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TIME-SERIES ANALYSIS-BASED QUALITY MONITORING OF WATER, DISINFECTED WITH CHLORINE DIOXIDE

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Abstract

In wartime and post-war recovery conditions, the sustainable management of urban water resources has emerged as a critical priority in the context of global environmental challenges and public health demands. Among various disinfection methods, chlorine dioxide is increasingly recognized for its high efficacy in microbial control and lower potential for producing hazardous disinfection by-products compared to traditional chlorination. However, to ensure the reliability, safety, and environmental compliance of such systems, it is essential to employ rigorous analytical frameworks that can assess and predict system performance under variable conditions.

This study focuses on the mathematical analysis of chlorine dioxide-based water purification systems, using monitoring data from a Dniprovska municipal water treatment station in Kyiv, Ukraine. The integration of mathematical modeling with real-time water quality monitoring offers a robust approach to optimizing operational parameters, identifying anomalies, and improving overall treatment efficiency. Importantly, this research contributes to broader ecological objectives by supporting the reduction of chemical usage and minimizing environmental impact. Moreover, it aligns with the principles of sustainable development, particularly in enhancing the resilience of water infrastructure and advancing progress toward the United Nations Sustainable Development Goals. Monitoring of the selected set of water quality parameters over a two-year period revealed the expected average values and ranges for each of the investigated indicators. As the analysis showed, the drinking water complied with regulatory standards even under conditions of anomalous contamination of river water, which confirms both the effectiveness of the implemented technological solutions and the operational efficiency of the adopted treatment technology.

Keywords*: natural water treatment, water treatment plant, disinfection, chlorine dioxide, monitoring, statistical analysis, sustainable development goals.*

The provision of safe and clean drinking water remains one of the most pressing global challenges, particularly in the face of rapid urbanization, climate change, and the degradation of natural water sources. Ensuring the microbiological safety of drinking water while minimizing the formation of harmful disinfection by-products has driven the development and implementation of advanced treatment technologies. Among these, chlorine dioxide has gained increasing attention due to its strong oxidizing properties, broad-spectrum antimicrobial activity, and relatively low tendency to form trihalomethanes and other regulated by-products when compared to traditional chlorination methods [1, 2].

In the context of Ukraine, where municipal water treatment systems often operate under conditions of limited resources and outdated infrastructure, the adoption of chlorine dioxide as a primary or supplementary disinfectant is viewed as a promising strategy for improving water quality and operational efficiency. Nevertheless, the performance of chlorine dioxide-based disinfection systems is highly sensitive to multiple factors, including dosage accuracy, contact time, water temperature, and the presence of organic and inorganic substances in raw water. These variables necessitate a systematic, data-driven approach to performance evaluation and process optimization.

Currently, numerous studies are being conducted on chlorine dioxide-based oxidation processes used in water purification. Approaches for evaluating and controlling the formation of disinfection by-products (DBP) are being proposed, while kinetic and mechanistic data on the reactivity of ClO_2 toward micropollutants are also under active discussion. ClO_2 reacts selectively with electron-rich moieties (such as anilines, phenols, olefins, and amines) and removes certain inorganic ions and microorganisms with high efficiency. Nevertheless, the formation of chlorite and chlorate during the oxidation process remains a critical issue in ClO_2-based treatment.

Mathematical modeling offers a powerful tool for analyzing the dynamic behavior of water treatment systems. By integrating real-time monitoring data into predictive models, researchers and practitioners can gain deeper insights into the efficiency, stability, and potential risks associated with water purification processes. Such analyses enable the identification of critical control points, the simulation of various operational scenarios, and the support of decision-making aimed at reducing environmental impact and improving public health outcomes [3-6].

This study presents a mathematical analysis of a chlorine dioxide water purification system based on monitoring data collected from a Dniprovska municipal water treatment station in Kyiv, Ukraine. The primary objectives of the research are: 1) to evaluate the impact of key parameters on the effectiveness and stability of the system; and 2) to assess the ecological and sustainability implications of optimizing chlorine dioxide usage. By addressing these goals, the study aims to contribute to the broader discourse on sustainable water management and support Ukraine's progress toward achieving key targets of the United Nations Sustainable Development Goals (SDG), including SDG 6 (Clean Water and Sanitation), SDG 11 (Sustainable Cities and Communities), and SDG 12 (Responsible Consumption and Production).

Through the application of quantitative analysis and systems thinking, this research underscores the ecological significance of enhancing disinfection practices in municipal water treatment and highlights the role of scientific modeling in the transition toward more sustainable and resilient urban infrastructure.

According to the Target Program "Drinking Water of Kyiv for 2011-2020", approved by Resolution No. 220/5032 of the Kyiv City Council dated November 4, 2010, a comprehensive reconstruction of the Dnipro Water Treatment Plant was carried out. The designed treatment technology involves two stages of chlorine dioxide application: primary treatment (pre-oxidation) – prior to supplying water to the treatment facilities, and secondary treatment (post-disinfection) – chlorine dioxide disinfection of drinking water after rapid filtration. Additionally, ferrous chloride

($FeCl_2$) is applied to remove chlorites and residual chlorine dioxide concentrations. For chlorine dioxide production, hydrochloric acid and sodium chlorite are used as raw materials.

The primary treatment (pre-oxidation) is performed at the first lift pumping station, before water enters the treatment facilities. Chlorine dioxide is dosed into the water in quantities sufficient to oxidize organic and inorganic contaminants. To achieve this, a residual chlorine dioxide concentration of 0.2-0.4 mg/dm^3 must be maintained at the inlet of the mixing chambers.

After a certain contact time (20-30 minutes), during which oxidation of contaminants occurs and chlorites are formed, the water enters the mixing units. Prior to mixing, ferrous chloride ($FeCl_2$) is dosed to remove chlorites and any remaining chlorine dioxide. The $FeCl_2$ dosing unit in the mixing block consists of four injection points. Chlorine dioxide and residual chlorite concentrations are measured upstream of the mixers, and redox potential is monitored downstream. The dosing of $FeCl_2$ is automatically regulated to achieve near-zero concentrations of residual chlorine dioxide and chlorites. Compliance with these parameters is ensured through specialized instrumentation.

The secondary chlorine dioxide treatment (post-disinfection stage) is conducted after rapid filtration. This stage is intended to ensure microbiological safety and maintain a residual chlorine dioxide concentration of at least 0.1 mg/dm^3 in the drinking water as it enters the distribution network. To this end, the filter block is equipped with four dosing points for chlorine dioxide. The dosing of the disinfectant solution is also based on real-time data obtained from dedicated measurement devices.

Preliminary studies indicate a "dose-time" dependency in the use of chlorine dioxide in the Dnipro treatment process. The lowest doses are applied during the winter, while the highest are used in summer, late spring, and early autumn. Despite this seasonal variability, the residual chlorine dioxide concentration in disinfected drinking water after the clean water reservoir (CWR) consistently meets regulatory standards – no less than 0.1 mg/ dm^3 for ClO_2 and below 0.2 mg/ dm^3 for chlorites (with a current standard of 0.2 mg/ dm^3). However, during unfavorable seasonal periods, it is important to adopt a higher chlorite threshold (up to the WHO-recommended level of 0.7 mg/ dm^3) to enhance the barrier function of the treatment facilities and improve disinfection reliability. Currently, the Ministry of Health of Ukraine is considering updating the outdated Soviet-era chlorite standard of 0.2 mg/ dm^3 to 0.7 mg/ dm^3, in line with WHO recommendations and European Union practices. This transitional adjustment is allowed in Ukraine under Order No. 683 of the Ministry of Health of Ukraine, dated April 22, 2022.

Monthly data on a selected set of water quality parameters (color, pH, permanganate oxidizability, total organic carbon (TOC), phytoplankton, chlorine dioxide, chlorites), measured over a two-year period at control points of the water treatment process, are presented in Fig. 1.

The presented study was conducted within the framework of the research projects "Technological principles of minimizing the content of chlorites in drinking water after disinfection with chlorine dioxide" (State Registration Number: 0125U001784) and "Computer simulation and optimization of sustainable water management technological networks" (State Registration Number: 0124U002127).

The concentrations of chlorine dioxide and chlorites obtained at the treatment process control points by means of chromatographic and complementary analytical techniques correspond well to the water quality parameter data.

Boxplot diagrams (Figure 2, a-g) enabled a visual comparison of temporal changes in relative concentration values, assessment of the mean (central tendency), the range (variability) of the studied relative water quality characteristics, and the identification of outliers (abnormally high or low values) in the dataset. Anomalous values (outliers in the time series) of relative concentrations for phytoplankton and ClO_2 residual concentration are indicated with asterisks in Figures 2a and 2b, respectively. These anomalous values remain within the normative range. Figure 2h presents a typical interval distribution diagram of the treated water parameters using total organic carbon (TOC) as an example.

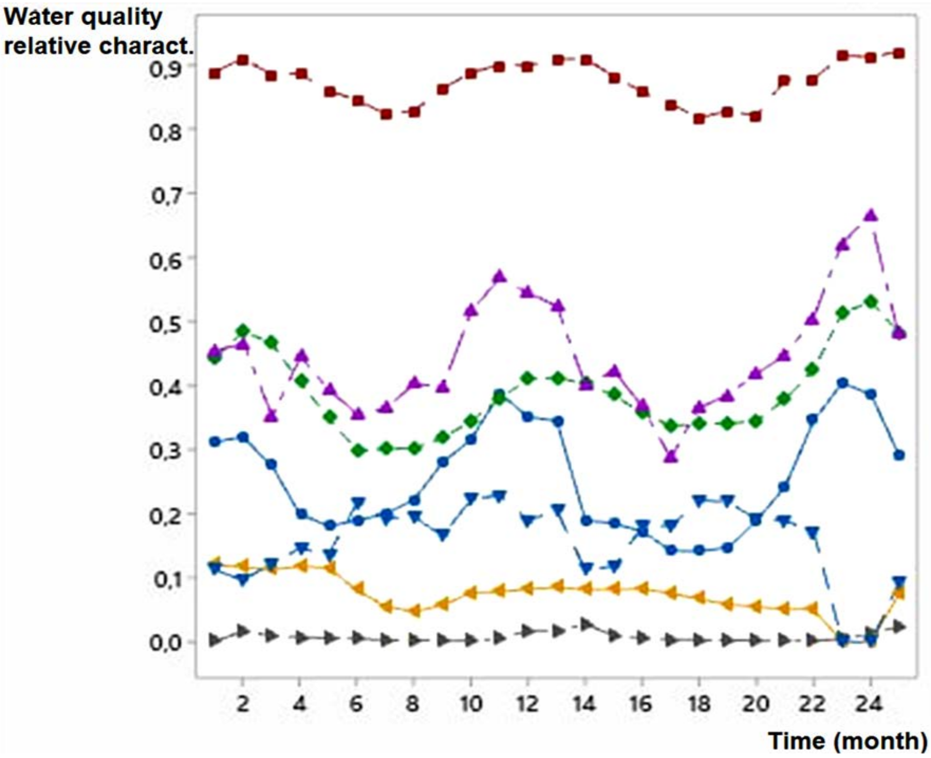

Figure 1. *Change in relative water quality characteristics over time by month:*
– color, – pH; permanganate oxidizability; – monomer total organic carbon (TOC);
– phytoplankton; – chlorine dioxide (residual); – chlorites (residual)

Monitoring of the selected set of water quality parameters over a two-year period revealed the expected average values and ranges for each of the investigated indicators. As shown in the diagrams, the drinking water complied with regulatory standards even under conditions of anomalous contamination of river water, which confirms both the effectiveness of the implemented technological solutions and the operational efficiency of the adopted treatment scheme.

Based on the mathematical analysis of the obtained results, a preliminary conclusion can be drawn that the adopted technological solutions and the operation of the implemented treatment network are effective in ensuring the epidemiological safety and chemical harmlessness of drinking water treated with chlorine dioxide. Moreover, it aligns with the principles of sustainable development, particularly in enhancing the resilience of water infrastructure and advancing progress toward the United Nations Sustainable Development Goals, including clean water and sanitation (SDG 6) and sustainable cities and communities (SDG 11).

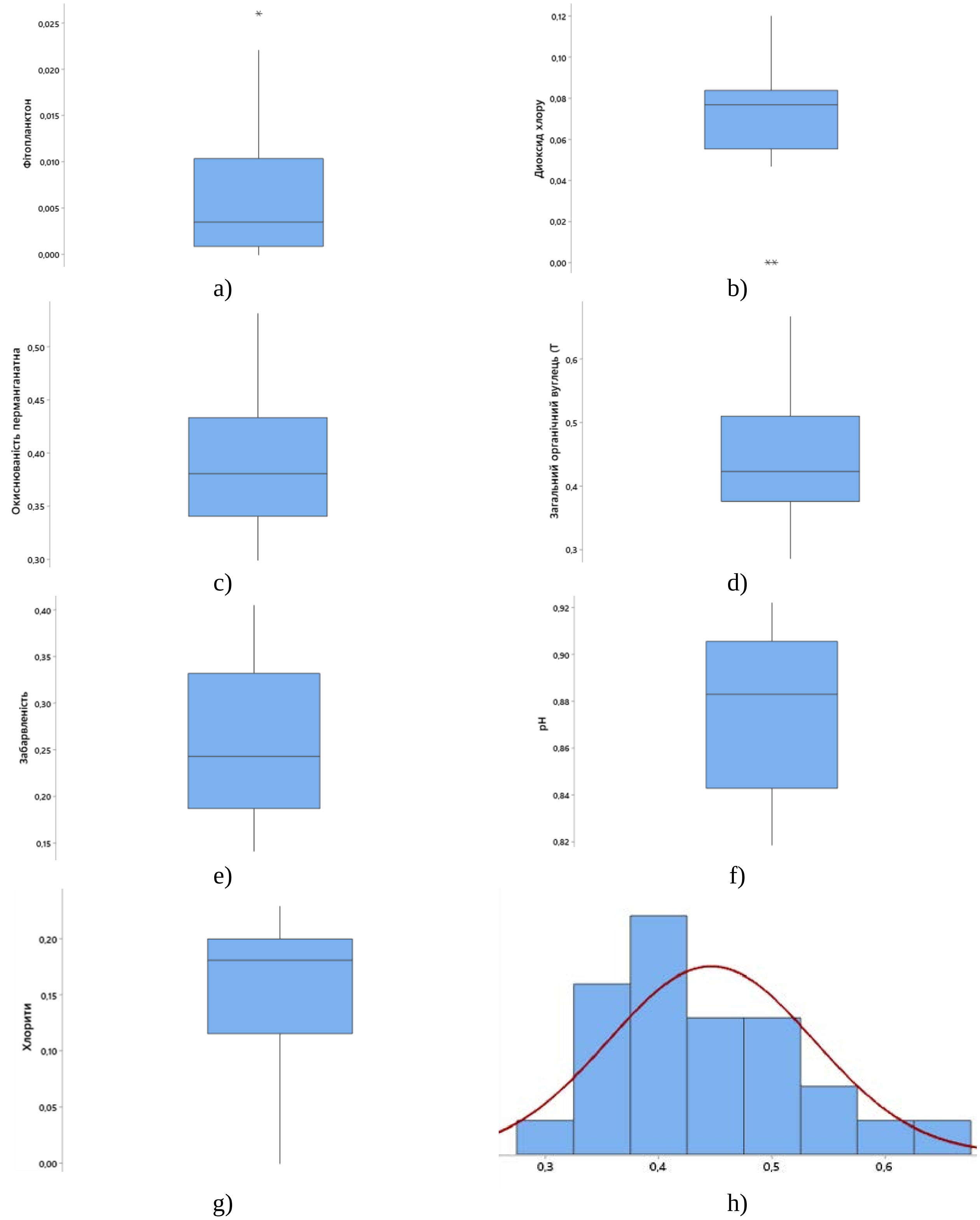

Fig. 2. *Statistical analysis of the relative parameters of the purified water quality: a) – g) – boxplot diagrams of the range of water quality characteristics (phytoplankton, residual chlorine dioxide, permanganate oxidizability, total organic carbon, color, pH, residual chlorites respectively); g) histogram of the distribution by "Total organic carbon"*

The presented study was conducted within the framework of the research projects "Technological principles of minimizing the content of chlorites in drinking water after disinfection with chlorine dioxide" (State Registration Number: 0125U001784) and "Computer simulation and optimization of sustainable water management technological networks" (State Registration Number: 0124U002127).

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МОНІТОРИНГ НА ОСНОВІ АНАЛІЗУ ЧИСЛОВИХ РЯДІВ ЯКОСТІ ВОДИ, ЗНЕЗАРАЖЕНОЇ ДІОКСИДОМ ХЛОРУ

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Анотація: В умовах військового часу та періоду повоєнного відновлення стале керування міськими водни ми ресурсами набуває великого значення у контексті глобальних екологічних викликів і вимог громадського здоров'я. З комплексом своїх характеристик діоксид хлору посідає ключове місце серед доступних нині методів дезінфекції води внаслідок його високої ефективності у боротьбі з мікроорганізмами та меншого потенціалу утворення небезпечних побічних продуктів дезінфекції. При цьому, для забезпечення ефективності, надійності, та безпечності систем знезараження води важливо доцільно керуватися системним науковим підходом до проєктування, оцінювання та прогнозування продуктивності таких систем в умовах змінного зовнішнього середовища.

Представлене дослідження мало на меті математичний аналіз систем очищення води на основі діоксиду хлору з використанням даних моніторингу Дніпровської водоочисної станції в м. Києві. Інтеграція математичного моделювання з моніторингом якості води в реальному часі пропонує надійний підхід до оптимізації робочих параметрів, виявлення аномалій і підвищення загальної ефективності очищення.

Моніторинг за обраним набором параметрів якості води протягом дворічного періоду виявив очікувані середні значення та діапазони для кожного з досліджуваних показників. Як показав аналіз, навіть за умов аномального забруднення річкової води питна вода відповідала нормативним нормам, що підтверджує як ефективність впроваджених технологічних рішень, так і ефективність роботи прийнятої схеми очищення.

На підставі математичного аналізу отриманих результатів зроблено висновок про ефективність прийнятих технологічних рішень та роботи впровадженої технології очищення води щодо забезпечення епідеміологічної безпеки питної води, обробленої діоксидом хлору.

Ключові слова: очищення природних вод, водоочисні споруди, знезараження, діоксид хлору, моніторинг, статистичний аналіз, цілі сталого розвитку.