Evaluation of different methods supporting swimming pool water disinfection in the aspect of removing organic micropollutants

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Abstract. As a result of the intensive development of analytical techniques that allow to reduce the detection limits of tested compounds, the latest scientific research alerts the growing number of organic micro-pollutants identified in the swimming pool water environment. These compounds can both react with the disinfectant, causing the formation of highly toxic disinfection by-products or constitute a serious health risk to swimmers due to their biological activity. The aim of the research presented in this paper is to evaluate the modern methods supporting disinfection used in swimming pool systems, in the aspect of removing compounds from the group of organic microorganisms. The total content of organic matter in systems using UV radiation and ozonation was compared. The identification of organic micropollutants was also carried out. The presence of two phthalates in the tested pools has been documented. It has been shown that their concentration depends on the disinfection method used. Photocatalytic degradation of phthalates in the pool water system allowed to obtain over 35% removal rate, while the efficiency of ozonation in the most favourable case was just over 16%.

1 Introduction

In the light of current legal regulations and technical guidelines [1–3], water in public swimming pools should meet a number of microbiological and physico-chemical requirements that guarantee it will not endanger swimmers' health. Such properties are ensured by a properly designed pool water treatment system, which consists of basic unit processes, i.e. coagulation, filtration, pH correction and disinfection. The choice of pool water treatment method depends on many factors. At the first stage, it is extremely difficult to predict which kind of system will be the most beneficial in particular case. Investment and operating costs are often very important when deciding in this regard.

The basic process of water treatment is filtration, which allows removal of impurities with a diameter > 0.1 μm. In order to increase efficiency, filters are often preceded by coagulation. The essence of this process is to reduce the dispersion of the colloidal system as a result of combining individual particles of the dispersed phase into larger clusters that can be effectively retained on the filter beds. To destroy the living and spore

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forms of pathogenic organisms and to prevent their secondary development, water must be disinfected. Mainly chemical methods involved the dosing of strong oxidants such as chlorine, sodium hypochlorite or chlorine dioxide are used for disinfection of swimming pool water. One of the strongest oxidants is ozone - almost twice stronger than chlorine. An important disadvantage of ozone as a disinfectant, is its low durability, and the danger of secondary bacterial growth. In the absence of an active disinfectant in water, the growth of bacteria can occur even in the presence of ozone products. Therefore, in the swimming pool water it is necessary to provide the remaining concentration of the disinfectant, and ozonation can only be used as a method of disinfection support.

During chemical oxidation processes, new impurities may be formed in the water, as by-products of the oxidation reaction with organic components of the treated water. One of the ways to reduce the efficiency of disinfection by-product formation is to reduce the dose of disinfectant. It is possible only as a result of chemical disinfection preceded by the physical method of destroying microorganisms, e.g. with UV irradiation [4]. The most bactericidal properties are UV-C radiation. Microorganisms have the highest sensitivity to radiation with a wavelength of 254 nm. This radiation causes rapid photochemical reactions in the DNA, thus microorganisms are destroyed or they lose the ability to reproduce [5].

As a result of the intensive development of analytical techniques that allow to reduce the detection limits of tested compounds, the latest scientific research alerts the growing number of organic micro-pollutants identified in the swimming pool water environment. This group includes a number of chemical compounds, e.g. Pharmaceuticals and Personal Care Products (PPCPs), flame retardants (FRs) or insecticide compounds [6]. All mentioned compounds can react with the disinfection agent introduced into the pool water, contributing to the formation of toxic or irritating products, leading to a decrease in the comfort of use of swimming pool facilities or even a health risk to swimmers [7]. Some of micropollutants recently identified in swimming pool water are biologically active even in trace concentrations. Among the health effects of human exposure to these compounds the most frequent are the occurrence of reproductive system diseases, hormonal disorders and even cancer [8, 9]. The classical methods used to treat swimming pool water are not effective in removing most of the organic micro-pollutants [10]. The closed-circuit system may even contribute to the accumulation and increase their concentration level [11]. The contamination level of pool water with micropollutants depends on many factors [12], among which the technology of water treatment is mentioned.

The aim of the research presented in this paper is to evaluate different disinfection methods used in swimming pool systems in the aspect of organic micro-contaminates removal. The content of organic matter, a precursor of dangerous disinfection by-products in systems, using UV radiation and ozonation was compared. A qualitative and quantitative analysis of the organic micropollutants profile was also carried out.

2 Materials and methods

2.1 The research subject

Sampling took place in accordance with the guidelines of the Polish standard PN-ISO 5667-5:2003. Swimming pool water samples were collected from the aqua park equipped with four water circuits, independent of each other. All of them are equipped with the same pressure filters, before which the aluminum sulfate by Kemipol of 0.1–0.8 mm granulation is dispensed as a coagulant, containing 17% Al_2O_3.

Filters contain a multi-layer filter bed consisting of:
- 15cm of quartz gravel, fraction 3–5mm,
- 15 cm of quartz gravel, fraction 1–2mm,
- 80 cm of quartz sand,
- 20 cm of activated carbon Sorbotech LGCO100,
- 20 cm of Hydro-flit bed, fraction 1.5–2mm.

The entire aquapark is equipped with a homogeneous system of disinfection by chlorination with Chlorox (Sodium Sodium Chloride Specification S) from NTCE, which is dosed for installation before entering each pool basin. In three cycles (P1, P2, P3), disinfection is supported by the ozonation using the Prominent Bono Zon ozone generator (Fig. 1), while one of the circuits (P4), which provides water treatment in the swimming pool for learning to swim, is an exception. Instead of the ozone generator, the UV lamp by Lifetech (Figure 2) is used. This is the only difference in the technological system of analyzed circuits.

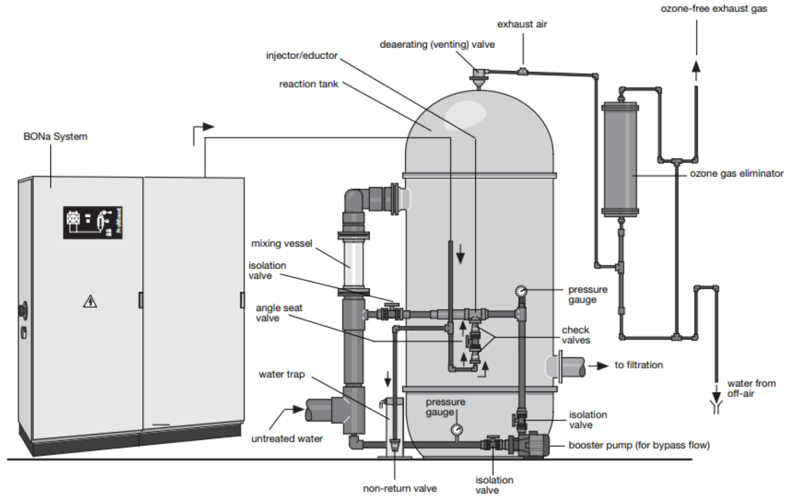

Fig. 1. The technological scheme of the Bono Zon system applied in the technological circuits of the analyzed swimming pool (*source: Prominent's catalog*).

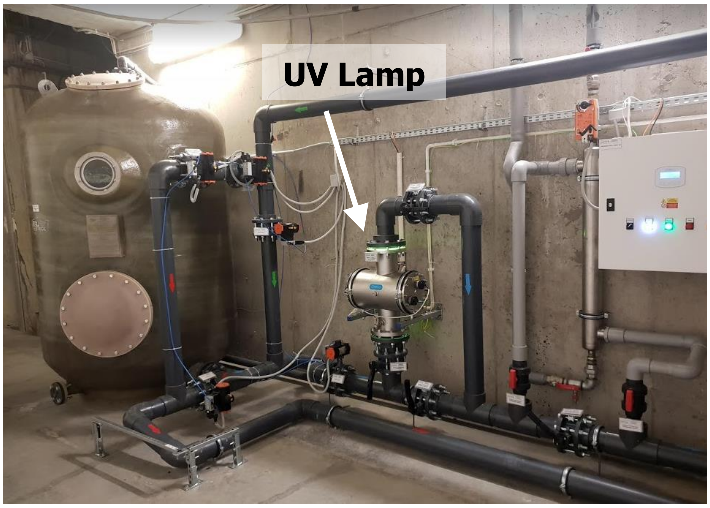

Fig. 2. Technological system equipped with a Lifetech UV lamp.

2.2 Analysis of selected indicators of organic swimming pool water contamination

The assessment of water quality before and after the treatment process was done on the basis of selected parameters related to the presence of organic matter in water:
- ultraviolet absorbance (UV_{254}) measured at a wavelength of 254 nm in a cuvette with a luminal length of 1 cm, using the Analytik UV VIS Cecil 1000,
- the content of total organic carbon (TOC) measured by Shimadzu's TOC-L analyzer.

2.3 Methodology for the determination of organic micropollutants in pool water

Determination of micropollutants in water was carried out in two stages:
1. Extraction of compounds from water by solid phase extraction (SPE).
2. Qualitative and quantitative analysis of extracts by gas chromatography coupled with mass spectrometry (GC-MS).

Organic solvents (methanol and acetonitrile) with analytical purity from Avantor (Gliwice, Poland) and columns for SPE, ENVI-18 by Sigma Aldrich (Poznań, Poland) were used. Details of the applied analytical method and its validation are presented in paper [13].

2.4 Evaluation of research and results analysis

The results presented in the paper are arithmetic mean values from four replications of individual tests. In all cases, the error estimated on the basis of standard deviation did not exceed 5%.

3 Results and discussion

Both indicators of water pollution (TOC and UV_{254}) showed an increase in the organic matter content after water treatment in relation to the measurement before treatment in all circuits using ozonation as a disinfection method (Fig. 3). The results of research [14] indicated that ozonation increases the share of hydrophilic fractions in sewage organic matter, especially in hydrophilic acids, which leads to the increase of the potential of formation the specific haloacetic acids in chlorination. In the same studies [14], the potential of creating trihalomethanes decreased after the initial ozonation but increased with further ozonation. Probably these two phenomena caused the increase in the organic matter content in swimming pool installations using ozone. In system equipped with the UV lamp, after irradiation of water, there was a marked decrease in organic matter content in comparison to the level of pollution at the inlet to the treatment system (Fig. 3). The TOC removal rate was 19.5%, and absorbance decreased by over 33%. Among the known methods for reducing the concentration of disinfection by-products, the removal of precursors present in water in the form of organic matter is considered as the most effective [5]. Significantly higher results of absorbance in one of ozonation system compared to the others, result from the specific physico-chemical properties of brine water.

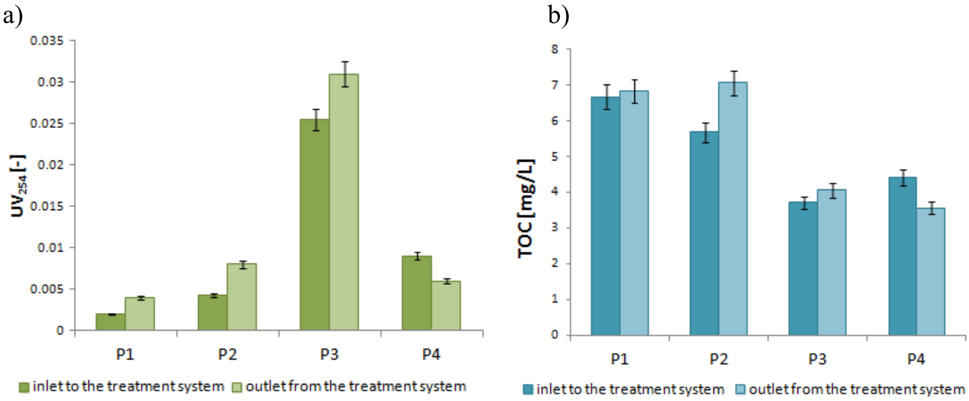

Fig. 3. Change of the organic matter content before and after ozonation (P1, P2, P3) and UV radiation processes (P4), expressed by pollution indicators: a) UV_{254} b) TOC.

Chromatographic analysis showed the presence of many different organic micro-pollutants in the tested water samples. The content of three compounds was clearly distinguishable (Figure 4).

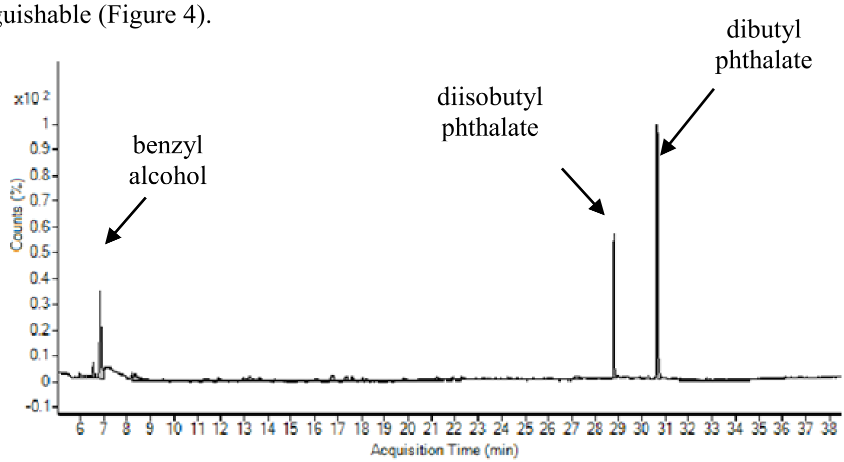

Fig. 4. An example of a chromatogram obtained as a result of testing one of the pool water samples.

Benzyl alcohol, due to its pleasant smell, is a component of many cosmetics, it is found among others in body butter, creams, lotions or balms. It can also be found in basic cosmetics for daily care, such as shampoos and foot creams. It is also used as a regulator of the product consistency. Moreover, it prevents the growth of microorganisms during storage, protecting the cosmetic against bacterial infection. This compound can also be used in the production of paints, varnishes, waxes and resins, while its derivatives are used in the pharmaceutical industry as a preservative.

Phthalates are synthetic compounds mainly used for the production of plastics, paints and cosmetics. This results in their wide application in many everyday products. They are an additive that increases flexibility, durability and strength of materials, mainly containing PVC. Both dibutyl phthalate (DBP) and diisobutyl phthalate (DIBP) are often found in personal care products, e.g. for cleaning nails. They can also be used as an additive to printing inks or glues. They are widely used as plasticizers in various products, ie floor coverings, balls, shower curtains. Due to their widespread use, phthalates can potentially occur even in drinking water sources. For example, the study of water samples from the

Mopanshan reservoir as a source of drinking water for the city of Harbin in north-east China [15] showed the presence of DBP in the concentration range from 52.5 ng/L to 4498.2 ng/L and DIBP from 40.0 ng/L to 658.8 ng/L. The fate of phthalates in two water supply networks capturing water from the Mopanshan reservoir was also analyzed. There were no significant differences in the level of concentrations of the subject compounds in the purification of water in a conventional purification station in relation to the concentration level in raw water [15].

The presence of DBP and DIBP in swimming pools seems to be particularly worrying, as they have been included in the list of high-risk substances REACH as compounds suspected of having a negative impact on the human endocrine system. The harmfulness is that they affect the human endocrine system, disrupting its proper functioning, due to its chemical structure. This may lead to fertility problems, cancer of the reproductive system, abnormal fetal development, early maturation of girls, genital damage or decreased production of semen, metabolic disorders, obesity and diabetes [16]. They may also increase the risk of allergies, asthma or cancer. Pursuant to Commission Delegated Directive (EU) 2015/863 of 31 March 2015 amending Annex II to Directive 2011/65 / EU of the European Parliament and of the Council, these compounds will be subject to a restriction on application from 22 July 2019.

The comparative analysis showed the smallest content of identified phthalates in the pool equipped with the UV lamp (Figure 5). Lau et al. [17] showed in laboratory tests that under the influence of UV radiation, up to 90% DBP can degrade during one hour of irradiation. The actual exposure time in working swimming pool system is much shorter and amounts to only a few to several seconds, which has reduced the content of diisobutyl phthalate 37.3% in water and 35.1% dibutyl phthalate (Figure 6).

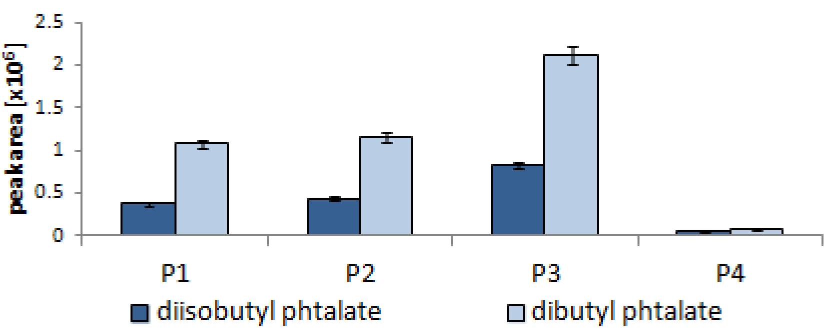

Fig. 5. Comparison of concentration levels of phthalates depending on the disinfection method used – ozonation (P1, P2, P3) and UV radiation (P4).

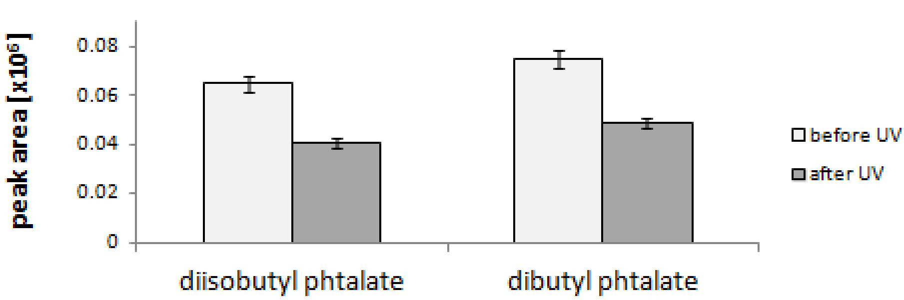

Fig. 6. The content of phthalates in swimming pool water before and after applying the UV lamp (P4).

The efficiency of ozonation in the aspect of removing the subject compounds was much lower, it was 6.96%–16.39% for diisobutyl phthalate (Figure 7a) and 5.32%–13.46% for dibutyl phthalate (Figure 7b).

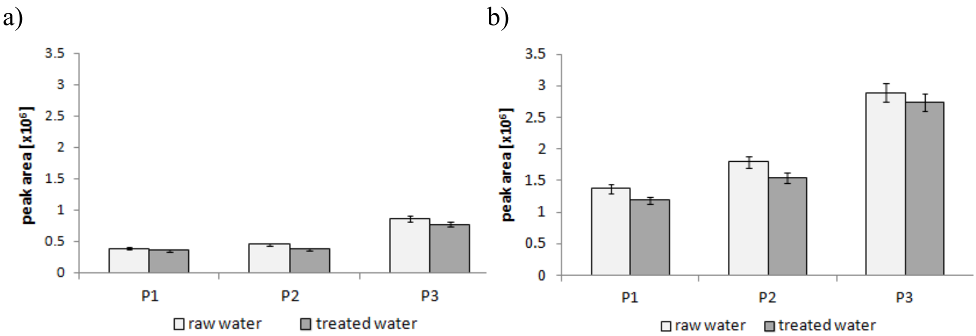

Fig. 7. The content of a) diisobutyl phthalate b) dibutyl phthalate in swimming pool water before and after ozonation (P1, P2, P3).

Research [17] documented six major intermediates of final DBP photodegradation products, including: butyl benzoate, benzoic acid, and phthalic acid, and butyl mono phthalate (MBP) and its derivatives: alcoholic and ketone or aldehyde. These compounds affect human health. For example, monobutyl phthalate may adversely affect the thyroid, reproductive and respiratory systems, resulting in lung function decline, allergies and asthma [18-20]. It can also reduce both sperm concentration and motility [21, 22]. However, the effect of long-term chronic exposure to benzoic acid in animal studies resulted in decreased appetite and reduced growth. This compound also caused an increased number of resorptions and malformations in hamsters. Clinical data indicate that it may produce non-immune contact urticaria and non-immune direct contact reactions characterized by the appearance of blisters, erythema and pruritus [23].

In paper [24] it was shown that in the initial period of photocatalysis there is an increase in water toxicity as a result of formation by-products of oxidation. For this reason, it has been recommended to use a long exposure time. In pool installations, this solution has not yet been applied. UV lamps work in these systems as flow devices, so the exposure time for their rays is very short.

4 Conclusions

- In order to minimize the concentration of disinfection by-products in swimming pool water, disinfectants should be dosed after the removal of organic compounds. The use of UV radiation is an effective method in this regard.

- In the assessed pools, the presence of micropollutants, among others dibutyl phthalate and diisobutyl phthalate was documented. It has been shown that their concentration depends on the disinfection support method used in the technological system.

- Photocatalytic degradation of phthalates in the pool water system allowed to obtain over 35% removal rate, while the efficiency of ozonation in the most favorable case was just over 16%.

- UV radiation is a more beneficial method of supporting disinfection of pool water than ozonation in the aspect of removing organic micropollutants from swimming pool water. However, this process often leads to the formation of by-products, that can significantly degrade the quality of the treated water streams. Therefore, the key role in assessing the effectiveness of advanced oxidation processes should not only be the assessment of the removal rate of parent compounds, but also the identification and evaluation of toxicological by-products of their degradation.

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