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Evaluation of water quality parameters and trihalomethane formation in breakpoint chlorination of wastewater

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Highlights:

- EAW was compared with sodium and calcium hypochlorite in breakpoint chlorination of anaerobic effluent. Water quality parameters and trihalomethane formation were evaluated.

Keywords: Electroactivated water; calcium and sodium hypochlorite; anaerobic effluent.

INTRODUCTION

This study aims to evaluate the water quality parameters and trihalomethane formation during breakpoint chlorination of wastewater, focusing on comparing the efficacy of electroactivated water (EAW) treatment to that of sodium and calcium hypochlorite treatments.

An increasing number of wastewater treatment plants (WWTPs) are adopting disinfection technologies to enhance operational and environmental safety (Scialdone et al., 2021). Electrochemical technology for wastewater treatment has gained significant attention over the last two decades, such as reduced chemical use, improved worker safety, elimination of liabilities associated with transport, and improved occupational health and safety management (Sousa Filho et al., 2022).

EAW is an oxidizing solution produced through the electrolysis of a brine solution. This process generates a solution containing hypochlorous acid in equilibrium with the hypochlorite ion and other chlorine species (Scialdone et al., 2021). EAW consists of a multi-oxidant solution that includes hydrogen peroxide, ozone, dichlorine, chlorine dioxide, and sodium hypochlorite (Wu et al., 2019).

Despite its potential benefits, the organic matter in WWTP effluent acts as a precursor for disinfection by-product (DBP), which can pose health risks. The formation of DBPs, such as trihalomethanes (THMs), is influenced by treatment levels and concentrations of ammonia, dissolved organic nitrogen, and bromide or iodide (Richardson et al., 2007) in wastewater effluents.

METHODOLOGY

Disinfection processes were conducted using sodium hypochlorite, calcium hypochlorite, and an oxidizing solution produced by the Hidrogeron® GE-150 static chlorine generator. These disinfectants were applied to anaerobic effluent from Upflow Anaerobic Sludge Blanket (UASB) reactors at the Mangueira Wastewater Treatment Plant (WWTP) in Recife, Brazil.

Chlorination was performed at the breakpoint. The experiment was conducted with three contact times (CT): 10, 20, and 30 minutes, and the chlorine doses applied were 25 to 100 $mg \cdot L^{-1}$ as Cl_2. Key parameters, including temperature, pH, chemical oxygen demand (COD), and ammonia nitrogen, were monitored, according to APHA (2022). Residual chlorine was analyzed following the disinfection

process. Trihalomethane (THM) concentrations were measured using liquid-liquid extraction (Franco et al., 2018) and analyzed by gas chromatography coupled with mass spectrometry (GC-MS).

RESULTS AND CONCLUSIONS

The formation of trihalomethanes (THMs) was monitored during the wastewater chlorination using different disinfectants: sodium hypochlorite, calcium hypochlorite, and an electroactivated water (EAW). The THMs measured included trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM).

High levels of combined residual chlorine (CRC) were observed even after the breakpoint occurrence. This was observed at all doses, contact times, and for all three oxidants. This is related to the levels of ammoniacal nitrogen and COD in the effluent. The breakpoint curves for the contact times studied were similar. The occurrence of the breakpoint depended only on the concentration of chlorine applied. Due to the presence of organic nitrogen, among other compounds, which can alter the shape of the breakpoint curve, such a sharp valley at the breakpoint was not seen when calcium hypochlorite was used.

The final pH of the chlorinated sample increased compared to that of the raw sample. Sodium hypochlorite was the oxidant that most increased the pH value, making the effluent basic. High pH values, such as those obtained, can favor the formation of THM. Total solids did not differ significantly from the raw sample when sodium and calcium hypochlorites were used. However, the high chloride content caused by chlorination with EAW interfered with its quantification. TSS decreased after chlorination, which is consistent with the results obtained for turbidity since both are associated. The quantification of COD by the colorimetric method was strongly influenced by the presence of chloride ions in the samples, which caused a significant increase in the COD value in the experiments carried out with EAW.

Although the effluent studied contained many precursors for the formation of THMs, their amount in the chlorinated effluent may have been lower due to the selectivity of the reaction with ammonia and the slower rate of reaction with THM-forming compounds in the presence of combined chlorine. TCM was the most abundant compound for all oxidants, followed by BDCM, DBCM, and TBM. For sodium hypochlorite, TCM accounted for more than 60% of the THM_4 and, in some cases, up to 99%. For calcium hypochlorite and EAW, TCM accounted for more than 87% of all tests. TBM and DBCM accounted for less than 1% in almost all tests, except for a few tests with sodium hypochlorite, with less than 3%.

In the case of sodium hypochlorite, the maximum trichloromethane (TCM) concentration observed was 213 µg/L at a contact time of 20 minutes and a dosage of 85 mg/L. The formation of brominated trihalomethanes (THMs) remained below 25 µg/L throughout the process. Interestingly, the data revealed increased brominated THM formation after the breakpoint, while TCM concentrations remained relatively stable along the breakpoint curve. For calcium hypochlorite, a much higher peak of TCM was recorded, reaching 702 µg/L at a contact time of 10 minutes and a dosage of 62 mg/L. Brominated THMs were consistently below 20 µg/L. The results indicated that the highest THM formation occurred at the breakpoint. Beyond this point, the rate of THM increase was more gradual as the dosage increased. In the case of electroactivated water, two notable TCM peaks were detected: 643

µg/L at 10 minutes with a dosage of 70 mg/L and 640 µg/L at 20 minutes with a dosage of 100 mg/L. Brominated THM levels remained under 25 µg/L, similar to sodium hypochlorite. However, a higher formation of THMs was observed after the breakpoint, particularly at contact times of 10 and 20 minutes.

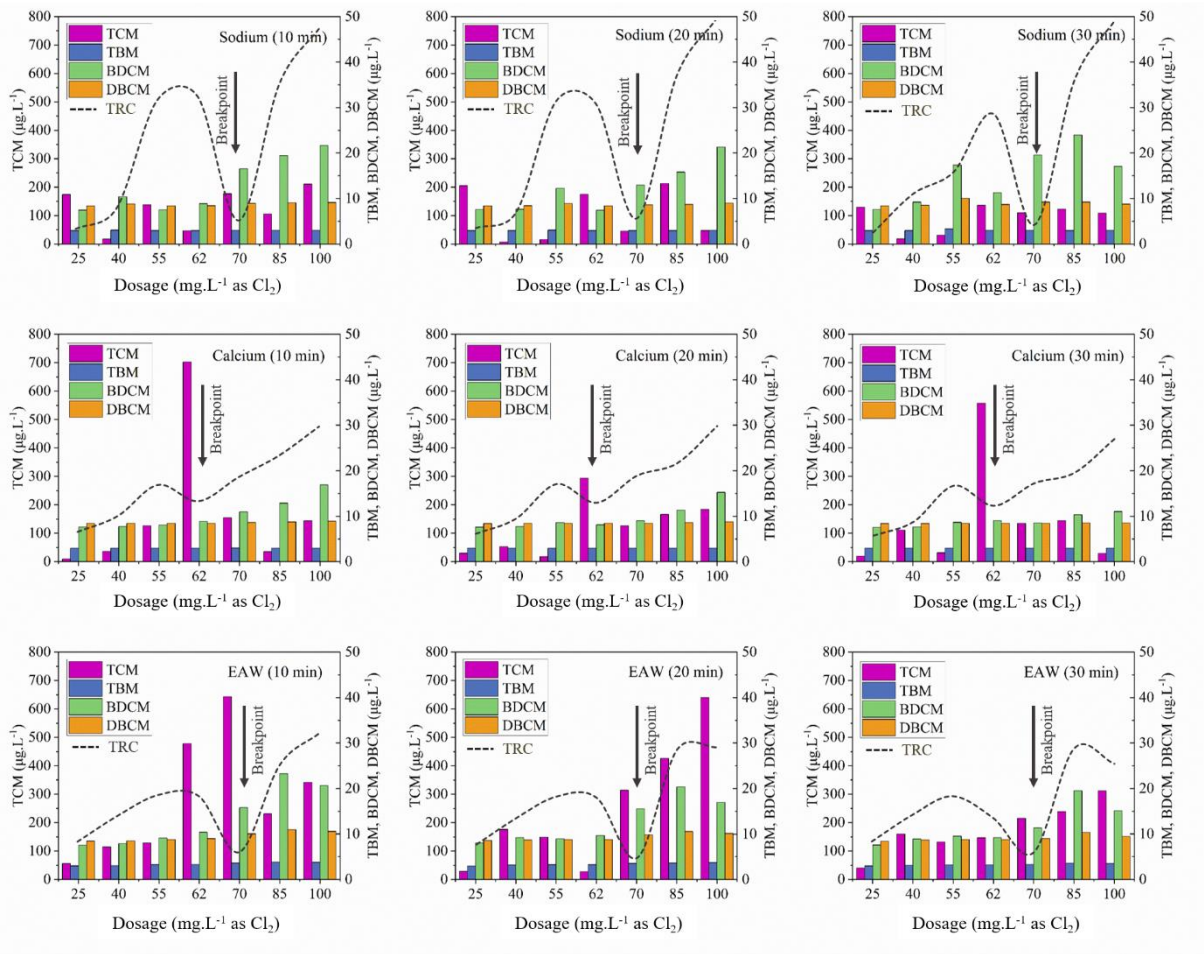

Figure 1 – Trihalomethane formation throughout the breakpoint chlorination curve.

Higher dosages and longer contact times were particularly associated with elevated THM formation, especially with electroactivated water producing the highest THM levels after reaching the breakpoint, compared to sodium and calcium hypochlorite treatments. These results suggest that, while EAW demonstrates promising disinfectant properties, its use after reaching the breakpoint may considerably elevate the risk of disinfection by-product formation, particularly trihalomethanes, compared to traditional chlorination methods.

Sodium hypochlorite was the oxidant that demonstrated the lowest levels of by-product formation. However, when comparing the results obtained for pathogen inactivation, satisfactory levels of disinfection were received before the breakpoint. Thus, disinfection with dosages before the breakpoint may be feasible for all oxidants studied since THM levels remained below the regulated levels and

efficiency in pathogen inactivation was achieved. EAW proved to be a competitive sanitizer with commercially available hypochlorites.

Future research should explore the chlorination process using electrolyzed water by varying the contact time and applying lower dosages. It should also evaluate the formation of other organochlorine compounds, such as halo acetic fatty acids, which are by-products of chlorine disinfection. Furthermore, a comparative economic analysis of replacing conventional chlorine with electrolyzed water in wastewater treatment plants should be applied.

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REFERENCES

APHA. (2022). *Standard Methods for the Examination of Water and Wastewater* (24º ed). American Public Health Association, American Water Works Association, and Water Environment Federation.

Franco, E. S., Pádua, V. L., Giani, A., Rodríguez, M., Silva, D. F., Ferreira, A. F. A., Júnior, I. C. S., Pereira, M. C., & Rodrigues, J. L. (2018). Validation of a robust LLE-GC-MS method for determination of trihalomethanes in environmental samples. *Environmental Monitoring and Assessment*, *190*(8), 473. https://doi.org/10.1007/s10661-018-6835-8

Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R., & DeMarini, D. M. (2007). Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutation Research/ Reviews in Mutation Research*, *636*(1–3), 178–242. https://doi.org/10.1016/j.mrrev.2007.09.001

Scialdone, O., Proietto, F., & Galia, A. (2021). Electrochemical production and use of chlorinated oxidants for the treatment of wastewater contaminated by organic pollutants and disinfection. *Current Opinion in Electrochemistry*, *27*, 100682. https://doi.org/10.1016/j.coelec.2020.100682

Sousa Filho, J. W., Lenza, G. A., Tonhela, M. A., Araújo, K. S., Fernandes, D. M., & Malpass, G. R. P. (2022). Full-scale application of an electrochemical disinfection solution in a municipal drinking water treatment plant. *Water and Environment Journal*, *36*(1), 86–95. https://doi.org/10.1111/wej.12763

Wu, C.-T., Chang, C.-Y., Li, Y.-Y., & Lin, P.-H. (2019). Feasibility study for the production of multi-oxidants from the desalination of seawater brine. *Water Quality Research Journal*, *54*(3), 242–248. https://doi.org/10.2166/wcc.2018.160