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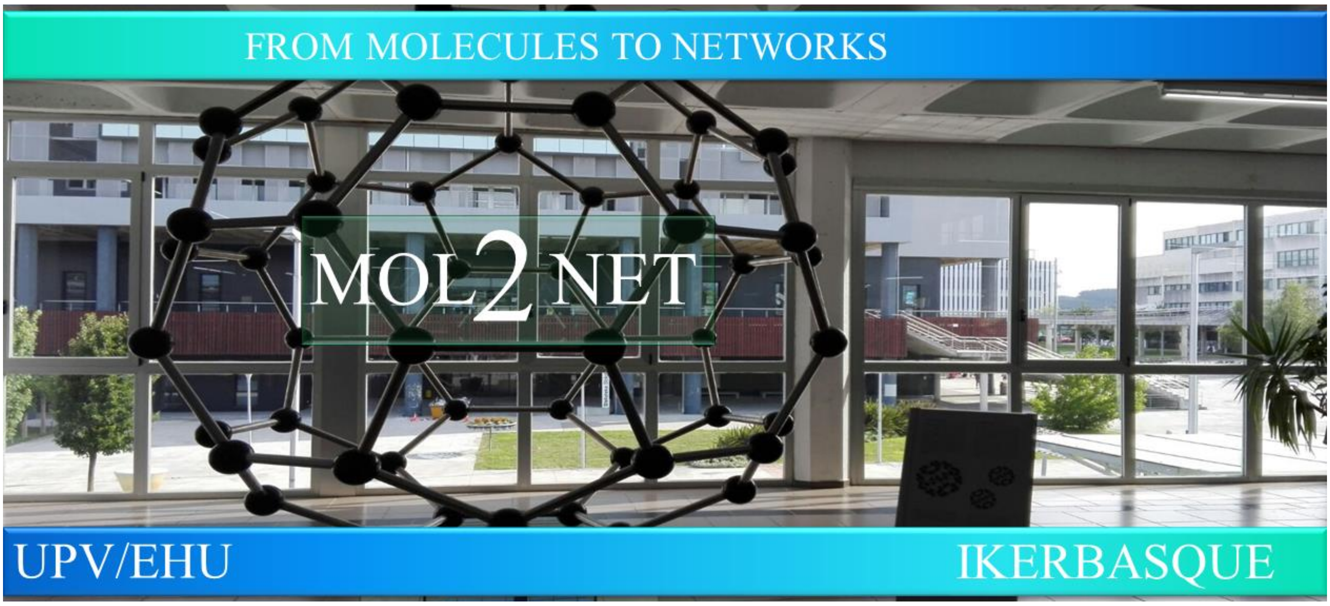

Public Health and Water Treatment: A Simulation Study on the Ozonation of Taste-and-Odor Compounds in Surface Water Resources in the Philippines

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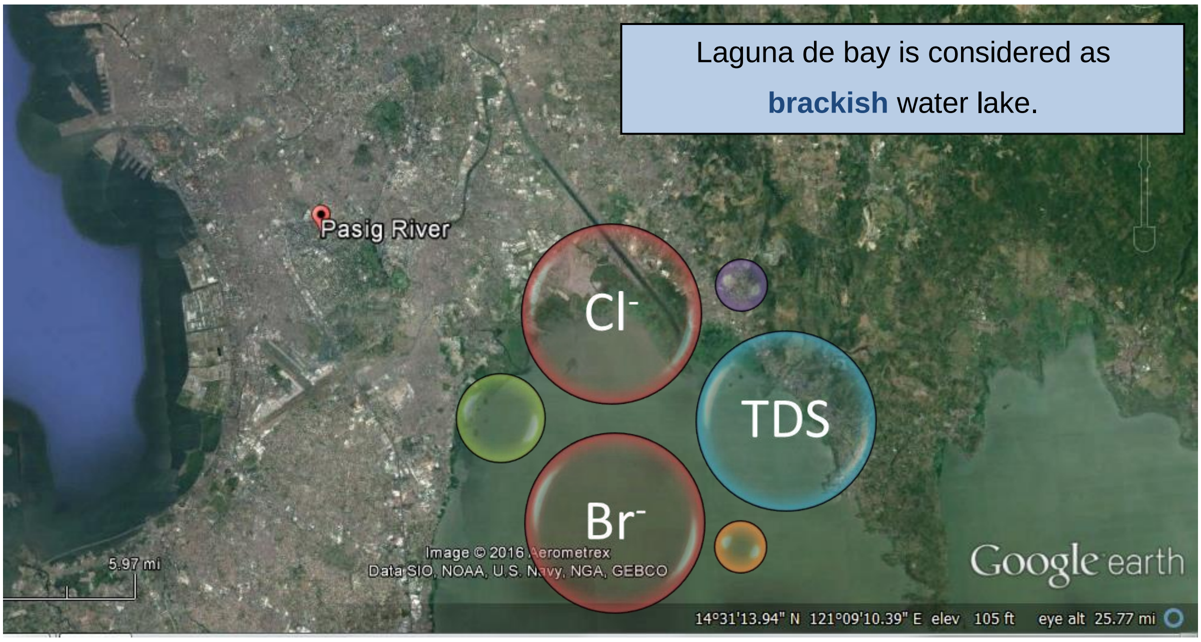
Abstract

The current raw water supply from Angat Dam is insufficient to address the demand in Metropolitan Manila, Philippines. One of the alternatives is the Laguna Lake, the largest freshwater lake in the country, and at the same time the world's largest septic tank last 2007. Currently, there are drinking water treatment facilities around the lake and soon-to-be constructed for future purposes. Different water quality problems have been reported such as taste and odor (T&O). Geosmin and 2-Methylisoborneol (2-MIB) are two of the most recognized T&O compounds from blue-green algae and can be treated through ozonation. However, presence of bromide is also expected since the lake is connected to seawater. This study used advanced chemical reaction kinetics using Polymath™ software to verify the extent of treating these contaminants without spending for actual ozonation. Results showed that 3 mg/L of ozone can treat 55 ng/L of each of T&O compounds for 20 minutes while 0.45 mg/L of bromate was also produced. Simulation studies like these are recommended for institutions that are in-search for scientific solutions but quite hesitant to spend high capital costs at

first. Simulations can also be used as guidance from conceptualization up to the actual operations of the facility.

Graphical Abstract



By: Dexter Cabalza - Reporter / @dexcabalzaINQ Philippine Daily Inquirer / 05:04 AM June 10, 2019

SMELLY PROBLEM Muntinlupa residents living near the Laguna de Bay have been complaining since last month about the foul odor coming from the lake. They likened the smell to the stench emanating from pig pens and decaying fish. —MUNTINLUPA PIO/DEPUTY ADMINISTRATOR RJ PATDU SMITH

Introduction

Since 2010, Laguna Lake has been using as an alternative drinking water source of the Metropolitan Manila, Philippines. The raw water coming from the second major freshwater lake in terms of volume in Southeast Asia is being treated by the country's largest membrane-based water treatment facility which is also the first of its kind to use large-scale ultrafiltration and reverse osmosis system [1]. However, due to rapid urbanization and industrialization, the water quality of the lake started to deteriorate. In the western bay of the lake, wastewater discharge and run-offs from industries pose some threats to the water body while the eastern portion serves as a catchment of agricultural land-uses [2]. Several water quality related problems have been reported recently including taste-and-odor [3, 4, 5, 6]. Two of the known compounds which contribute to the taste-and-odor problems in lakes worldwide are geosmin and 2-methylisoborneol (2-MIB) which are also commonly caused by algae [7]. However, only few process trains can treat these two compounds in the influent at the moment, such as adsorption and ozonation [8, 9].

On the other hand, Laguna Lake is also considered as a brackish water lake due to the backflows of saline water from Manila Bay through Pasig River. This happens during the events when the water level of the lake is less than that of Manila Bay. The typical chloride concentrations of the lake are approximately between 250 to 350 mg/L but can increase to 4,000 mg/L during intrusion of the saltwater [10]. In addition to chlorides, seawater can also contain bromides [11]. Although there are no reports of bromide concentrations in the Laguna Lake yet, considering it as one of the water quality parameters in designing a water treatment plant that would use the lake as raw water can be beneficial at the present and future operations. However, treating bromide-containing waters using ozone can also produce another problem in the form of bromate. Bromate is considered as one of the disinfection-by-products which threatens human's health[12]. In fact, it is categorized as carcinogenic by World Health Organization [13].

With the above scenarios, an institution such as a water utility company, might be hesitant to immediately use ozonation in treating a certain raw water that contains geosmin, 2-MIB, and bromides despite ozone's capability to efficiently eliminate the taste-and-odor compounds due to the carcinogen formation. Aside from high costs involved, practical limitations must also be considered in implementing plant-scale studies into a live and operating plant. Knatz et al. 2015 experienced some constraints in maintaining existing plant operations and the urgency to incorporate a new treatment process within the same hydraulic profile of the existing plant. While Amato et al. 2009 used computational fluid dynamics to further verify the performance of the modified tank design in an existing water treatment plant.

In actual plant operations, simulation studies can help engineers to test different process scenarios even before it happened. This is another way of proceeding with experiments especially if there are major risks to consider. For a wastewater treatment system, process modeling is considered as an important part of its design and operation [16]. Plant-scale studies usually start from laboratory scale and if the results are promising, bench-scale studies could commence eventually. However, both these methods demand resources such as time and costs. Conducting laboratory experiments are usually comprise of intensive procedures, such as sampling preparation, and might involve rigorous analysis. Moreover, there is also a need to invest on several laboratory apparatuses and equipment to proceed with water analysis, which also require highly skilled professionals to perform. Upscaling laboratory scale setups also poses some technical risks such as appropriate design methods to use. This is in addition to the fact that results may still differ from laboratory and bench scale experiments. In both methods, engineers and operators had spent significant time to come up with unknown outcomes.

On the contrary, numerical simulations offer simpler yet reliable way to proceed with process experiments without the need to absorb some major risks mentioned previously. The computer aided simulation of wastewater is identified as one of the effective tools to enhance the operation of their existing plants or to support the design of new facilities [17]. Computational studies may also require expertise for software use, but this still outweighs the higher costs and longer time spent in conducting laboratory and bench scales studies. Furthermore, the risk of delivering a non-complying treated water to the customers would almost be eliminated, if not its entirety, when the engineers will simulate the chemical reactions first using the computers. Given the above circumstances, this study aims to promote the use of computational process simulations from design conceptualization up to its treatment plant operations phase.

Materials and Methods

Bibliometric Analysis

Scopus database was utilized to see the current trends between published journal articles regarding certain keywords from this study. Scopus is a comprehensive, diverse, and trusted abstract & citation database where it provides access to high-quality data and content. It uses analytical tools to provide information based on categories such as year, country, and subject area [18].

Simulations

Polymath™ Software was used to calculate the differential equations involved in this study. Polymath™ is a numerical calculation package for solving different kinds of mathematical equations including ordinary differential equations [19].

Results and Discussion

Bibliometric Analysis

Different keywords were used to understand the recent scholarly trends about the topic of this study. Among these terminologies, the keywords “ozone, water, treatment” resulted with the highest number of Scopus published articles equal to 14, 778 as of November 27, 2023. China is the top country with 3,098 Scopus published documents while the Philippines has 8.

It can also be spotted from Table 1 that China and US are two common territories that conduct research on the five keywords considered, while Environmental Science is the top subject area in all keywords. The number of published research related to geosmin and 2-MIB are quite low compared to bromide and bromate, respectively. This might be due to the related health concerns on the production of bromate from treating bromide using ozone. Bromate is classified as B2 by US Environmental Protection Agency (US EPA) as probable human carcinogen [20]. While bromide ion is one of the precursors such that ozonation of bromide-containing waters would result to bromate formation [21].

On the other hand, it is noticeable from Table 1 that the Philippines currently has only eight Scopus published journals related to "ozone, water, treatment" keywords and none for the rest. One of the possible reasons of not having Scopus published articles related to geosmin, 2-MIB, bromide, and bromate is due to the limited capacity of local laboratories. It is a practice to preserve water samples based on standards and sending these to external laboratories abroad for analysis. The four chemical species involved require highly sophisticated analytical methods that also need technical expertise in using the advanced laboratory apparatus. However, this can also be an opportunity to local scientists to explore research topics related to these four chemical compounds through partnerships with international institutions. Besides, the increasing demand on potable water seems to be inevitable nowadays. Hence, it is also inevitable to treat raw water sources with geosmin, 2-MIB, and bromide soon.

Table 1. Summary of bibliometric analysis

Keywords used	Number of Scopus published articles	Top 5 countries	Top 3 subject areas	Number of Scopus published articles from rank 1 country	Number of Scopus published articles form the Philippines
ozone AND water AND treatment	14, 778	China, US, Japan, Germany, Spain	Environmental Science, Engineering, Chemistry	3,098	8
ozone AND geosmin	110	US, China, Japan, South Korea, Canada	Environmental Science, Engineering, Chemistry	31	0
ozone AND 2-methylisoborneol	104	China, US, Japan, South Korea, Canada	Environmental Science, Engineering, Chemistry	38	0
ozone AND bromate	712	US, China, Switzerland, France, Netherlands	Environmental Science, Chemistry, Engineering	213	0
ozone AND bromide	1,507	US, China, Germany, UK, Japan	Environmental Science, Chemistry, Agricultural and Biological Sciences	598	0

Chemical Reactions

The corresponding oxidation reactions of the chemical species involved were initially determined and setup. The reaction kinetics of ozone with the considered compounds in this study were assumed to be second order as von Gunten 2002 discussed in his paper. In his study, it was stated that the second-order form of the ozone reaction kinetics comes from both the first orders of ozone and the other involved compound.

The reaction rate constants considered in this paper came from various references as seen in Table 2. These constants are usually determined through series of experiments by measuring the concentrations of either the reactants or products involved in the chemical reaction. This study has taken five reactants, namely, ozone, geosmin, hydroxyl radical, 2-MIB, and bromide, while bromate is the sole product.

Table 2. Oxidation Reactions and Rate Constants

Reaction*	Rate Constant Value ($M^{-1}s^{-1}$)	Reference
$A + B \xrightarrow{k1} Products\ 1$	k1 = 8	[23]
$C + B \xrightarrow{k2} Products\ 2$	k2 = 2.5 x 10^9	[23]
$A + D \xrightarrow{k3} Products\ 3$	k3 = 6.5	[23]
$C + D \xrightarrow{k4} Products\ 4$	k4 = 3.5 x 10^9	[23]
$A + E \xrightarrow{k5} F$	k5 = 50	[22]

*A = ozone, B = geosmin, C = hydroxyl radical, D = 2-methylisoborneol, E = bromide, F = bromate

After setting-up the reactions involved and their respective rate constants, the appropriate mole balances, rate laws, and relative rates per chemical specie were combined into general rate equations as shown below. These expressions are in the form of ordinary differential equations which can be directly encoded and solved using Polymath™ Software.

General rate equations*:

$$\frac{dC_A}{d\tau} = -k_1 C_A C_B - k_3 C_A C_D - k_5 C_A C_E$$
$$\frac{dC_B}{d\tau} = -k_1 C_A C_B - k_2 C_B C_C$$
$$\frac{dC_C}{d\tau} = -k_2 C_B C_C - k_4 C_C C_D$$
$$\frac{dC_D}{d\tau} = -k_2 C_B C_C - k_4 C_C C_D$$
$$\frac{dC_E}{d\tau} = -k_5 C_A C_E$$
$$\frac{dC_F}{d\tau} = k_5 C_A C_E$$

Treatment Simulation

Concentrations and Operating Parameters

Prior to the simulation using Polymath™ Software, several variables must be considered. Table 3 shows the assumed initial concentrations of different chemical species present in the untreated water. The initial amount of bromate in the raw water is assumed to be 0 mg/L since it is a product of ozone and bromide reaction. The potable water standard value of 10 ng/L is used for the target final concentrations for geosmin and 2-MIB concentrations. This value is the odor threshold used by Australian Drinking Water Guidelines [24]. Currently, the local drinking water standards in the Philippines do not regulate these two taste-and-odor compounds. On the other hand, the 0.01 mg/L bromate concentration was adopted from the Philippine National Standards for Drinking Water [25].

Table 3. Concentrations of concerned species

Specie	Initial Concentrations	Target Final Concentrations
Geosmin	55 ng/L	10 ng/L
2-MIB	55 ng/L	10 ng/L
Bromide	0.33 mg/L	-
Bromate	0 mg/L	0.01 mg/L

In addition to the species concentrations, values of the necessary operating parameters were also attained from reputable design references for ozonation. Table 4 summarizes the typical design parameters from Kawamura 2000 with the rationales behind of the chosen values. Since ozone is unstable and reacts very fast once injected in the water, minimizing its concentration is one of the safety measures that an engineer can apply as early as its conceptual stage.

Table 4. Operating Parameters

Parameter	Value	Remarks
Ozone Dosage	3 mg/L	Safety considerations
Detention Time	20 minutes	Maximum design value

Polymath™ Software Simulation Results

After conducting the process simulation of ozonation using the software, it was found out that geosmin and 2-MIB were successfully treated as shown in Table 5. However, as expected bromate was formed with an amount of 0.45 mg/L. Figure 1 shows the consumption of bromide ions and the formation of bromate as oxidation takes place. It is recommended to conduct another study to determine at what level these two taste-and-odor compounds could be eliminated without compromising bromate formation.

Table 5. Concentrations of concerned species

Specie	Initial Concentrations	Target Final Concentrations	Simulated Final Concentrations
Geosmin	55 ng/L	10 ng/L	0 ng/L
2-MIB	55 ng/L	10 ng/L	0 ng/L
Bromide	0.33 mg/L	-	0 mg/L
Bromate	0 mg/L	0.01 mg/L	0.45 mg/L

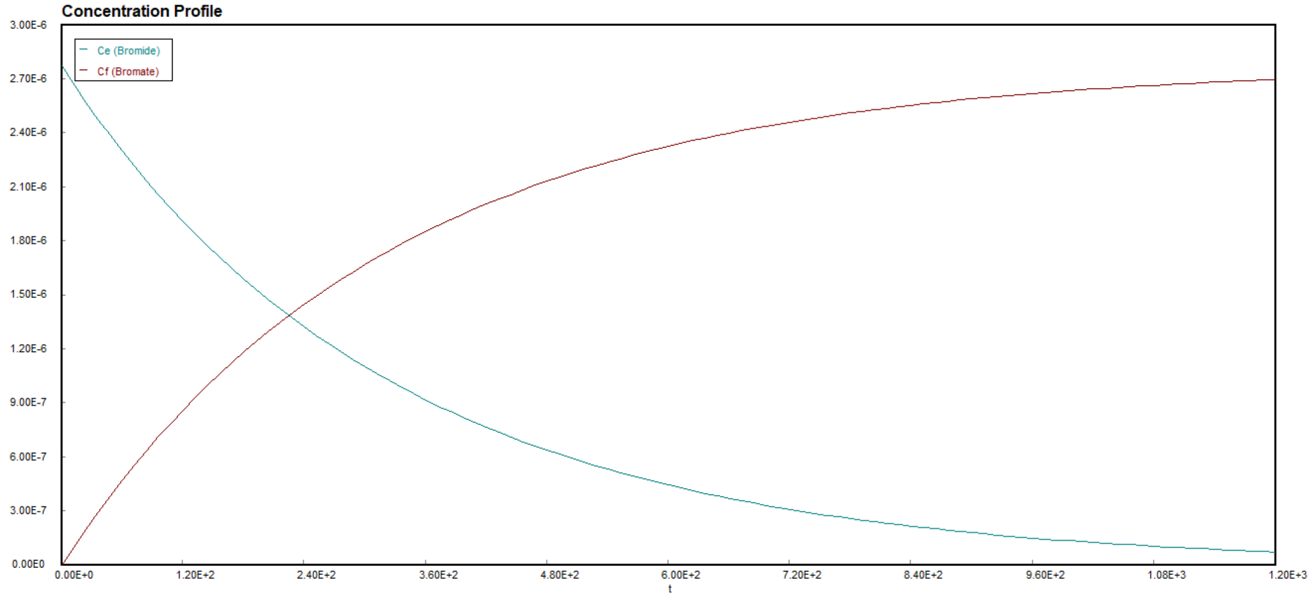


Figure 1. Concentration profiles of bromide and bromate during ozonation

Application of the study

After the chemical kinetics simulation, bromate was formed and the concentration is above the limit set by the local water drinking standards. With the assumption that there are no other viable options to avoid treating a particular raw water source which contains significant amounts of geosmin, 2-MIB, and bromide, the concerned water utility can still plan by utilizing the simulation outcomes as basis and guidance of future mitigating actions. Below are some considerations that the water utility company can adopt:

1. The design engineer may opt to lower the concentrations of geosmin and 2-MIB prior to ozonation through other treatment processes such as adsorption.
2. The planners can conceptualize how to control the algal proliferation as producers of the two taste-and-odor compounds.
3. Consider another downstream process immediately right after ozonation that can remove the bromate formed.
4. Have a dedicated process that could reduce the concentration of bromate prior to network distribution.

Updated designs with the above recommendations are also possible to investigate using computational simulations and can be conducted up to the operating stage of the facility. Hence, if time and costs are at the utmost concerns, process simulations can provide an overview of the possible solutions.

Conclusions

This paper has shown that 0.45mg/L of bromate was produced when 0.33 mg/L of bromides in the water is eradicated by 3 mg/L of ozone for 20 minutes, while simulation results for taste-and-odor treatment was found desirable as ozone completely remove geosmin and 2-MIB in the raw water. Due to practical limitations of conducting experiments in an existing plant, process simulation studies can be initially accomplished at minimal costs and shorter period compared with the conventional laboratory-to-upscale experiments. In the end, laboratory and simulation methods can really work together, and yet actual plant-scale outcomes may still deviate. But taking immediate actions upon considering the results from simulation studies could really make a significant difference in solving process-related upsets, not just in the design stage but also during its operation, on a minimal expense.

References

[1] Maynilad Water Services (2023). Maynilad. Retrieved from Maynilad: https://www.mayniladwater.com.ph/our-company/facilities/

[2] Varca, L. M. (2012). Pesticide residues in surface waters of Pagsanjan-Lumban catchment of Laguna de Bay, Philippines. Agricultural Water Management, 35-41.

[3] Context.Ph. (2023, May 4). Laguna Lake fish catch smell as El Nino bites. Retrieved from Context.ph: https://context.ph/2023/05/04/laguna-lake-fish-catch-smell-as-el-nino-bites/

[4] Lopes, J. (2019, June). Muntinlupa Health Office explains Laguna Lake algal bloom. Retrieved from Metro News Central: https://metronewscentral.net/muntinlupa/metro-cities/muntinlupa-health-office-explains-laguna-lake-algal-bloom

[5] Hicap, J. (2022, June 14). Muntinlupa LGU, LLDA to address algal bloom problem in Laguna Lake. Retrieved from Manila Bulletin: https://mb.com.ph/2022/06/13/muntinlupa-lgu-llda-to-address-algal-bloom-problem-in-laguna-lake

[6] Cabalza, D. (2019, June 10). Algae in Laguna de Bay not harmful despite smell. Retrieved from Inquirer.Net: https://newsinfo.inquirer.net/1128336/algae-in-laguna-de-bay-not-harmful-despite-smell

[7] Zhang, R., Qi, F., Liu, C., Zhang, Y., Wang, Y., Song, Z., … Sun, D. (2019). Cyanobacteria derived taste and odor characteristics in various lakes in China: Songhua Lake, Chaohu Lake and Taihu Lake. Ecotoxicology and Environmental Safety, 181, 499–507. https://doi.org/10.1016/j.ecoenv.2019.06.046

[8] Nie, S., Wang, Q., Liao, Y., Zhang, J., Yang, F., Wang, S., … Yu, J. (2023). Algal organic matter impact on 2-methylisopropanol and geosmin adsorption by activated carbon: Variation with algae growth and decay, prediction by fluorescence surrogates. Separation and Purification Technology, 320, 124206-. https://doi.org/10.1016/j.seppur.2023.124206

[9] Yuan, B., Xu, D., Li, F., & Fu, M.-L. (2013). Removal efficiency and possible pathway of odor compounds (2-methylisoborneol and geosmin) by ozonation. Separation and Purification Technology, 117, 53–58. https://doi.org/10.1016/j.seppur.2013.04.029

[10] Santos-Borja, A., & Nepomuceno, D. N. (2006). Laguna de Bay: Institutional development and change for lake basin management. Lakes & Reservoirs : Research and Management, 11(4), 257–269. https://doi.org/10.1111/j.1440-1770.2006.00310.x

[11] Chen, Y., & Compton, R. G. (2023). A bespoke reagent-free amperometric bromide sensor for seawater. Talanta (Oxford), 253, 124019-. https://doi.org/10.1016/j.talanta.2022.124019

[12] Dorji, P., Choi, J., Kim, D. I., Phuntsho, S., Hong, S., & Shon, H. K. (2018). Membrane capacitive deionisation as an alternative to the 2nd pass for seawater reverse osmosis desalination plant for bromide removal. Desalination, 433, 113–119. https://doi.org/10.1016/j.desal.2018.01.020

[13] Guidelines for drinking-water quality: fourth edition incorporating the first addendum. Geneva: World Health Organization; 2017. Licence: CC BY-NC-SA 3.0 IGO.

[14] Knatz, C., Rafferty, S., & Delescinskis, A. (2015). Optimization of water treatment plant flow distribution with CFD modeling of an influent channel. Water Quality Research Journal of Canada, 50(1), 72–82. https://doi.org/10.2166/wqrjc.2014.024

[15] Amato, T., & Wicks, J. (2009). The practical application of computational fluid dynamics to dissolved air flotation, water treatment plant operation, design and development. Journal of Water Supply : Research and Technology - AQUA, 58(1), 65-. https://doi.org/10.2166/aqua.2009.003

[16] Wu, X., Yang, Y., Wu, G., Mao, J., & Zhou, T. (2016). Simulation and optimization of a coking wastewater biological treatment process by activated sludge models (ASM). Journal of Environmental Management, 165, 235–242. https://doi.org/10.1016/j.jenvman.2015.09.041

[17] Köhne, M., Shuhen, M., & Schönberger, D. (1999). Modelling and Simulation of Purification Processes in Wastewater Treatment Plants Using the Modular Toolbox KSIM. Mathematical and Computer Modelling of Dynamical Systems, 5(4), 285–297. https://doi.org/10.1076/mcmd.5.4.285.3676

[18] VOSviewer. (2023). Retrieved from VOSviewer: https://www.vosviewer.com/

[19] Polymath Software. (2008). Retrieved from Polymath Software: https://websites.umich.edu/~elements/5e/software/polymath-legal.html

[20] Bromate. (2017). Retrieved from United States Environmental Protection Agency: https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance_nmbr=1002

[21] Lim, S., Shi, J. L., von Gunten, U., & McCurry, D. L. (2022). Ozonation of organic compounds in water and wastewater: A critical review. Water Research (Oxford), 213, 118053-. https://doi.org/10.1016/j.watres.2022.118053

[22] von Gunten, U. (2003). Ozonation of drinking water: Part I. Oxidation kinetics and product formation. Water Research, 37(7), 1443–1467. https://doi.org/10.1016/S0043-1354(02)00457-8

[23] Westerhoff, P., Nalinakumari, B., & Pei, P. (2006). Kinetics of MIB and Geosmin Oxidation during Ozonation. Ozone: Science & Engineering, 28(5), 277–286. https://doi.org/10.1080/01919510600892836

[24] NHMRC, NRMMC (2011) Australian Drinking Water Guidelines Paper 6 National Water Quality Management Strategy. National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia, Canberra.

[25] Philippine National Standards for Drinking Water of 2017 (PNSDW) (2017, June 23). Department of Health (DOH). Republic of the Philippines.

[26] Kawamura, S. (2000). Integrated Design and Operation of Water Treatment Facilities. New York: John Wiley & Sons.