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Influence of the Use of an Additional Oxidant (Chlorine Dioxide) in Water Treatment on Swimming Pool Water Quality

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Abstract: This article presents the results of experiments on the effect of chlorine dioxide, applied as an additional oxidant, on swimming pool water quality. Three doses of chlorine dioxide were applied: 22, 44 and 66 mg/m^3. At each research stage, prior to the actual experiment, in which the oxidant was dosed, the background was tested, i.e., water samples were taken from a conventional treatment system (without chlorine dioxide). The experiments showed that chlorine dioxide effectively removes organic compounds and their chlorine derivatives. For the highest dose of ClO_2, COD_{Mn} decreased by almost 88% and chloroform concentration by 75%. Chlorine dioxide also effectively supports water disinfection. At the highest dose, the number of mesophilic bacteria decreased by 60% and the number of psychrophiles by 94%. However, after the dosing of this oxidant had been discontinued, a deterioration of the microbiological water quality and the secondary growth of microorganisms were observed. Chlorine dioxide also caused an increase in conductivity and the concentration of inorganic compounds (nitrates, total chlorates and chlorites). The effect of this agent on the combined chlorine concentration was not observed. The reported experiments have shown that this measure is not unequivocally beneficial in terms of improving swimming pool water quality.

Keywords: swimming pool water treatment; chlorine dioxide; disinfection by-products

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1. Introduction

The main goal of swimming pool water treatment is to ensure the best possible water quality, so that the pool is safe to use. Swimming pool water is treated in a closed circuit, which, in the standard system, requires the removal of organic matter by means of rapid filtration via a single- or multi-layer pressure filter (with prior dosing of coagulants) and water chlorination (usally with sodium hypochlorite as a basic disinfectant and oxidant). However, such a treatment system is often insufficient to maintain the required water quality and is supplemented with additional processes. It is becoming more and more popular to use chlorine dioxide to support water disinfection, but also to oxidize organic pollutants in swimming pool water.

The effectiveness of microorganism inactivation with chlorine dioxide is comparable to disinfection with chlorine in a case of water with neutral pH. However, when the pH changes, the disinfecting effect of chlorine decreases, while the disinfecting effect of chlorine dioxide remains stable. Nowadays, an important factor may also be that chlorine dioxide kills viruses more effectively than chlorine or even ozone [1]. In the presence of organic matter, ClO_2 is a stronger antiviral agent against SARS-CoV-2 than sodium hypochlorite [2].

Reactions of water components with chlorine dioxide are based on a different mechanism than those with chlorine disinfectants. ClO_2 is not a chlorinating agent, but a strong oxidant. Oxidation by ClO_2 occurs through the mechanism of one electron exchange, attacking electron-rich centers of organic molecules [3]. When one electron is transferred, the chlorine dioxide is reduced to chlorite (ClO_2^-). During oxidation reactions with organic matter, about 50–70% of the ClO_2 is usually converted into ClO_2^-, while the rest is converted into chlorate (ClO_3^-) and chloride (Cl^-) [3]. Thus, the reaction of dissolved organic matter and inorganic compounds with chlorine dioxide results in the formation of undesirable inorganic disinfection byproducts, i.e., chlorates (ClO_3^-) and chlorites (ClO_2^-) [1]. Chlorates and chlorites do not show acute or chronic toxicity [4]. Additionally, chlorites are not classified as carcinogenic to humans (group 3, according to the International Agency for Research of Cancer (IARC)), but they can cause oxidative stress, leading to changes in red blood cells. This is related to exposure to these compounds through ingestion. As inorganic compounds, chlorates and chlorites do not permeate the skin and are not a significant risk to swimmers. This is confirmed by the regulations for the use of these compounds for swimming pool water in the German DIN standard (30 mg/L) [5]. Regarding the impact on the formation of organic halogen disinfection by-products such as trihalomethanes (THM), when chlorine dioxide is used as the sole disinfectant or oxidant, significantly fewer THM are formed than with chlorination [6]. In the case of swimming pool water treatment, chlorination is obligatory and chlorine dioxide can be used as an additional oxidant. Research on THM formation in drinking water showed that the combined use of ClO_2 and Cl_2 reduced THM formation potential, which decreased gradually with an increasing ClO_2 to Cl_2 ratio [7–9]. In research conducted on swimming pool water, Kim et al. [3] showed that with mass ratio of ClO_2 to Cl_2 equal to 1:25, there was no significant difference in THM formation, while increasing this ratio to 1:1 resulted in a significant decrease in THM concentration in the sample with the addition of ClO_2.

As the result of the application of chlorine dioxide for water disinfection or in the oxidation process, in addition to inorganic chlorates and chlorites, many organic by-products are formed, such as aldehydes and short-chain carboxylic acids (formic, acetic, oxalic). Similar by-products are observed in the case of water ozonation, despite the fact that the reaction of organic compounds with chlorine dioxide is much slower than with ozone. The application of ClO_2 for water disinfection, like ozonation, leads to an increase in the amount of biodegradable and available organic matter [10,11], which may reduce the biological stability of water. This is defined as the inability of water or materials in contact with it to support the growth of microorganisms in the absence of a disinfectant [12,13]. Relating the above-described properties of chlorine dioxide in swimming pool water, it can be assumed that this compound will perfectly support the water disinfection, which is routinely carried out with chlorine compounds. Swimming pool users, during their time in the pool, release organic matter (saliva, sweat, mucus, urine and skin particles), as well as soap residues, cosmetics and sunscreen [3]. Chlorine dioxide, as a strong oxidant, can degrade these organic compunds into smaller particles, which can lead to the excessive growth of microorganisms, e.g., in circulation systems. Moreover, the consumption of chlorine dioxide in reactions with water contaminants may limit its disinfecting effect.

Although chlorine dioxide has been used in swimming pools for several years, studies on its use as an additional oxidant are largely absent from the literature. This article presents the results of experiments using chlorine dioxide as an additional oxidant before the chlorination process. The present research was carried out in a real-world context, and a number of physicochemical and microbiological parameters regarding water quality were measured and assessed.

2. Materials and Methods

2.1. Study Facility

The experiments were conducted at the AGH UST Swimming Pool, an indoor swimming pool located at ul. Buszka 4 in Krakow (Poland). Water samples were taken from the sport pool basin (dimensions 25 m × 16 m; depth 1.35 m to 1.8 m; volume 630 m^3 and water surface 400 m^2). The circulating water flow in the system is 177 m^3/h. Water treatment includes coagulation, filtration and disinfection with sodium hypochlorite. For the experiments described in this article, chlorine dioxide was periodically dosed into the treatment system after the filtration process and before disinfection. It was procured from Dwuaxan TECH, Dwuaxan

Company (Zabierzow, Poland), in which the precursor of the active chlorine dioxide is a mixture of sodium hypochlorite and sodium chlorite. Figure 1 shows a diagram of the water treatment technology with the location of chlorine dioxide dosing.

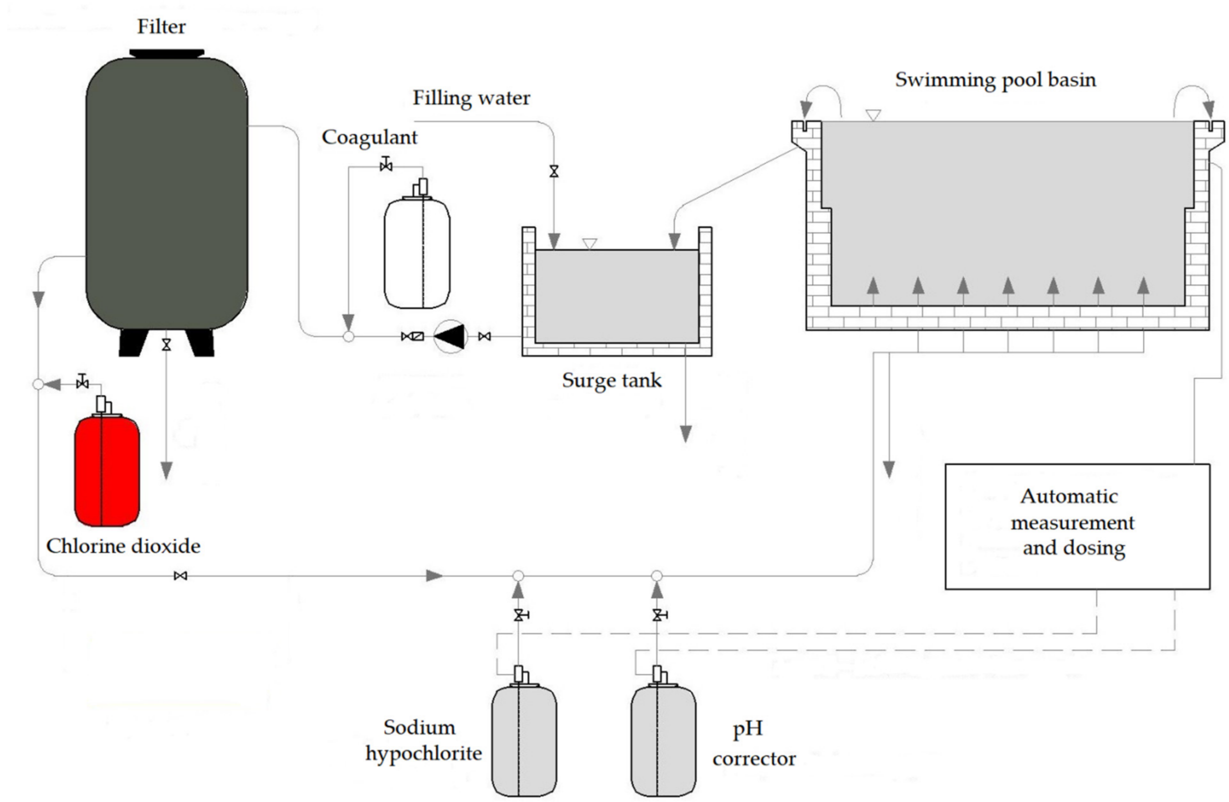

Figure 1. Schematic of swimming pool water treatment in the study facility, showing the localization of chlorine dioxide dosing.

The experiments were conducted from November 2019 to March 2020 in three stages. At each stage, a different amount of chlorine dioxide was dosed into the treatment system:

- Stage I—Dwuaxan TECH dose 50 g/h → ClO_2 dose 22 mg/m^3;
- Stage II—Dwuaxan TECH dose 100 g/h → ClO_2 dose 44 mg/m^3;
- Stage III—Dwuaxan TECH dose 150 g/h → ClO_2 dose 66 mg/m^3.

At each research stage, before the period in which the oxidant was dosed, the background water was tested, i.e., the samples were taken from water treated in a standard system (without chlorine dioxide). This was due to the fact that the quality of swimming pool water deteriorates over time, as well as due to changes resulting from the use of an oxidant (oxidants increase the concentrations of inorganic pollutants, which are not removed in standard swimming pool water treatment processes). Thus, at each research stage, the swimming pool was operated in normal water treatment mode (variant Cl_2) for 2–3 weeks before the additional dosing of chlorine dioxide (variant ClO_2/Cl_2) for another 2–3 weeks. The samples were taken twice a week on Tuesdays and Thursdays, always at the same time to ensure the same bather loads. Double sampling and double laboratory analysis were applied for each sample.

2.2. Analytical Methods and Statistical Analysis

Physicochemical and microbiological parameters were analyzed in the tested swimming pool water. Trichloromethane (chloroform) was determined in the collected water samples using a Trace Ultra DSQII GC-MS gas chromatograph by Thermo Scientific. Concentrations of free and total chlorine and chlorine dioxide were determined by the colorimetric method with DPD (N, N-diethylphenylendiamine), using a Cecil Instruments Aurius 2021 UV-VIS spectrophotometer. Concentrations of nitrates were determined photometrically using Nanocolor tests on a Nanocolor UV-Vis spectrophotometer by Macherey-Nagel. Conductivity was determined by the electrometric method. Microbiological analyses of psychrophilic and mesophilic bacteria were performed using the pourplate method [14]. The number of heterotrophic bacteria was determined using both standard yeast extract medium and R2A medium. Mesophilic bacteria were incubated at 36 ± 2 °C, while psychrophilic bacteria were incubated at 22 ± 2 °C. In the case of the yeast extract medium, the incubation time was 48 h for mesophiles and 72 h for psychrophiles. In the case of the R2A medium, this time was longer, i.e., 7 days for both mesophilic and psychrophilic bacteria. The results for mesophilic and psychrophilic bacteria grown on R2A agar are presented below. The number of bacteria incubated on the yeast agar plates was 0 cfu/cm^3 for all analyzed samples. Chlorates and chlorites, as well as the permanganate index (COD_{Mn}), were determined with the titrimetric method, as recommended by APHA-AWWA-WPCF [15]. Turbidity was determined on a Turbidineter 2100 AN by Hach.

For all tested water quality parameters, statistical analyses were conducted to assess the influence of the addition of chlorine dioxide on the swimming pool water treatment system, i.e., the differences between the variant Cl_2 and the variant ClO_2/Cl_2 were analyzed for each tested dose of chlorine dioxide, as well as differences between the stages, i.e., between the different doses of ClO_2. Analyses were performed with the Student's *t*-test. Before performing this t-test, the equality of variance was tested with the Lavene's test, and the normalilty of data distribution was tested using the Shapiro-Wilk test. The significance level was 0.05. All these analyses were performed with Statistica (version 10.0) by StatSoft.

3. Results and Discussion

3.1. Chlorine and Chlorination By-Products

Figure 2 shows the research results for free chlorine and chlorination by-products.

As shown in Figure 2A,B, the concentration of free and combined chlorine was not constant. The highest free chlorine concentration was observed in stage I with the Cl_2 variant (0.83 mg/L), while in stages II and III (the same variant, i.e., when only chlorination was used), the average free chlorine concentrations were 0.61 and 0.69 mg/L, respectively. With the ClO_2/Cl_2 variant, the average free chlorine concentrations were more even, amounting to 0.59, 0.56 and 0.58 mg/L for research stages I, II and III, respectively. The combined chlorine concentration in the samples from variants with and without chlorine dioxide dosing did not differ significantly in each stage of the experiments, except for stage III, in which this parameter differed statistically significantly ($p < 0.05$) between the Cl_2 and the Cl_2/ClO_2 variants. In the variant without chlorine dioxide, the average combined chlorine concentration was 0.85 mg/L in stages II and III, and 0.87 mg/L in stage I. For the ClO_2/Cl_2 variant, the lowest average combined chlorine concentration was observed for stage I (0.84 mg/L); this was slightly higher (0.85 mg/L) for stage II, and the highest values were noted for the stage III (0.98 mg/L). In the Cl_2/ClO_2 variant, the combined chlorine concentration was statistically significantly ($p < 0.05$) higher in stage III compared to stages I and II. There were no significant differences ($p > 0.05$) among the three stages with the Cl_2 variant. It can therefore be concluded that in the case of a standard treatment system, dosing with chlorine dioxide will not reduce the concentration of combined chlorine in swimming pool water. However, the dosing of an additional oxidant reduces the chloroform content in swimming pool water (Figure 2C). The conducted research showed that for each tested dose of chlorine dioxide, the chloroform concentration was lower than in water without the addition of this oxidant. For stages I and III, these differences were statistically significant ($p < 0.05$). For stage I, the average chloroform concentration decreased by 56% (from 9.25 µg/L with the Cl_2 variant to 4.05 µg/L with the ClO_2/Cl_2 variant). In stage II, a slightly lower decrease (32%) in the chloroform concentration in water with chlorine dioxide compared to only chlorinated water (from 11.95 to 8.08 µg/L) was noted. Statistically significant differences ($p < 0.05$) for the chloroform concentration were noted between stages I and II and between stages II and III with the Cl_2/ClO_2 variant. The greatest decrease in the average chloroform concentration was observed for stage III, in which the highest dose of chlorine dioxide was used. The average chloroform concentration in the water samples when the pool was operated in normal treatment mode (Cl_2) was 13.42 µg/L; this decreased to 2.12 µg/L (by 75%) after including chlorine dioxide in the treatment process. Thus, the lowest chloroform concentrations were observed for the lowest and highest tested doses of chlorine dioxide. This phenomenon may be attributed to the influence of chlorine dioxide on organic matter and the specificity of THM formation in water. Thus, chlorine dioxide degrades organic matter into forms with lower molecular weights, such as aldehydes and short-chain carboxylic acids (formic, acetic, oxalic) [10,11]. These small molecules react much more easily with chlorine, and organochlorine compounds are formed. subsequently, an increase in THM concentrations in water can be observed, as in stage II. Organic matter in water, under the influence of higher doses of strong oxidants, e.g., chlorine dioxide, can be mineralized, and then organochlorine compounds such as THM form in lower amounts. As shown in our results, the application of a dose of chlorine dioxide such as that used in stage III (66 mg/m^3) inhibits the formation of chloroform and significantly decreases its concentration in water. Such an increase in THM concentration with the combined use of ClO_2 and Cl_2 has been described by other authors [9]. In a study on spring waters, the authors of that report showed that the THM formation potential decreased gradually with increasing ClO_2 to Cl_2 ratio, as ClO_2 reacted with humic acids, making them non-reactive or unavailable for THM formation.

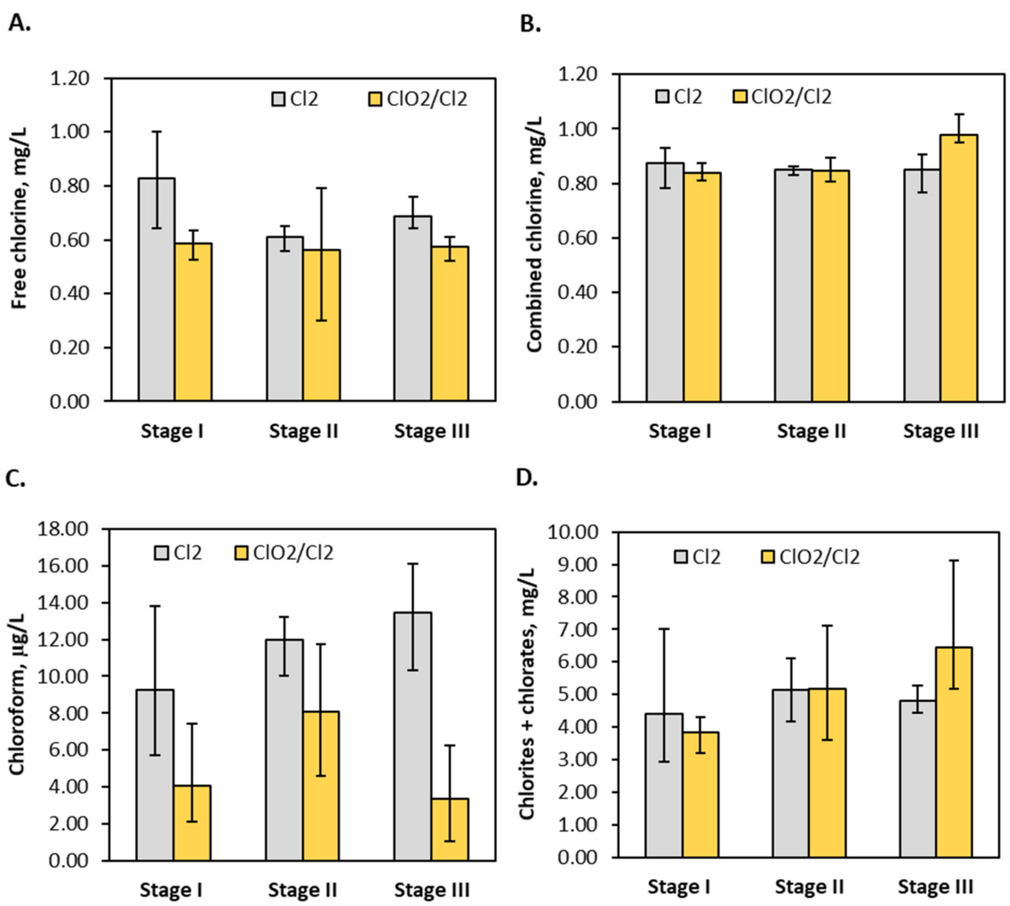

Figure 2. The influence of chlorine dioxide on the physical and chemical parameters of swimming pool water: (**A**) free chlorine; (**B**) combined chlorine; (**C**) chloroform; (**D**) sum of chlorates and chlorites.

As a result of the reaction of dissolved organic matter and inorganic compounds with chlorine dioxide, inorganic disinfection by-products are formed, such as chlorates (ClO_3^-) and chlorites (ClO_2^-) [1]. Chlorites are the predominant form of by-products in disinfection with chlorine dioxide. The amount of produced chlorites corresponds to 50–70% of the chlorine dioxide dose, while the concentration of chlorates is at most 7% [5]. Chlorites and chlorates are also products of the decomposition of chlorine dioxide in an aquatic environment. Chlorates can also be formed during the storage of sodium hypochlorite, and can therefore be present in water disinfected with this compound [16]. These compounds are not removed from swimming pool water with conventional treatment processes; therefore, they tend to accumulate in swimming pool water. As shown in Figure 2D, the application of chlorine dioxide may actually increase the amount of chlorates and chlorites in water. However, this increase was observed only for the highest dose tested (by 34%, from 4.82 to 6.44 mg/L). There was a statistically significant difference ($p < 0.05$) in the concentration of these compounds between stages I and III with the ClO_2/Cl_2 variant. However, no statistically significant differences ($p > 0.05$) were found between the sum of chlorates and chlorites between variants Cl_2 and ClO_2/Cl_2 in the individual stages. For stage II, the average concentration of the sum of chlorates and chlorites in the variant with chlorine dioxide did not differ from that in the background samples, amounting to 5.15 and 5.18 mg/L for the Cl_2 and ClO_2/Cl_2 variants, respectively. In stage I, where the lowest dose of chlorine dioxide was used, the average concentration of total chlorates and chlorites in the swimming pool water samples with the ClO_2/Cl_2 variant was 3.84 mg/L, i.e., 13% lower than in the samples collected during the standard operation of the swimming pool (4.41 mg/L).

3.2. Organic and Inorganic Matter

Figure 3 shows the concentrations of organic and inorganic compounds in the swimming pool water, obtained during the experiments with the dosing of chlorine dioxide.

The Polish Ministry of Health regulations [17] impose the obligatory monitoring of several physicochemical and microbiological parameters in pool water. Organic compounds are represented by COD_{Mn} and indirectly by turbidity, and inorganic compounds by nitrates. Figure 3A,B show that both turbidity and COD_{Mn} decrease with increasing doses of chlorine dioxide. In stage I, the average value of turbidity decreased by 22%, from 0.22 NTU in the Cl_2 variant to 0.17 NTU in the ClO_2/Cl_2 variant. In stage II, after the use of chlorine dioxide, a 12% decrease in turbidity was recorded (from 0.14 to 0.12 NTU). However, in stage III, after using the highest dose of chlorine dioxide, the turbidity was 0.14 NTU, i.e., 32% lower in comparison to the average value in water disinfected with only Cl_2 (0.21 NTU). Only in the case of stage II were the differences in turbidity in the Cl_2 and ClO_2/Cl_2 variants statistically significant different ($p < 0.05$). These differences were not noted between the turbidity in water with different doses of chlorine dioxide ($p > 0.05$). Turbidity in swimming pool water mainly indicates a problem with the removal of organic compounds by the treatment system, but the precipitation of insoluble inorganic compounds may also increase it. Oxidation processes favor the precipitation of insoluble inorganic compounds, such as silica or compounds that cause water hardness [18]. The average COD_{Mn} value decreased with increasing the dose of chlorine dioxide; however, statistically significant differences ($p < 0.05$) were noted between stages II and III, and between stages I and III. In the variant using only the standard swimming pool water treatment system (Cl_2), the average COD_{Mn} values were 2.24 mgO_2/L in stage II and 2.69 mgO_2/L in stages I and III. After the use of chlorine dioxide, the average COD values decreased by 45% in stage I, by 57% in stage II and by as much as 88% in stage III. The COD_{Mn} values with the ClO_2/Cl_2 variant were 1.49, 0.96 and 0.34 mgO_2/L in stages I, II and III, respectively. In all cases, these differences were statistically significant ($p < 0.05$).

Nitrates (NO_3^-) are the end products of the oxidation of nitrogen-containing compounds released into water via sweat from bathers [19]. Thus, nitrates can be used as an indicator of the water age and the effectiveness of its purification. Oxidation processes may favor the increase of their concentration in water (Figure 3D). The average background concentrations of nitrates (in the variants without chlorine dioxide) were 7.83, 9.74 and 12.12 mg/L for stages I, II and III respectively. As a result of dosing with chlorine dioxide, the average value of nitrates increased—to 8.97 mg/L (by 14%) in stage I, to 10.35 mg/L (by 6%) in stage II and to 12.51 mg/L (by 3%) in stage III. However, these differences were not statistically significant ($p > 0.05$). Although the increases in nitrate concentrations were not too high in the individual stages, the effect of the accumulation of these compounds in swimming pool water can be noticed. These compounds are not removed in the processes used to treat swimming pool water; as such, by the end of the experiment, they had accumulated considerably, showing a statistically significant increase ($p < 0.05$) of 60% from 7.83 mg/L in the Cl_2 variant of stage I to 12.51 mg/L with the ClO_2/Cl_2 variant in stage III. A statistically significant increase ($p < 0.05$) in the concentration of nitrates for different doses of ClO_2 was also observed for the ClO_2/Cl_2 variant between stages I and stage III and between stages II and stage III.

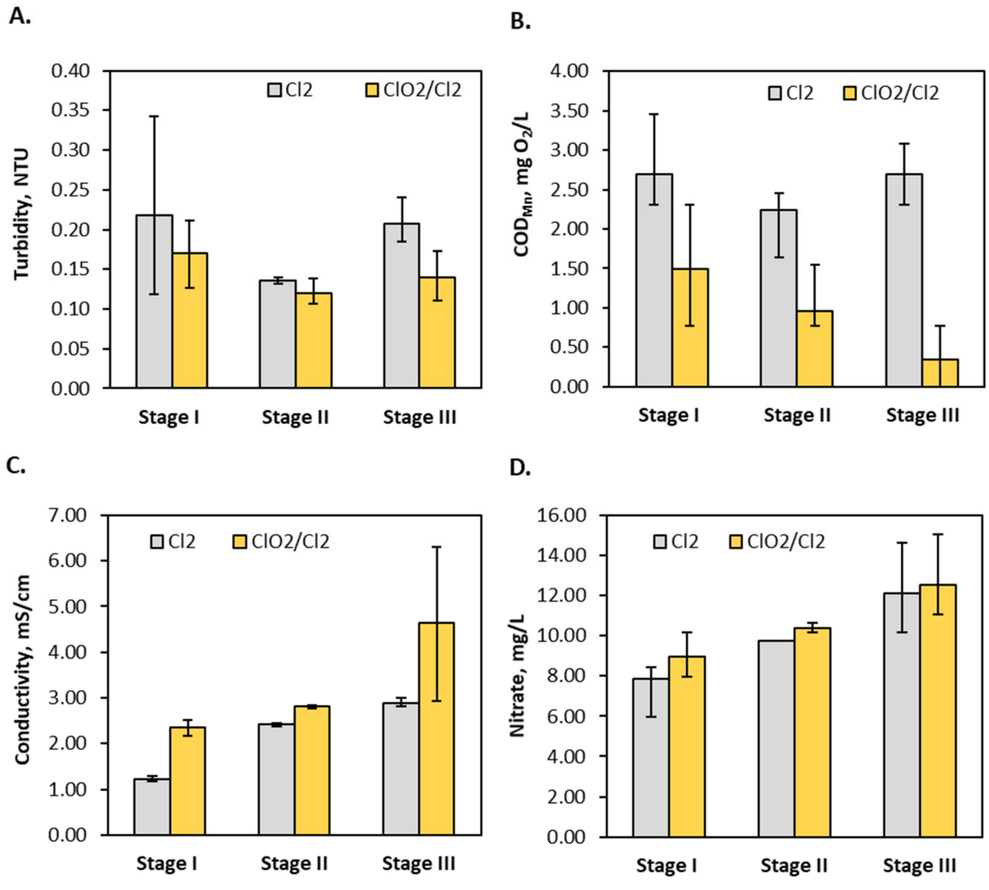

Figure 3. The influence of chlorine dioxide on the physical and chemical parameters of swimming pool water: (**A**) turbidity; (**B**) COD_{Mn}; (**C**) conductivity; (**D**) nitrates.

Chlorides are other inorganic compounds that can be used as indicators of water aging in swimming pools. They are formed mainly as a result of the reduction of free chlorine, and a simple method of assessing their concentrations is to measure the conductivity of the water. The concentration of nitrates is usually positively correlated with the concentration of chlorides [20]. As the conducted research showed, the dosing of an additional oxidant in the water treatment process causes an increase in water conductivity (Figure 3C). The highest increase in conductivity was observed in stage I, in which the conductivity of water treated with the ClO_2/Cl_2 variant was 93% higher (a statistically significant increase ($p < 0.05$) from 1.22 mS/cm in the standard treatment system to 2.35 mS/cm after the application of chlorine dioxide in a dose of 22 mg/m^3). In stage II (chlorine dioxide dose:

44 mg/m^3), the average conductivity value of the Cl_2 variant was 2.41 mS/cm; as a result of dosing with chlorine dioxide, it increased statistically significantly ($p < 0.05$), by 17% to 2.81 mS/cm. Following the application of chlorine dioxide at a dose of 66 mg/m^3, the average value increased statistically significantly ($p < 0.05$), i.e., by 61% (from 2.88 mS/cm for the Cl_2 variant to 4.63 mS/cm for the ClO_2/Cl_2 variant). In the case of this indicator, as in the case of nitrates, the termination of chlorine dioxide dosing did not decrease the conductivity value, as observed prior the use of the oxidant. During the whole experiment, conductivity increased by 270%, from 1.22 mS/cm in the Cl_2 variant in stage I to 4.63 mS/cm in the ClO_2/Cl_2 variant in stage III. There was no statistically significant increase ($p > 0.05$) in conductivity with different doses of chlorine dioxide.

3.3. Microbiological Pollutants

Figure 4 shows the results of testing water samples for microbiological pollutants.

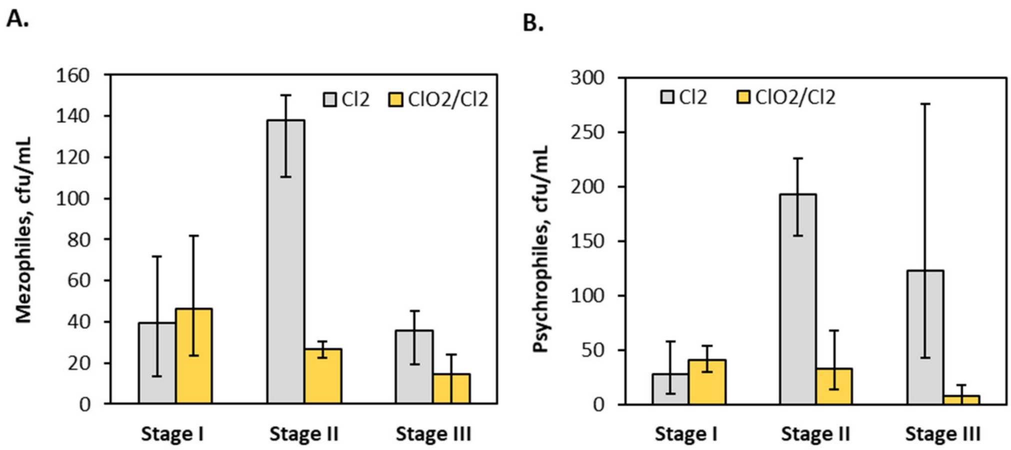

Figure 4. The influence of chlorine dioxide on the microbiological parameters of swimming pool water: (**A**) mesophiles; (**B**) psychrophiles.

As shown in Figure 4, the use of chlorine dioxide as an additional oxidant and disinfectant has a positive effect on the swimming pool water microbiological quality. As indicated in the research methods, the R2A medium was used. Under unfavorable conditions, microorganisms are in a state of low metabolic activity and cannot multiply and grow on conventional microbiological media. These are therefore viable but not culturable (VNBC) microorganisms, which are in a kind of transitional state due to the unfavorable conditions that occur in swimming pool water in the presence of an active disinfectant. When favorable conditions appear, the microorganisms can once again breed after undergoing a so-called resuscitation [21–23]. The R2A medium, with a very large amount of nutrients, certainly promotes such a return; therefore, by growing microorganisms on such a medium, many more colonies of microorganisms are obtained than on a standard medium (e.g., agar with yeast extract). Favorable conditions for the recovery of microorganisms from a VNBC state may also appear in swimming pool water. It is enough to reduce the disinfectant dose or to employ a treatment process that favors the degradation of organic matter into smaller particles, which become an additional source of food for microorganisms. The use of strong oxidants, which are strong disinfectants, can increase the amount of biodegradable and assimilable organic matter in water [12,13] and paradoxically promote the multiplication of microorganisms (or their exit from the VNBC state) if the concentration of such a compound is lowered. As shown in Figure 4, after the periods of chlorine dioxide dosing at the lowest tested dose, when moving to the next stage and collecting background samples, in the absence of the disinfectant, there was an increase in the numbers of both mesophiles and psychrophiles in the swimming pool water samples. The average number of mesophilic bacteria in the Cl_2 variant of stage I was 39 cfu/mL, while in the same variant, but in stage II, it increased by 252% to 138 cfu/mL. In stage

III, the number of background mesophils (with the Cl_2 variant) was similar to that in stage I, i.e., 36 cfu/mL. Statistically significant differences ($p < 0.05$) between the numbers of mesophilic bacteria in the Cl_2 and ClO_2/Cl_2 variants were noted only in stage II, in which there were significantly more background bacteria. Regarding the effect of chlorine dioxide on the number of mesophils, statistically significant differences ($p < 0.05$) were noted between stages I and III. In the case of psychrophilic bacteria, the average numbers in the Cl_2 variant in stage I was 28 cfu/mL; this increased by 599% to 193 cfu/mL in stage II. In stage III in the same variant, i.e., in the standard treatment system, the amount of psychrophiles reached 123 cfu/mL, i.e., 346% higher than in the water from stage I. As with mesophilic bacteria, statistically significant differences ($p < 0.05$) were noted in the number of psychrophilic bacteria in the Cl_2 and ClO_2/Cl_2 variants in stages where the numer of bacteria was higher in the Cl_2 variant. For psychrophiles, this was the case in stages II and III. Regarding the effect of the dose of chlorine dioxide on the number of psychrophiles, no statistically significant differences ($p > 0.05$) were found between the analyzed doses of ClO_2.These results clearly show that after discontinuing the use of chlorine dioxide, the biological stability of the water decreased.

Comparing the numbers of microorganisms in the water in the Cl_2 and ClO_2/Cl_2 variants in the individual stages, it can be seen that the application of chlorine dioxide had an impact on the water microbiological quality. With the use of the smallest dose of chlorine dioxide (22 mg/m^3), the number of microorganisms increased in relation to the background, i.e., water in the standard water treatment system. The amount of mesophilic bacteria increased by 18% (from 39 cfu/mL in the Cl_2 variant to 46 cfu/mL in ClO_2/Cl_2), while the number of psychrophilic bacteria increased by 48% (from 28 to 41 cfu/mL). The application of higher doses of chlorine dioxide had a positive effect on the water microbiological quality. For stage II, in which the dose of this compound was 44 mg/m^3, the numbers of mesophilic bacteria decreased by 81% (from 138 to 26 cfu/mL) and that of psychrophilic bacteria by 83% (from 193 to 32 cfu/mL). For stage III (chlorine dioxide dose: 66 mg/m^3), the number of mesophilic bacteria was reduced compared to the variant without chlorine dioxide, i.e., from 36 to 14 cfu/mL (by 60%), and that of psychrophilic bacteria by as much as 94%, from 123 to 8 cfu/mL. The higher doses problably caused the mineralization of organic matter, as well as the disintegration of microorganism cells. Despite the relatively high values for microorganism numbers obtained on the R2A medium during a routine microbiological control on a standard medium (performed by an accredited laboratory servicing the pool), the amount of microorganisms capable of growing at 36 °C (mesophiles) was 0 cfu/mL.

4. Conclusions

The present research results have shown that the application of chlorine dioxide, in the form of Dwuaxan TECH, effectively removes organic compounds and their chlorine derivatives, such as THM. Chlorine dioxide also turned out to be an effective agent to support water disinfection, and as such, may be useful in dealing with all kinds of microbiological problems in swimming pool water, as well as in circulation systems. When used in small doses, it is recommended to continuously dose the agent in order to prevent the secondary development of microorganisms (with the use of higher doses, such a phenomenon does not occur). Like any strong oxidant, chlorine dioxide increases the content of inorganic compounds in water, as well as its conductivity. The effect of this agent on the combined chlorine concentration in swimming pool water was not observed. In order to reduce the Cl concentration, additional individual processes should be included in water treatment technology. This will be the subject of further research by the authors and the results will be reported.

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