REMOVAL FROM WASTEWATER OF BENZETHONIUM CHLORIDE (BZT) BY PHOTOCATALYSIS

Alexandru VISAN[1], Leon COVALIU[1], Cristina Ileana COVALIU-MIERLĂ[1]*

Benzethonium Chloride (BZT) is still an important pollutant even though was banned from household disinfectants market in EU. It is still largely used outside developed countries in hospitals and beauty industry. There are few studies regarding the impact of BZT in nature and even less studies that propose a method for water treatment. The article is focused on researching the effect of TiO_2 nanoparticle in the process of photocatalysis considering a simple and efficient configuration of the photocatalytic reactor. The results set a new point from where it can be developed new wastewater reactors with real life applications.

Keywords: Benzethonium chloride, photocatalysis, wastewater

1. Introduction

Quaternary ammonium compounds (QACs) are extensively employed as surfactants and biocides. Quaternary Ammonium Compounds (QACs) possess the capacity to reach into the environment through several means, including home, agricultural, and industrial utilization. Consequently, comprehending the dispersion and origins of these substances within aquatic systems holds significant importance. Quaternary ammonium compounds (QACs) were detected in both sediments and wastewater, whereas molecules possessing a side-chain consisting of twelve or more carbon atoms exhibited higher occurrence rates in both matrices. The environmental predominance of quaternary ammonium compounds (QACs) is influenced by wastewater treatment techniques and utilization rates, as indicated by data obtained from several wastewater treatment plants employing different unit operations, as well as from sediment cores [1].

The Benzethonium chloride Group (BZT) is still under-researched in the field of environmental protection despite the large usage, with only incipient and casuistically limited studies to establish the impact on the environment. The most important studies are those of Sarah G. Pati and Adams [1] and Elsa López Loveira [14] who managed to measure and propose a reliable explanation for creating a basis for knowing the environmental impact of BZT.

The increase in the concentrations of quaternary ammonium compounds in municipal and industrial wastewaters is due to the increasing in the need for surface disinfectants, both in the case of the food industry and in the case of the sanitary field, especially in a pandemic period in which they have occupied an important

[1] National University of Science and Technology POLITEHNICA Bucharest, Romania,
* Contact author's e-mail: cristina_covaliu@yahoo.com

place [2]. Benzalkonium chloride (BAC) finds application in diverse settings including private dwellings, industrial facilities, and healthcare establishments, where it serves as an antiseptic and disinfectant. It may be part of an extended range of products, including medications and personal care items. [3]. Such an increase can lead to concentrations that cannot be eliminated from the wastewater by classical treatment methods [4]. In case of the classical methods concentration of BACs in the systems are dangerously close to the limit level that they can handle without affecting the entire purge cycle. For example, membrane filtration is becoming inefficient at a concentration greater than 2 mg/L of such quaternary ammonium salts. Given that this concentration is one that can be easily exceeded in some situations it is clear that a specific alternative method for the treatment of these pollutants is required [1, 5].

The initial product containing BACs was officially registered with the United States Environmental Protection Agency (EPA) in the year 1947. Subsequently, the utilization of this substance has experienced a significant surge. [3]. Quaternary ammonium compounds (QACs), which include benzalkonium chloride (BAC), have biocidal properties against yeast, bacteria, and fungi. Although QACs do not possess biocidal properties against bacterial spores, they do exhibit the ability to hinder spore germination, particularly in the case of mycobacteria [6-8]. Quaternary ammonium compounds (QACs) have been found to have virucidal properties against viruses that possess lipid membranes, this is attributed to the ability of the alkyl chain to destroy the integrity of it. Moreover, disinfectants containing quaternary ammonium compounds (QACs) are frequently employed for disturbing biofilms [9]. The most frequently detected benzylalkyldimethyl ammonium compounds (BACs) (C12–C18) (Table 1) have in the molecular configuration a minimum of one hydrophobic hydrocarbon chain that is connected to a nitrogen atom carrying a positive charge. This particular configuration grants them the ability to easily adhere to sewage sludge, soil, and sediments, which mostly possess a negative charge [10].

Table 1:

Types of BACs

	Name	**Molecular structures**
BAC C12	Dodecylbenzyldimethylammonium chloride	$CH_3(CH_2)_{11}N(Cl)(CH_3)_2CH_2C_6H_5$
BAC C14	Tetradecylbenzyldimethylammonium chloride	$CH_3(CH_2)_{13}N(Cl)(CH_3)_2CH_2C_6H_5$
BAC C16	Hexadecylbenzyldimethylammonium chloride	$CH_3(CH_2)_{15}N(Cl)(CH_3)_2CH_2C_6H_5$
BAC C18	Octadecylbenzyldimethylammonium chloride	$CH_3(CH_2)_{17}N(Cl)(CH_3)_2CH_2C_6H_5$

1.1. Photolysis of benzothonium chloride in nature and avantages of TiO_2 nanomaterial

The effects of BZT release in nature and half-life of the substance have been studied in rivers and laboratory condition [10, 11]. This parameters of the research were used to further define a starting point in the present research.

The studied research was done both in natural light conditions and under UV-C light spectrum effects in order to fully understand the photolysis degradation process [11], photolysis in the case of those types of QACs has promising results.

Another variable introduced in research is the use of a photooxidant source. Such an advanced photocatalytic degradation process presents advantages in case SMX and LEVO QACs on the other hand, in case of CAR and ATR, the indirect photodegradation have a minimal impact in results [11]. In the experiments, for a series of samples, hydrogen peroxide was used as an OH sensitizer, of course, the presence of hydroxyl improves the results, but only in limited cases.

The results obtained in the case of BZTs for the half-life period are ~28 days, during which it can cause environmental damage on the one hand, and on the other hand, to develop a commercial solution based on photodegradation, the time and yield of the process must be enhanced.

The photocatalytic process using nano scaled TiO_2 catalyst has a major advantage of its nanoscale dimensions related to the effect of quantum size, which improves energy band space and reduces particle size [13].

1.2. Photocatalyst in BZTs removal from wastewater – previously research

As Elsa López Loveira [14] concludes in their research from 2011; the findings suggest that BZT can undergo photocatalytic degradation when exposed to high-pressure treatment (HP) within an acceptable period of irradiation. However, it is worth noting that the degree of mineralization is relatively lower, indicating the production of compounds that are more resistant to degradation. The efficacy of the method can be enhanced by subjecting the samples to a treatment that is integrated with a biological system. In order to achieve this objective, many arrangements of interconnected photocatalytic-biological reactors can be employed, with the specific configuration being determined primarily by the concentration of biologically treated wastewater (BZT) and the overall organic load [14].

The treatment setup exhibits certain advantages for BZT concentrations of up to 100 mg/L. Within the biological reactor, the degradation of 50% benzalkonium chloride (BZT) occurs, resulting in a significant reduction in the chemical oxygen demand of the effluent. The subsequent use of photochemical treatment results in the complete elimination of benzalkonium chloride (BZT) without compromising its effectiveness, as it selectively oxidizes other easily degradable chemicals that are also present in the compound [14].

When BZT concentrations fall below 100 mg/L, the effectiveness of HP pretreatment is compromised due to the elevated toxicity of the photodegradation byproducts on the biofilm, surpassing that of pure BZT [14].

When higher concentrations of benzalkonium chloride (BZT) at 180 mg/L are present in water, the bacterial biofilm cannot be maintained over time. Consequently, it becomes necessary to conduct a preliminary high-pressure treatment to decrease the BZT concentration [14].

Previously researches of photocatalysis effect on surfactants, included BZTs group, were conducted by Hisao Hidaka et al. in 1992, their findings include sodium dodecylbenzenesulfonate (DBS), benzyldodecyldimethylammonium chloride (BDDAC), sodium benzenesulfonate (BS), benzyltrimethylammonium chloride (BTAC), sodium dodecyl sulfate (DS) and hexadecyltrimethylammonium bromide (HTAB). In conclusion they conclude that the degradation of anionic DBS and cationic BDDAC surfactants, together with their reference compounds BS, DS, BTAC, and HTAB, was investigated in a TiO_2 dispersion under irradiation. The rates of photodegradation in the early phases are modeled using the Langmuir-Hinshelwood equation. The decomposition rate of the DBS surfactant is comparatively slower as compared to the BS surfactant, which lacks a lengthy alkyl chain. The aromatic component inside the DBS structure undergoes photodegradation at a faster rate compared to the alkyl chain. The cationic DBBAC system demonstrates a similar tendency [15].

The degradation rate of the anionic surfactant DBS is higher compared to that of the cationic surfactant BDDAC. The results of the electron spin resonance (ESR) analysis suggest the presence of hydroxyl (OH) radicals in the irradiated titanium dioxide (TiO_2) increase dispersions. The surfactant undergoes degradation when it is exposed to hydroxyl radicals ('OH) and/or hydroperoxyl radicals ('OOH), resulting in the production of carbon dioxide (CO_2) gas. This degradation process involves the formation of oxidized species such as peroxides, aldehydes, and carboxylates [15].

2. Experimental part

2.1. Materials and methods

M. W. Lam et al. shows us the mechanism by which BZT absorbs light waves from the UV-C spectrum [11], which is why it was chosen a Philips brand 30W UV-C lamp for photocatalysis. At the same time, this lamp that emits in the UV-C spectrum was chosen also due to the fact that TiO_2 was used for photocatalysis, a catalyst that is activated only in UV light.

By using TiO_2 for photocatalysis, we aim to reduce the usage of hydrogen peroxide or other OH sensitizer in the process of water depollution. The results are measured using the UV-VIS photometer SPECORD PLUS 200 Series, in UV

spectrum at wavelength of 273 nm, measured both at the end of exposure and at 12 h after.

The TiO_2 catalyst nanoparticles powder was deposited on a polycarbonate plate by spraying which was submerged under pure BZT solution. The UV-C lamp was placed above the wastewater at a distance of 50 mm, also, the wastewater depth was set to maximum 25 mm. In this configuration the UV light have to travel between 2 mediums; air and wastewater for a total distance of 75 mm in order to reach the TiO_2 particles as we can see in Fig. 1. Moreover, the configuration has economic advantages, since a low electrical power consumption lamp was used and no need of a quartz shield for submersion.

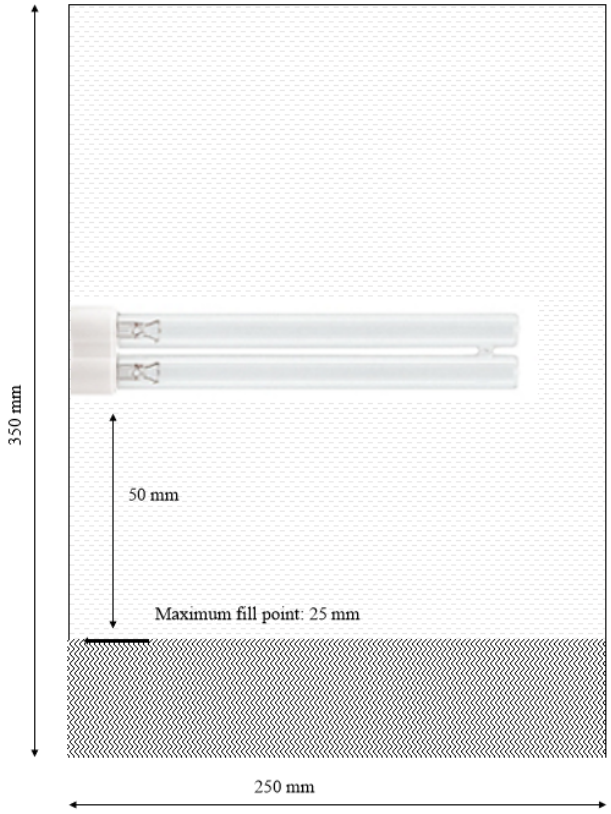

Fig. 1: System configuration used in experiments.

3. Results and discussion

For the calculation of the yield, we used the following formula where the light absorbance was measured using UV-VIS spectrophotometer. The absorbance was measured on an *in-situ* calibration curve, calculated with an accuracy of $R^2 >$ 99.98% for all 6 variables (in situ standard concentrations solutions).

$$\eta = \frac{\Delta absorbance}{i\ absorbance} \times 100$$

In the experiments were used six concentrations, starting from 12.5 mg/L to 75 mg/L. Concentrations were chosen considering the limits of the UV measurement method, the method by which concentrations lower than 5 mg/L are difficult to measure, the absorption of light being very low at similar concentrations. On the other hand, according to specialized studies, normal concentrations in nature are found between 0.06 mg/L and 5 mg/L, and a possible increase in concentrations *in situ* can lead to inhibition of microorganisms or to decreased yield by membrane filtration from classical wastewater treatment plants. Moreover, for low concentrations, the current technology used in wastewater treatment plants can be considered sufficient to maintain a balance between cost and efficiency.

Analyzing the results from Fig. 2 and Fig. 3 we note that by using the above method, we can identify a rate of increase in yield in constant time for all six concentrations.

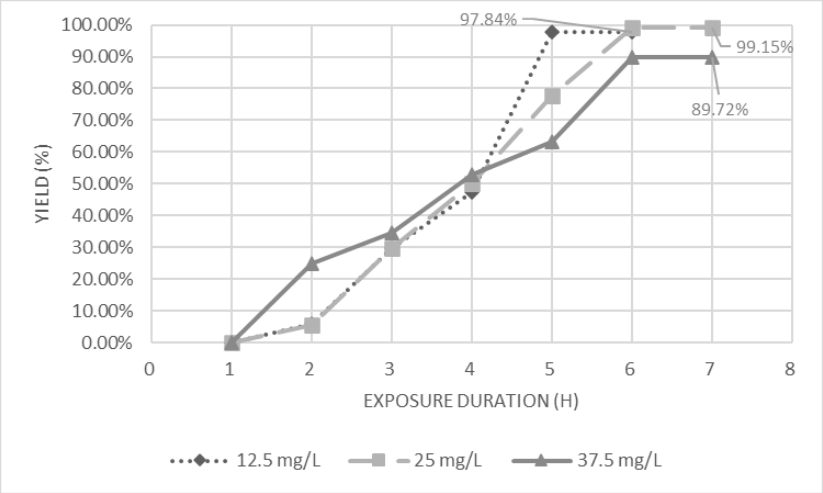

Fig. 1: The yield of photocatalysis using TiO_2 of BZT removal from wastewater - concentration 12.5 mg/L, 25 mg/L and 32.5 mg/L.

The results were obtained in a much shorter time than the natural conditions, managing to obtain yields of over 80% in a period of time between 8 and 13 hours of exposure, depending on the initial concentration tested. In Fig. 2, the yield obtained in case of concentrations 12.5 mg/L and 25 mg/L are similar, around 98%-99%, but the time needed to be obtained the yield was 1 hour shorter for 12.5 mg/L.

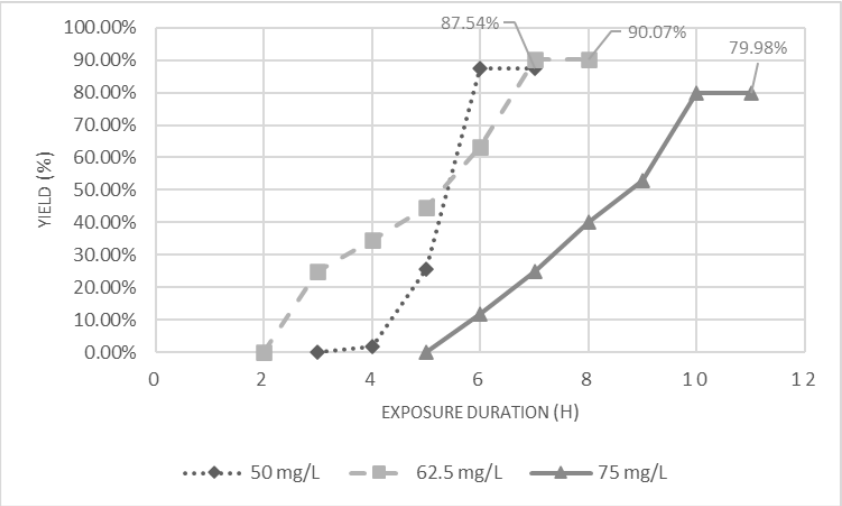

Fig. 2: The yield of photocatalysis using TiO_2 of BZT removal from wastewater- concentration 50 mg/L, 62.5 mg/L and 75 mg/L.

Comparing the two concentrations results with 37.5 mg/L concentration show that is a direct relation between the efficiency of the reactor and the concentration of BZTs in wastewater. Moreover, the trend is also followed in the case of the other concentrations in Fig. 3. In Fig. 3, in the case of 75 mg/L concentration the yield was obtained in 10 hours, moreover, the process of degradation has results only after a continuum exposure of 5 hours. For 50 mg/L and 62.5 mg/L the yield obtained was around 90% in 6 hours for 50mg/L and 7 hours for 62.5 mg/L.

4. Conclusions

Using the TiO_2 catalyst and described photocatalytic reactor configuration we achieved close to maximum yields, in a time up to 92% less than the natural half-life. Consequently, we expect increased results regarding time exposures by introducing new economical functions in our system configuration such as aeration and agitation of solution during exposure or changing the pH. From the research presented above, as well as from the preliminary tests that were conducted in the laboratory, will expect a reduction in exposure time below four hours, in the case of lower concentrations.

R E F E R E N C E S

[1] S. G. Pati and W. A. Arnold, "Comprehensive screening of quaternary," The Royal Society of Chemistry 2020, pp. 430-441, 2020.

[2] C. Zhang, F. Cui, G.-m. Zeng, M. Jiang, Z.-z. Yang, Z.-g. Yu, M.-y. Zhu and L.-q. Shen, "Quaternary ammonium compounds (QACs): A review on occurrence, fate and toxicity in the environment," Science of the Total Environment, Vols. 518-519, pp. 352-362, 2015.

[3] T. I. Merchel Piovesan Pereira B, "Benzalkonium Chlorides: Uses, Regulatory Status, and Microbial Resistance.," Appl Environ Microbiol., 2019.

[4] Y. Cui, J. Gao, M. Zhao, Y. Guo, Y. Zhao and Z. Wang, "Deciphering the interaction impacts between antiseptic benzethonium chloride and biofilm nitrification system: Performance, resistance mechanisms and biodegradation," Water Research, vol. 240, 2023.

[5] C. Zhang, U. Tezel, K. Li, D. Liu, R. Ren, J. Du and Spyros G. Pavlostathis, "Evaluation and modeling of benzalkonium chloride inhibition and biodegradation in activated sludge,," Water Research,, vol. 45, pp. 1238-1246, 2011.

[6] S. E. Longo, F. Brigadeci, A. Segimiro, S. Voyron, M. Cardinali, M. Girlanda and R. Piervittori, "Biocide efficacy and consolidant effect on the mycoflora of historical stuccos in indoor environment.," Journal of Cultural Heritage,, vol. 34, pp. 33-42, 2018.

[7] T. Sandle, R. Vijayakumar, S. A. Aboody, M. and S. Saravanakumar, "In vitro fungicidal activity of biocides against pharmaceutical environmental fungal isolates.," Journal of Applied Microbiology, vol. 117(5), p. 1267–1273, 2018.

[8] M. Tretiach, S. Bertuzzi and O. Salvadori, "Chlorophyll A fluorescence as a practical tool for checking the effects of biocide treatments on endolithic lichens," International Biodeterioration & Biodegradation, vol. 64(6), p. 452–460.

[9] E. Tuladhar, M. C. de Koning, I. Fundeanu, B. R. and E. Duizer, "Different virucidal activities of hyperbranched quaternary ammonium coatings on poliovirus and influenza virus.," Applied and Environmental Microbiology, vol. 78(7), p. 2456–2458, 2012.

[10] H. Olivia, W. Barber and E. M., "Benzalkonium chloride: A systematic review of its environmental entry through wastewater treatment, potential impact, and mitigation strategies," vol. 52:15, 2022.

[11] M. W. Lam and S. A. Mabury, "Photodegradation of the pharmaceuticals atorvastatin, carbamazepine, levofloxacin, and sulfamethoxazole in natural waters," Aquat. Sci., vol. 67, p. 177–188, 2005.

[12] C. B. Anucha, I. Altin, E. Bacaksiz and Vassilis N. Stathopoulos, "Titanium dioxide (TiO_2)-based photocatalyst materials activity enhancement for contaminants of emerging concern (CECs) degradation: In the light of modification strategies,," vol. 10, 2022.

[13] F. Irfan, M. Tanveer and M. Moiz, "TiO2 as an effective photocatalyst mechanisms, applications, and dopants: a review.," vol. 95, 2022.

[14] E. L. Loveira, P. S. Fiol, A. Senn, G. Curutchet and R. Candal, "TiO2-photocatalytic treatment coupled with biological systems," vol. 91, 2012.

[15] H. Hidaka, J. Zhao, E. Peiizzetti and N. Serpone, "Photodegradation of Surfactants. 8. Comparison of Photocatalytic Processes between," vol. 96, 1992.

[16] J. Yang, U. Tezel, K. Li and S. G. Pavlostathis, "Prolonged exposure of mixed aerobic cultures to low temperature and benzalkonium chloride affect the rate and extent of nitrification," Bioresour. Technol., vol. 179, p. 193–201, 2015.

[17] D. Dulin and T. Mill, "Development and evaluation of sunlight actinometers," Environ. Sci. Technol, vol. 16, p. 815– 820, 1982.

[18] H. Hidaka, S. Yamada, S. Suenaga, J. Zhao, N. Serpone and Ezio Pelizzetti, "Photodegradation of surfactants: Part vi complete photocatalytic degradation of anionic, cationic and nonionic surfactants in aqueous semiconductor dispersions," Journal of Molecular Catalysis, Vols. Volume 59, Issue 3,, pp. 279-290, 1990.