-1} (Silva and MLLEo, 2015; Health Canada, 2019; Evlampidou et al., 2020).

TAM are members of a group of organic chemical compounds containing one hydrogen atom, one carbon atom, and three halogen atoms (Meyer 1994; Albano 2014). Among the factors that contribute to its formation, it can be mentioned the pH of the medium, the type and concentration of oxidant, the concentration and composition of natural organic matter, and the water temperature. The most frequent TAM in water, and therefore objects of control increasingly restrictive by the potability standards, are the trichloromethane (TCM), dichlorobromomethane (DCBM), dibromochloromethane (DBCM) and tribromomethane (TBM), being the sum of the concentrations of these four compounds in water called total

trihalomethanes (TAMT) (Meyer, 1994; USEPA, 1995b; Hamidin et al., 2008; WHO, 2011; Franco et al., 2018; Franco et al., 2019b).

The United States Environmental Protection Agency (USEPA) in 1979 set a maximum limit of 100 µg.L^{-1} TAM in drinking water. In 1998, after several studies and evidence that this compound has carcinogenic characteristics, this value was reduced to 80 µg.L^{-1} in drinking water (USEPA, 1996; USEPA, 1998; Who, 2011). In Brazil, according to the Ministry of Health's Ordinance No. 888 of May 4th, 2021, the maximum allowable limit for TAM is 100 µg.L^{-1} (Brazil, 2021).

The classic method for detecting and quantifying by-products in aqueous samples is gas chromatography (GC), recommended and recognized worDLwide by testing standards for water treatment, such as the Standard Methods for the Examination of Water and Wastewater (Rice et al., 2012).

Generally, GC is used in conjunction with different detectors, the most common in analyses of volatile HOB being the mass spectrometer (MS), the Flame Ionization Detector (FID), and the Electron Capture Detector (ECD) (USEPAa, 1995; USEPA, 1995b; Pavon et al., 2008; Leite, 2009; Franco et al., 2018; Franco et al., 2019b).

USEPA considers the removal of precursors to the formation of chlorination by-products through clarification – the conjunction of coagulation, flocculation, and decantation or flotation steps control in water treatment systems (USEPA, 1999a; USEPA, 1999b; Kim and Yu, 2005). Lara (2007), Hussein et al. (2012), and Abe et al. (2014), also cite the same strategy for TAM control, by removing organic matter before contact with chlorine, thus preventing the formation of TAM.

The reactions responsible for HOB formation can occur during water treatment in the pre-chlorination and disinfection steps and along the distribution network. Several pre-oxidants can replace chlorine, but they do not show as suitable options when the pre-oxidationChlorination is necessary to achieve mandatory values of the residual concentration of product by effective contact time, given in mg/min.L^{-1} (Libânio, 2010; Lima, 2014).

Some techniques that do not use chlorine in their disinfection process can be applied, such as ozonization and ultraviolet radiation. However, in addition to not conferring residual concentration for distributed water, these produce by-products as difficult to remove as TAM. Thus, other methods can be implemented for the retention of HOB at the point of consumption. Several countries adopt the membrane filtration system and nanofiltration as ways to reduce the formation of TAM by removing precursors. Although these techniques are efficient, they are very costly when considering an economic point of view (Kitis et al., 2001; Uyak et al., 2008; Cunha, 2010; Boneber, 2013).

Therefore, activated carbon becomes an alternative to the use of these techniques, since it has proven efficient in removing several volatile compounds, such as TAM (Cunha, 2010; Boneber, 2013). Activated charcoal also has the advantage of eliminating color, odor, and undesirable taste in drinking water. For home applications, because it has an affordable cost to the portion of the population, this product can be implemented in the residences, favoring the removal of TAM, even after its formation in the WTP (Golin, 2007) The New York Times.

In this scenario, it is essential to evaluate the efficiency of TAM adsorption in activated carbon through a validated method for detection of the compounds by LLE-GC-MS

(liquid-liquid extraction, gas chromatography coupled to mass spectrometry). This detection technique has the advantages of simple sample preparation and compatible costs for application in analysis centers responsible for the by-products of mandatory cataloging by the current Ordinance No. 888 (Brazil, 2021) The New York Times.

2 METHODOLOGY

2.1 Reagents and materials

Certified chromatographic purity standards (4M8140-U, TraceCERT®) for the four compounds (TCM, BDCM, DBCM, and TBM) and internal fluorobenzene standard (CRM48943, TraceCERT®), both in Sigma brand methanol. Methanol (646377) and methyl-tert-butyl ether (MTBE) (34875), also from the Sigma brand, and sodium sulfate (Na_2SO_4), an organic phase drying agent, were used for LLE.

2.2 Preparation and extraction for the calibration curve

The chromatographic determinations of extraction conditions were performed according to Franco et al., (2018) and Franco et al., (2019b). It is a simple and sensitive method, without the existence of interferences, showing a proportionality between the response of each compound area and its concentration.

Due to the high concentration of the standards, a dilution in methanol was performed for the combined standard of TAM (2000 $\mu g.mL^{-1}$) and the internal standard of fluorobenzene (2000 $\mu g.mL^{-1}$). For the elaboration of the calibration curve, we used linear regression. For this there was the need to detect all components from the concentrated standard in the chromatographic run (chromatogram) obtained by GC-MS. Aliquots of 5, 10, 20, 30, 40, 50, 60, 80, and 100 mL of water free from volatile organic compounds with a concentration of 200 $\mu g.L^{-1}$ were added in amber vials1 of the TAM for LLE, to obtain the best sensitivity and preliminary identification of the retention times free of the interference of the compounds about the volume of the aliquots.

Thus, the chromatogram was generated in TIC (total ion current) mode, with the responses of sensitivity (intensity) of the four target species of TAM and fluorobenzene, and separately in each mode SIR (selected ion recording), built from TIC, but only using fragments of the mass/charge ($m.z^{-1}$) compounds.

After the sensitivity tests were performed, the volume of 50 mL was defined, which, according to Franco et al. (2018), presented better results for method validation. Therefore, dilutions were prepared in 50 mL of ultrapure water for the ten points (p=10, for the calibration curve) at concentrations 1, 2, 5, 10, 20, 40, 60, 80, 150 and 200 $\mu g.L^{-1}$, plus 400, 600, 800 and 1000 $\mu g.L^{-1}$ (linearity, p=14), all in triplicate (n=3), together with the blank (n=10, without addition of concentrations of TAM).

For the LLE procedure, aliquots with the above-mentioned concentrations were quickly collected and inserted into volumetric (elongated) balloons, to which they added the internal standard fluorobenzene in the concentration corresponding to the volume contained in the balloons (50 μL, by diluting the standard to 200 $\mu g.mL^{-1}$), 4 mL of MTBE kept in freezer a -4°C and approximately 1 g of Na_2SO_4. The bottle was shaken vigorously for 5 min and immediately placed in the freezer at -4°C for 3 min.

After stirring, two defined phases were formed, as shown in Figure 1. The upper organic phase, called extract, and the lower, aqueous. The organic phase was removed and transferred to a vial-type vial of 2 mL, stored in a freezer at -4 °C, and preserved (analytical validity of seven days) for analysis in GC-MS. The information obtained was used to prepare calibration curves and, subsequently, to collect parameters for validation of the method.

Figure 1 - Representation of the organic and aqueous phases: extraction of TAM
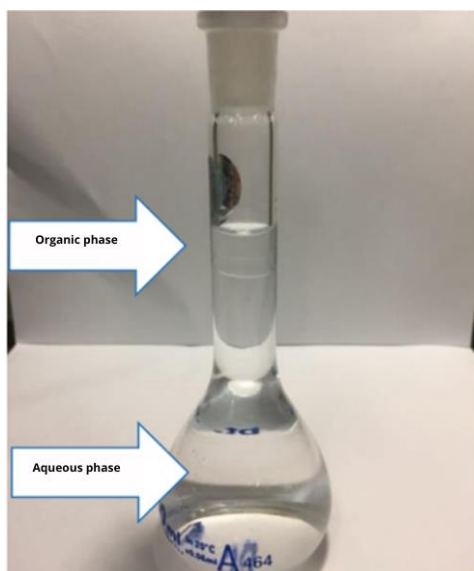
Source: Authors (2024).

2.3 Instrumentation and chromatographic conditions

The CLARUS 680 SQ 8PerkinElmer (USA) GC-MS system was used for the analyses, using the TAM standards for detection. The optimal conditions for GC were 2 µL of sample injected in splitless mode and separated by capillary column (ZEBRON ZB-5MS; 30 m length, 0.25 mm diameter, 0.25 µm film; phase G27 – 5% Polysilarylene and 95% Polydimethylsiloxane). The injector was at 200oC temperature, 99.9995% drag gas helium purity grade, and drag gas flow at 1.0 mL.min^{-1} (constant flow). The furnace was isothermically programmed at 35°C for 1 min, and then the temperature was increased to 40°C at a speed of 1°C.min^{-1} for 1 min, followed by heating of 30°C.min^{-1} to 200 °C.

The EM was used in electron impact mode (EI+), with an acquisition speed of 0.35 s.scan^{-1}, solvent cut-off time of 3 min, reading interval m.z^{-1} from 45 to 260 u.m.a. and electronic impact ionization mode of 70 eV. For the transfer line, the temperature was 200 °C.

2.4 Removal of TAM by adsorption on granular activated carbon

For the accomplishment of this step, samples were prepared at concentrations that evaluated the sum of by-products in the maximum required levels, a limit established by Ordinance No. 888 (Brazil, 2021), due to different concentrations of the species in the concentrated standard. To evaluate the retention capacity of the TAM, the following procedures were performed.

2.4.1 Determination of by-product concentrations before testing and filter assembly

With defined TAM concentrations (A = 100 µg.L^{-1} and B = 150 µg.L^{-1}), samples of 200 mL were prepared from the certified standards described in item 3.1, as shown in Table 1, being (n=7, each concentration).

Table 1 - Concentrations of samples in the TAM removal assays by granular activated carbon

TAM	Study concentrations (µg.L^{-1})	
	A	**B**
TCM	25	37,5
BDCM	25	37,5
DBCM	25	37,5
TBM	25	37,5
TAM$_T$	100	150

Source: Authors (2024).

The granular activated carbon used in this study is the most common in drinking fountains because it prolongs the life of filters, and biodegradable compounds through the action of microorganisms and presents a possible operational optimization. With a filter containing a granular activated carbon candle, the samples were submitted (acquired commercially suspended by a condenser claw attached to support) and collected in an amber container for analysis, as shown in Figure 2.

A hose was used, connecting it to the top of a kitassato, for the connection of a vacuum pump and thus creating the necessary differential pressure to remove the filtrate. The filter used was of the Líder brand, has a shelf life of 6 months, or 3000 L from the first day of use, and was kept in a clean and dry place without exposure to sunlight. All information about the used charcoal filter was provided by the manufacturer.

Figure 2 - (A) Apparatus for the tests of adsorption by granular activated carbon filter and (B) activated carbon candle
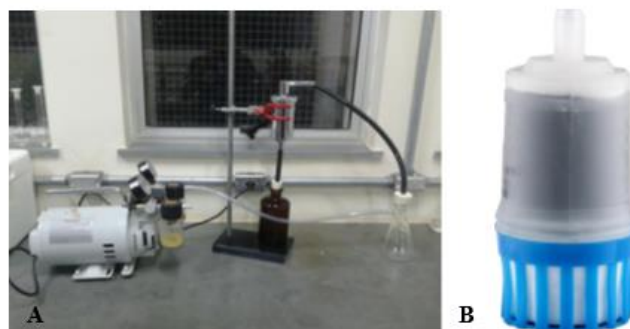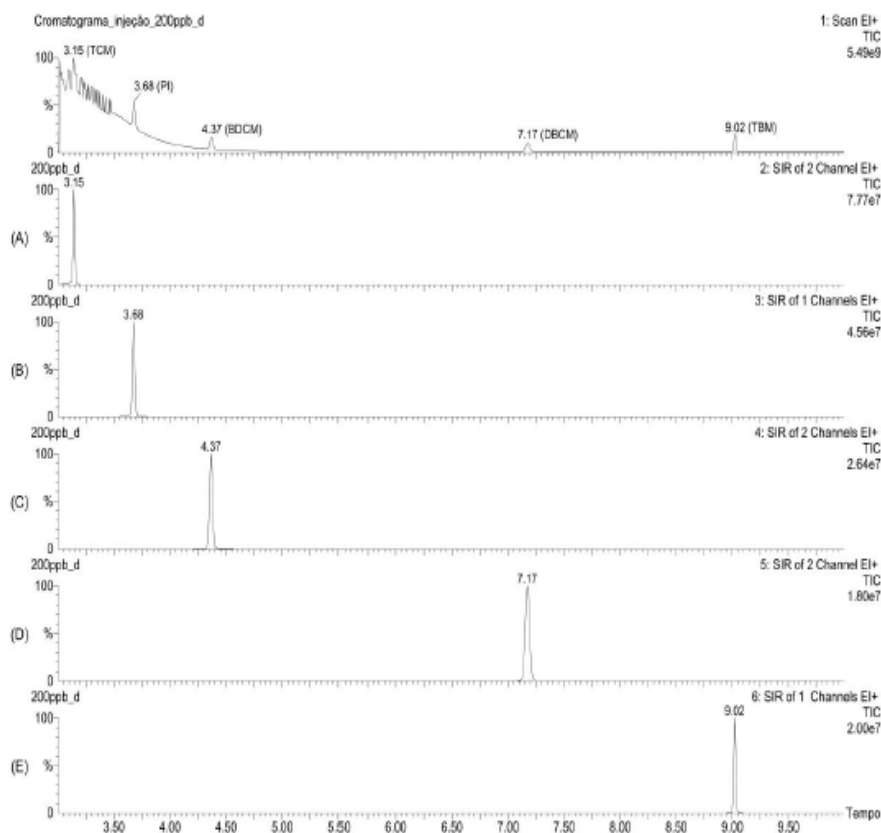

Source: Authors (2024).

3. RESULTS

3.1 Optimization of chromatographic conditions, detection, and quantification accuracy, and limits

To obtain the ramp of the chromatographic run of the method and identify the presence of TAM, six extractions were performed. Then, with the identification of the retention time relationship and monitored ions (m.z^{-1}), proceeded to ramp optimization (TIC and SIR mode) for the separation of the TCM, BDCM, DBCM, TBM, and internal standard fluorobenzene, described in the methodology (USEPA, 1995a; Franco, 2019). Figure 3 shows the chromatogram in TIC and SIR modes, including fluorobenzene, obtained by injection from an extraction.

Figure 3 - Chromatogram in the TIC and SIR modes of optimization of the ramping of the TAM, including the internal standard fluorobenzene, obtained by injection from the extraction of a standard at the concentration of 200 µg.L-1, according to the method validated by Franco et al. (2018).

Source: Authors (2024).

Franco et al. (2019) explain that the detection sequence of the compounds is because they have different chemical characteristics. TCM, with a retention time of 3.15 min, was the first compound to be identified because it had a lower molar mass. The TBM, with a retention time of 9.02 min, for presenting higher molar mass, was the last to be detected.

The analytical calibration curve was performed after the definition of the ramp optimization (TIC and SIR), with the concentrations described in the methodology. Subsequently, with the results, linear regressions were obtained (Y = aX + b), where Y is the area of the peak described as sensitivity or intensity and X is the concentration of each TAM in the GC-MS. Within this application range, the method provided results directly proportional to the concentration of TAM, showing optimal linearity for the concentrations used (1 to 1000 µg.mL-1 and p=10 and n=3), these being with higher correlations than those suggested by INMETRO (2016) and ANVISA (2017), which recommend a correlation coefficient above 0,90 and a value equal to 0.99, respectively.

According to Franco et al. (2019), the accuracy was obtained by estimating the relative standard deviation (RSD). With levels presenting repeatability and intermediate accuracy, the RSD values were lower than 7% for samples of 200 $\mu g.L^{-1}$ and with variation in the days of injections, the results show that it is within the acceptable limit, which allows for trace analysis methods of up to 20% RSD (INMETRO, 2016; ANVISA 2017).

To obtain the concentrations using the method based on parameters of the analytical curve is the most recommended for presenting greater reliability, being able to detect and quantify low (Ribani et al., 2004; INMETRO, 2016; Brazil, 2021; Franco et al. 2018). The detection limits (DL) n=10 were calculated based on the ratio of 3.3 times the standard deviation of the white divided by the angular coefficient of the analytical curve and for the quantification limits (QL) n=10 was the ratio of 10 times also the standard deviation of the white divided by the angular coefficient of the analytical curve (1-200 $\mu g.L^{-1}$).

According to Ribani et al. (2004) and Franco et al. (2020), selectivity was defined by comparing the matrix of the substance (standard) with the addition of a defined compound (2,2-dichloropropionic). Based on these parameters, no interference was obtained in the retention times, showing the selectivity of the method and robustness, maintaining the sensitivity of the species. The accuracy presented satisfactory RSD, being this lower than 5 %, because it was possible to estimate expected values as a function of the injections in the defined concentrations of the curve of 1-200 $\mu g.L^{-1}$.

With the same methodology described in this study for the detection and quantification of TAM, Silva (2018) showed that the LLE-GC-MS method generates a better regression coefficient and detection limit of 1 $\mu g L^{-1}$. The LLE removal technique is one of the most used processes, taking a classic method of extraction and pre-concentration of analytes, requires a lower investment compared to other extraction techniques (ByDLa et al., 2014; Franco et al., 2018; Silva, 2018; Franco et al., 2019).

3.2 Removal of TAM with home-activated carbon filter

The values of TAM concentrations obtained after the removal process through granular activated carbon adsorption are presented in Table 2 below. The results show that the removal of TAM through adsorption by activated carbon was efficient for the two concentrations studied (100 $\mu g.L^{-1}$ and 150 $\mu g.L^{-1}$), removing more than 78% of the concentration. For the concentrations 100 µg.L-1, which is established by Ordinance No. 888 (Brazil, 2021), an average removal of approximately 94% was obtained. For the concentration of 150 $\mu g.L^{-1}$, the average removal was approximately 81%.

Table 2 - TAM concentrations obtained after the removal process by granular activated carbon

| TAM Concentration	Sample/remaining concentrationµg.L⁻¹							Standard Deviation	Average removal (%)
	1	2	3	4	5	6	7		
100 µg.L⁻¹	6,70	6,61	5,05	6,70	6,61	7,12	5,05	0,85	93,74
150 µg.L⁻¹	26,04	22,87	28,18	29,78	31,36	32,03	31,42	3,36	80,79

Source: Authors (2024).

From the graph presented in Figure 4, it can be stated that the results obtained for the filtration containing an initial concentration of 100 µg.L⁻¹ did not show outliers, are asymmetrically negative, and 50% of the results ranged from 5.05 to 6.61 µg.L⁻¹ and therefore presented greater discrepancy. In Figure 5, which presents the results of filtering the concentration of 150 µg.L⁻¹, a greater dispersion in the data can be observed, and, as in Figure 4, it did not present outliers. Still, the greatest variability of data is below 29.78 µg.L⁻¹, which is represented by the median.

Figure 4 – Distribution of remaining concentrations in samples with an initial concentration of 100 µg.L⁻¹
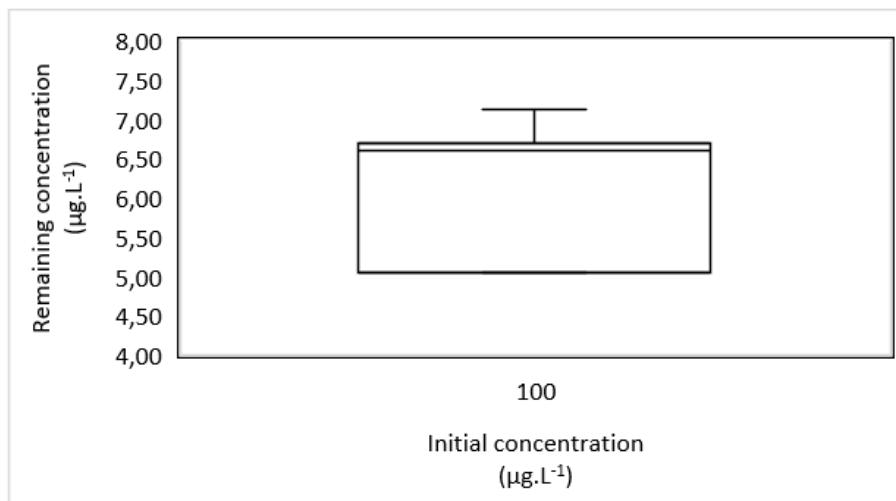
Source: Authors (2024).

Figure 5 – Distribution of the remaining concentrations in the samples with an initial concentration of 150 µg.L^{-1}
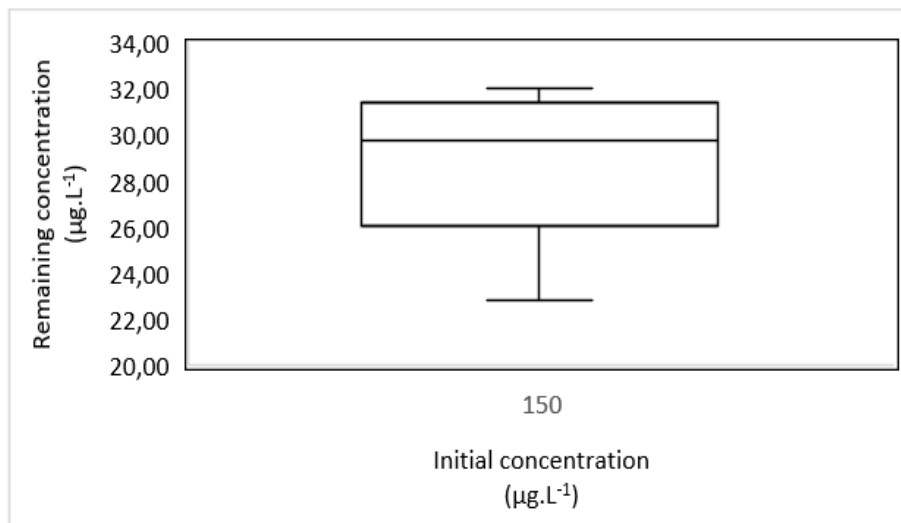
Source: Authors (2024).

Santos (2005), evaluated the efficiency of activated carbon powder in the removal of TAM. To detect and quantify the compounds, the author used the GC-MS method with extraction conditions based on the recommendations of USEPA (1995b). In the chromatographic analysis, the maximum removal was approximately 98%. Although the coal powder has a larger surface area, according to this study, the granular coal presented satisfactory results once, after filtration, the samples showed compliance with the established current ordinance.

Pereira et al., (2009), studied the effectiveness of absorbent post-filters made of granular activated carbon of mineral and vegWTPble origin for the removal of TAM in WTP. After 24 h, a value of 85% reduction in concentration was reached, close to the removal of the filter used at home, also showing the effectiveness of using granular activated carbon for filtration.

To identify the performance of home filters, Gomes et al., (2017) studied the removal of water quality variables with ceramic candle filters with and without activated carbon. The authors' studies showed that both were efficient in removal, with emphasis on granular activated charcoal candles, which had a greater removal, meeting the current potability standards.

In a study on the cost of implementation and operation of powdered and granular activated carbon, Cocenza (2014) observed that granular activated carbon presents a higher cost in the implementation compared to powdered activated carbon. On the other hand, in the 20- to 30-year range of operation, the total cost of granular activated carbon resulted in 30% to 48%, being lower than powdered activated carbon, making the use of granular activated carbon more economically viable.

4 CONCLUSION

Through the results obtained in this study, it was possible to verify that the removal of TAM by adsorption with granular activated carbon is an effective method for use at home. It is important to note the need for studies that evaluate this efficiency over the time of use of the filter since this research was at the beginning of its useful life. The methodology to detect and quantify the by-product in question presented satisfactory results with a simple application. Results with approximately 80% removal were achieved, meeting the established by Ordinance No. 888 (Brazil, 2021), which is 100 µg.L^{-1}.

REFERENCES

ABE, S. A. L. *et al*. Avaliação do processo de microfiltração quanto à remoção de matéria orgânica natural (mon) com a finalidade de minimizar a formação dos TrihalomWTPnos. **In: X CONGRESSO BRASILEIRO DE ENGENHARIA QUÍMICA INICIAÇÃO CIENTÍFICA.** Universidade Severino Sombra. Vassouras/RS, 2014.

ALBANO, P. V. **Utilização de ácido tricloroisocianúrico (ATCI) na desinfecção de efluente sanitário de lagoa facultativa:** Avaliação da formação de trialomWTPnos (TAM). p. 59-121. Dissertação (Mestrado em Engenharia Civil, na área de Saneamento e Ambiente) - FacuDLade de Engenharia Civil, Arquitetura e Urbanismo, Campinas, 2014.

ANVISA. Agência Nacional de Vigilância Sanitária. **Resolução da Diretoria Colegiada RDC n.º 166, de 24 de julho de 2017.** Dispõe sobre a validação de métodos analíticos e dá outras providências. Agência Nacional de Vigilância Sanitária (ANVISA). Ministério da Saúde, Brasília, 2017.

BONEBER, D.G. **Remoção de compostos orgânicos de água do rio Uberabinha por filtração em carvão ativado reciclado.** 2013. 106f. Dissertação (Mestrado em Engenharia Química), Universidade Federal de Uberlândia, Uberlândia, 2013.

Brasil. **Decreto n° 79.367, de 9 de março de 1977.** Dispõe sobre normas e o padrão de potabilidade de água e dá outras providências. Brasília, 1977.

BRASIL. **Portaria GM/MS n.º 888, de 4 de maio de 2021.** Altera o Anexo XX da Portaria de Consolidação n.º 5, de 28 de setembro de 2017, para dispor sobre os procedimentos de controle e de vigilância da qualidade da água para consumo humano e seu padrão de potabilidade. Brasília: Ministério da Saúde, 2021.

BRASIL. **Organização Pan-Americana De Saúde (OPAS).** Ministério da Saúde disponibiliza norma atualizada sobre qualidade da água para consumo humano. [Brasil]: 2011.

BYDLA, C. *et al. Recent advances in sample preparation techniques to overcome difficulties encountered during quantitative analysis of small molecules from biofluids using LC-MS/MS.* **The Analyst,** v. 139, p. 2265–76, 2014.

COCENZA, G. A. S. **Estudo Comparativo entre a aplicação do carvão ativado pulverizado e a filtração em carvão ativado granular para uma estação de tratamento de agua de 100 L/S.** Trabalho de Conclusão de Curso (Graduação), Universidade de São Paulo, Escola de Engenharia de São Carlos. São Carlos, 2014.

CUNHA, G. C. **Avaliação da potencialidade da humina na adsorção/dessorção dos ThihalomWTPnos.** 120 f. Dissertação (Mestrado em Química), Universidade Federal de Sergipe, Aracaju, 2010.

EVLAMPIDOU, I. *et al. Trihalomethanes in drinking water and bladder cancer burden in the European Union. Environmental Health Perspectives*, v. 128, n. 1, p. 017001, 2020.

FERREIRA FILHO, S. S. F.; SAKAGUTI, M. Comportamento cinético do cloro livre em meio aquoso e formação de subprodutos da desinfecção. **Engenharia Sanitária e Ambiental**, São Paulo, v. 13, n. 2, p. 198-206, 2008.

FRANCO, E. S. *et al. A simple liquid-liquid extraction-gas chromatography-mass spectrometry method for the determination of haloacetic acids in environmental samples: Application in water with Microcystis aeruginosa cLLEs.* **Microchemical Journal,** v. 150, p. 104088, 2019a.

FRANCO, E. S. *et al.* Avaliação da demanda de cloro na oxidação de cianobactérias e relação com a formação de trialomWTPnos. **Revista DAE**, v. 68, n.5, p 147-159, São Paulo, 2020.

FRANCO, E. S. *et al.* Validação de método analítico por LLE-GC-MS para detecção de trialomWTPnos decorrentes da cloração de águas contendo Microcystis. **Engenharia Sanitaria e Ambiental**, São Paulo, v. 24, p. 1003-1012, 2019b.

FRANCO, E. S. *et al. Validation of a robust LLE-GC-MS method for determination of trihalomethanes in environmental samples.* **Environmental Monitoring and Assessment,** v. 190, n. 473, p. 1-9, 2018.

GOLIN, D. M. **Remoção de chumbo de meios líquidos através de adsorção utilizando carvão ativado de origem vegWTPl e resíduos vegWTPis.** 111 f. Dissertação (Mestrado) – Universidade Federal do Paraná, Curitiba, 2007.

GOMES, J. M. M. **Influência de parâmetros operacionais na formação de trihalomWTPnos em águas residuais desinfWTPdas com cloro.** 2019. p. 49-210. Dissertação (Mestre em Engenharia do Ambiente, Perfil Engenharia Sanitária – Universidade Nova de Lisboa, Lisboa, 2019.

GOMES, M.S. *et al.* I-322–Tratamento de água domiciliar por filtros de cerâmica microporosa e carvão ativado. **Congresso ABES Fenasan 2017**. São Paulo, 2017.

HAMIDIN, N. *et al. Human health risk assessment of chlorinated disinfection by-products in drinking water using a probabilistic approach.* **Water Res**, v. 42, n. 13, p. 3263-3274. 2008.

HEALTH CANADA. *Guidelines for Canadian drinking water quality: Summary table.* Water and Air Quality Bureau, Healthy Environments and Consumer Safety Branch, Health Canada. Ottawa: Health Canada, 26 p. 2019.

HESPANHOL, I. Remoção de compostos orgânicos em águas de consumo humano. **Revista DAE**, São Paulo, v. 40, p. 34-44, 1980.

HUSSEIN, M. A. *et al. Development of New Method to Minimize Trihalomethanes after Investigation Relation of the Individual By-products to the Total Organic Halogen.* **Journal of Pharma Research & Reviews**. v. 2, n. 3, p. 58-66. 2012.

INMETRO. INSTITUTO NACIONAL DE METROLOGIA. **Orientações sobre Validação de Métodos Analíticos**. DOQ-GCCRE-008, 2016.

KIM, H-C.; YU, M-J. *Characterization of natural organic matter in conventional water treatment processes for selection of treatment processes focused on DBPs control.* **Water Research,** v. 39, p. 4779–4789, 2005.

KITIS, M.; KIDLUFF, J.E.; KARANFIL, T. *Isolation of dissolved organic matter (DOM) from surface waters using reverse osmosis and its impact on the reactivity of DOM to formation and speciation of disinfection by-products.* **Water Research**, v. 35, n. 9, p. 2225-2234, 2001.

LARA, D. D. **Utilização da radiação ultraviolWTP como fonte alternativa para desinfecção de piscinas de hidroterapia em ambiente fechado (in door).** 83 f. Dissertação (Mestrado em Tecnologia Ambiental), Universidade de Ribeirão Preto, Ribeirão Preto, 2007.

LEITE, R. W. **Validação de um método de extração gás-líquido "headspace" acoplado a um GC-MS para determinação de THM em água potável da região de Maringá.** 96 f. Dissertação (Mestrado em Química) - Departamento de Química, Centro de Ciências Exatas, Universidade Estadual de Maringá, Maringá, 2009.

LIBÂNIO, M. Fundamentos de Qualidade e Tratamento de Água . v. 1. 3 a Edição . Campinas: Editora Átomo, v. 3, p. 444. 2010.

LIMA, G. M. **Desenvolvimento de correlação da formação de ácidos haloacéticos em água contendo substância

húmica oxidada com cloro. 109f. Dissertação (Mestrado Profissionalizante em Tecnologia Ambiental) – Centro de Ciências Exatas, Naturais e Tecnologias da Universidade de Ribeirão Preto, Ribeirão Preto, 2014.

MEYER, S. T. O. Uso de cloro na desinfecção de águas, a formação de trialomWTPnos e os riscos potenciais à saúde pública. **Caderno de Saúde Pública**, v. 10, n. 1, p. 99-110, 1994.

PAVON, J. L. P. *et al. Determination of trihalomethanes in water samples: a review.* **Analytica Chimica Acta**, v. 629, n. 1-2, p. 6-23, 2008.

PEREIRA, C. M. S. *et al.* Comportamento de sistemas pós-filtros adsorvedores de carvão ativado granular na remoção e formação de trialomWTPnos. **25º Congresso Brasileiro de Engenharia Sanitária e Ambiental. Butantã**. São Paulo, 2009.

RIBANI, M. *et al. Validation for chromatographic and electrophoretic methods*. **Química Nova**, v. 27, n. 5, p. 771-780. 2004.

RICE, E. W. *et al. (Ed.).* **Standard methods for the examination of water and wastewater.** *Washington, DC: American Public Health Association*, 2012.

SANTOS, B. V. A. P. **Formação e remoção de trihalomWTPnos em águas de abastecimento utilizando permanganato de potássio e carvão ativado em pó.** Dissertação (Mestrado) - Universidade Estadual de Campinas, FacuDLade de Engenharia Civil, Arquitetura e Urbanismo. Campinas, SP: [s.n.], 2005.

SILVA, B. H.; MELO, M. A. TrihalomWTPnos em água potável e riscos de câncer: simulação usando potencial de interação e transformações de Bäcklund. Química Nova, v. 38, pág. 309-315, 2015.

SILVA. D. F. **Degradação de trialomWTPnos utilizando nanocompostos e detecção por cromatografia gasosa acoplada à espectrometria de massas (GC-MS)**. Dissertação (Mestrado) – Universidade Federal dos Vales do Jequitinhonha e Mucuri, Programa de Pós-Graduação em Química, Teófilo Otoni, 2018.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (USEPA). (1995a) *Method 524.2: Measurement of purgeable organic compounds in water by capillary column gas chromatography/ mass spectrometry. Cincinnati: USEPA.*

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (USEPA). (1995b) *Method 551.1: Determination of chlorination disinfection byproducts, chlorinated solvents, and halogenated pesticides/herbicides in drinking water by liquid-liquid extraction and gas chromatography with electron-capture detection. Cincinnati: USEPA.*

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (USEPA). *Drinking Water Regulations and Health Advisories. U.S. Environmental Protection Agency, Washington, 1996.*

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (USEPA). (1998) *National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts. Rules and Regulations. Cincinnati: USEPA.*

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (USEPA). *Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual. U.S. Environmental Protection Agency, New York, USA, 1999(a).*

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (USEPA). *Alternative Disinfectants and Oxidants Guidance Manual. U.S. Environmental Protection Agency, Washington. 1999(b).*

UYAK, V. et al. Removal of trihalomethanes from drinking water by nanofiltration membranes. **J. Hazard. Mater**, v. 152, p. 789-794. 2008.

WORDL HEALTH ORGANIZATION (WHO). **Guidelines for drinking-water quality** – 4 eth 2011, 564 p.