Chemical and Process Engineering: New Frontiers, 2023, 44(3), e22
DOI: 10.24425/cpe.2023.146724

# A new magnetic-hybrid photoreactor for photocatalytic water disinfection

Oliwia Paszkiewicz[1], Kunlei Wang[2], Marian Kordas[1], Rafał Rakoczy[1], Ewa Kowalska[2,3], Agata Markowska-Szczupak[1]*

[1] West Pomeranian University of Technology in Szczecin, Faculty of Chemical Technology and Engineering, Department of Chemical and Process Engineering, Piastow 42, 71-065 Szczecin, Poland
[2] Hokkaido University, Institute for Catalysis (ICAT), N21, W9, 001-0021 Sapporo, Japan
[3] Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Krakow, Poland

*** Corresponding author:**
e-mail:
agata.markowska@zut.edu.pl

Presented at 24th Polish Conference of Chemical and Process Engineering, 13–16 June 2023, Szczecin, Poland.

**Article info:**
Received: 14 May 2023
Revised: 3 July 2023
Accepted: 14 July 2023

**Abstract**
Environmental contamination is an urgent topic to be solved for sustainable society. Among various pollutants, microorganisms are believed to be the most dangerous and difficult to be completely inactivated. In this research, a new hybrid photoreactor assisted with rotating magnetic field (RMF) has been proposed for the efficient removal of two types of bacteria, i.e., gram-negative *Escherichia coli* and gram-positive *Staphylococcus epidermidis*. Three self-synthesized photocatalysts were used, based on commercial titanium(IV) oxide – P25, homogenized and then modified with copper by photodeposition, as follows: 0.5 Cu@HomoP25, 2.0 Cu@HomoP25 and 5.0 Cu@HomoP25 containg 0.5, 2.0 and 5.0 wt% of deposited copper, respectively. The response surface methodology (RSM) was employed to design the experiments and to deteremine the optimal conditions. The effects of various parameters such as copper concentration [% w/w], and treatment time [h] and frequency of RMF [Hz] were studied. Results: analysis of variance (ANOVA), revealed a good agreement between experimental data and proposed quadratic polynomial model ($R^2 = 0.86$ for *E. coli* and $R^2 = 0.69$ for *S. epidermidis*). Experimental results showed that with increasing copper concentration, time and decreasing of frequency of RMF, the removal efficiency was increased. Accordingly, the water disinfection efficiency of 100% in terms of the independent variables was optimized, including copper concentration $c = 5\%$ and 2.5% w/w, time $t = 3$ h and 1.3 h and frequency of rotating magnetic field $f = 50$ Hz and 26.6 for *E.coli* and *S. epidermidis*, respectively. This study showed that response surface methodology is a useful tool for optimizing the operating parameters for photocatalytic disinfection process.

**Keywords**
photocatalysis, rotating magnetic field, titanium dioxide, disinfection, water purification

## 1. INTRODUCTION

The search for new methods of water treatment, both in terms of microbiology and removal of solid and organic contaminants, has been an ongoing research topic for many years (Burkett et al., 1981; Srivastav et al., 2020; Manimegalai et al., 2023). Slow climate change is causing a steady decline in freshwater resources, resulting in problems with the availability of drinkable water.

The most common methods of water treatment (sedimentation, boiling, filtration, chlorination, ozonation) are cost-effective processes, but can produce harmful by-products (Li et al., 2008). In contrast, photocatalysis is a promising solution with still untapped potential for water treatment applications. The reactive oxygen species, produced by the photocatalytic reaction, lead to the decomposition of organic compounds into carbon dioxide and water, as well as the complete mineralization of microorganisms present in water (Maness et al., 1999). To initiate the process, electromagnetic radiation is required, as well as a photocatalyst, which is excited under the influence of electromagnetic radiation with the energy required to overcome the band gap (Kumar et al., 2017).

Another simple non-chemical method of water purification is magnetic water treatment (MWT). This is a physical method in which water is passed through a magnetic field that causes changes in the configuration of ions present in the water, affecting changes in the zeta potential and solubility of chemical compounds in the water. It has also been suggested that the magnetic field affects the changes in the surface charges in water, which might increase the coagulation or precipitation of particles that flow through the magnetic field (Vaskina et al., 2020).

The photocatalytic reactions of killing bacteria with UV or even visible light have been widely studied in recent years (Djurišić et al., 2020; Gong et al., 2019; Habibi-Yangjeh et al., 2020; Sun and O'Connell, 2022; Upadhyaya and Rincón, 2019). Moreover, it has also been shown that bacteriostatic properties of various substances could be changed by the magnetic field (Jabłońska et al., 2022). Accordingly, this has motivated us to investigate the magnetically-assisted photocatalysis.

The necessity for the development of combined photocatalytic reactor with a multi-step water treatment system has already been proposed by McMichael et al. (2021). In our previous studies, it has been proven that modified titania photocatalysts could be activated by a rotating magnetic field (Paszkiewicz et al., 2022; Rakoczy et al., 2021). It is unlikely that a combination of photocatalytic disinfection and magnetic treatment does not result in the significant enhancement of the process effectiveness. It is believed that the results of these studies should enable to scale-up these reactors (this step is often the most complicated (Gkantzou et al., 2018; Lin et al., 2020)). It seems that the main obstacle against the use of new technology for industrial applications lies in the large dose of photocatalysts and high energy consumption (resulting from the use of lamps). Therefore, the present work has focused on a new "hybrid" reactor, i.e., a photoreactor with a rotating magnetic field generator. Moreover, a model for optimization of photocatalyst dose, magnetic fields frequency and light intensity has been proposed.

## 2. MATERIALS AND METHODS

### 2.1. Preparation of copper-modified titanium photocatalysts

The photocatalysts used in this study were prepared by simple photodeposition method. In brief, an aqueous solution of $CuSO_4$ was added to 500 mg of titania (commercial P25, homogenized first to get high uniformity (Wang et al., 2018)) and suspended in 250 ml of methanol (50 vol%). Then, the suspension was deaerated with argon (15 min), and the testing tube was sealed with a rubber septum and irradiated under UV/vis for one hour. After irradiation, copper-modified titania samples were washed three times with methanol and five times with water, centrifuged and dried in an oven at 120 °C overnight. Three samples were prepared with different contents of copper, i.e., 0.5, 2.0 and 5.0% (in respect of titania), which were named accordingly to the content of copper, i.e., 0.5 Cu@HomoP25, 2.0 Cu@HomoP25 and 5.0 Cu@HomoP25, respectively.

### 2.2. Experimental setup for antimicrobial tests

All experiments were performed using the experimental setup shown in Figure 1. The self-constructed magnetically-assisted reactor was applied for this study. The reactor consists of housing (1), in which the RMF generator (2) is embedded. RMF is generated by means of the stator of a three-phase induction motor, connected to a power source with an inverter (13). The cylindrical conduit (4) is equipped with light-emitting diode (LED) strips (3). Each LED strip consists of twelve 12-V diodes (white cold light IP20 SMD2835; LTC Sp. z o.o., Poland), linked to a power supply (14). A thermostat (12) is connected to the heat exchanger (10). The circulating pumps (9, 11) are used to flow the liquid through the coil. The cooling system keeps the constant temperature inside the reactor chamber at 37 ± 0.5 °C. The housing (1) is equipped with an inlet and outlet for oil. The heat exchanger (8), three-way valve (6) with controller (7), and circulating pump (5) are used as a thermostat of the RMF generator. The dielectric methyl silicone oil (Polsil, OM-10, "Silikony Polskie" Ltd., Poland) is used as the coolant of the RMF generator (2). Test tubes (15) (PP, 15 mL, SARSTEDT AG & Co. KG, Germany) are placed inside the reactor chamber. The applied RMF is characterized by the measurements of magnetic induction.

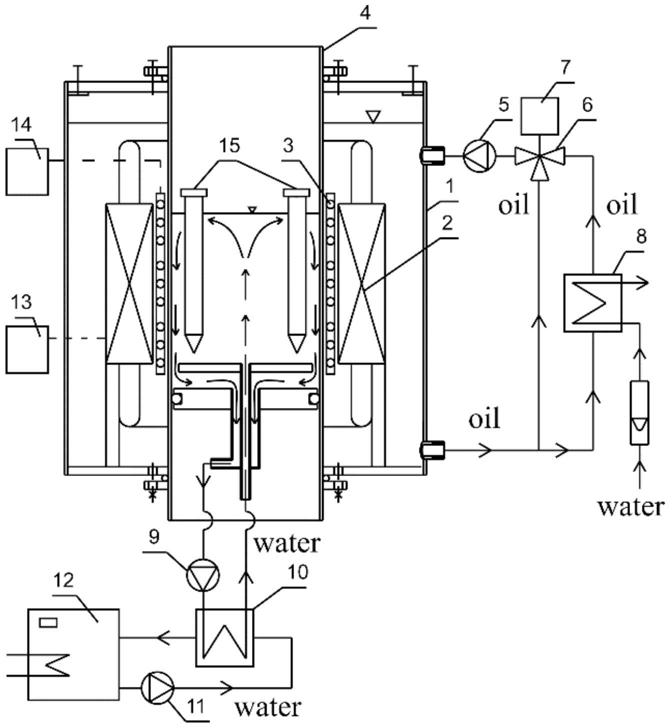


Figure 1. Experimental setup for antimicrobial tests.

### 2.3. Antimicrobial tests

Two reference bacterial strains, as follows: Gram-negative *Escherichia coli* (*E. coli*) K12 (ATCC 29425) and Gram-positive *Staphylococcus epidermidis* (*S. epidermidis*) (ATCC 49461), were used to determine the microbiological activity of copper-modified titania photocatalysts. Bacterial strains were cultivated in proper liquid media: nutrient broth (NB, BioMaxima S.A., Poland) for *E. coli* and Brain Heart Infusion broth (BHI, BioMaxima S.A, Poland) for *S. epidermidis*, for 24 h at 37 °C. Then, test cultures were centrifuged, and diluted using 0.85% sodium chloride buffer (NaCl, for *E. coli*) and phosphate-buffered saline (PBS, for *S. epidermidis*) to the final concentration of 0.5 in McFarland standard ($1 \cdot 10^8$ CFU·cm$^{-3}$).

The working bacterial suspension was obtained by adding 0.01 cm$^3$ of initial bacterial suspension to 1 L of proper buffer to obtain ca. $1 \cdot 10^3$ CFU·cm$^{-3}$ concentration of bacteria. Then, an appropriate weight of photocatalyst was added to 100 mL of the bacterial suspension to obtain a photocatalyst dose of 0.1 g·dm$^{-3}$.

In each test, 9 cm$^3$ of prepared suspension (with bacteria) was inserted into the reactor. Experiments were conducted in three variants, as follows: (i) in the presence of light, (ii) under rotating magnetic field (RMF) conditions, and (iii) the combination of light and RMF. Light-emitting diodes (LEDs) emitting radiation in the visible-light range were used as the light source. RMF in the frequencies of 5, 25, and 50 Hz was applied. Each experiment lasted 3 h, and the samples were taken in 0, 1, and 3 h of the process. A series of decimal working dilutions were made, and the diluted solutions were plated on solid media (Plate Count Agar for *E. coli*, Brain-Heart Infusion Agar for *S. epidermidis*). The positive control was conducted under the same conditions but without photocatalysts. The negative control experiment was conducted in a thermostatic incubator, without light and magnetic field. The inoculated plates were incubated at 37 °C for 24 h. Then, visible colonies were counted and the results was presented as N* [log CFU/mL].

## 2.4. Characterization of the applied RMF

In this study, the RMF with the frequency equal to 5 Hz, 25 Hz and 50 Hz was applied. The values of magnetic induction at different points inside the cylindrical process chamber were measured with the transverse Hall probe (STD18-0404), connected to the Gauss meter (FW Bell 5180 Magnetometer Gauss meter; Magnetic Science Inc, USA) with the measurement accuracy equal to ±2.5% of the reading. The experiments were performed according to the procedure of Rakoczy and Masiuk (2011). The contour patterns of the spatial distributions of the magnetic field in the selected cross-section of the RMF generator are shown in Figure 2. It should be noticed that the maximum values of magnetic induction were in the area near the RMF generator. The values of magnetic induction decreased towards the centre of the RMF generator. According to the experimental data, the values of magnetic induction are spatially distributed in the volume of the RMF generator. Therefore, the applied RMF might be characterized by employing the averaged values of magnetic induction.

Based on the experimental results, the obtained maximum and average values of the magnetic induction for the tested frequencies of the electrical current are listed in Table 1.

Table 1. The maximum and averaged values of the magnetic induction for the selected cross-sections of the RMF generator.

| Frequency of electrical current | The maximum value of magnetic induction for the selected cross-section of the RMF generator | The average value of magnetic induction for the selected cross-section of the RMF generator |
|---|---|---|
| 5 Hz | 25.36 mT | 13.13 mT |
| 25 Hz | 37.06 mT | 18.40 mT |
| 50 Hz | 42.64 mT | 19.92 mT |

The influence of individual variables from experiments was analysed with Statistica 13.3, and the data were fitted for the regression analysis to optimize the variables in the photocatalytic disinfection experiments. The evaluation of the statistical significance and quality of the model was obtained by an analysis of variance (ANOVA) test. The performance of the response surface was analysed with the regression polynomial equation. The regression coefficients of linear, quadratic, and interaction terms could be obtained by ANOVA analysis.

# 3. RESULTS AND DISCUSSION

The changes in the number of viable bacteria during the water disinfection process assisted with the rotating magnetic field are presented in Table 2, while those under LED light in Table 3.

It was found that single-step disinfection, i.e., only magnetic field or LED light, did not affect significantly the number of bacteria, which was further confirmed by the results of positive control experiments (Table 2 and Table 3). Under RMF exposition, the reduction of bacteria number depends mainly on the type of used photocatalyst. It has been found that 0.5 Cu@HomoP25 photocatalyst was the least active against both bacteria strains under magnetic field and irradiation. Under the same conditions, 5.0 Cu@HomoP25 exhibited the best bactericidal properties (Table 1 and Table 2). The application of photocatalysts with larger content of copper (2.0 Cu@HomoP25 and 5.0 Cu@HomoP25) and a rotat-

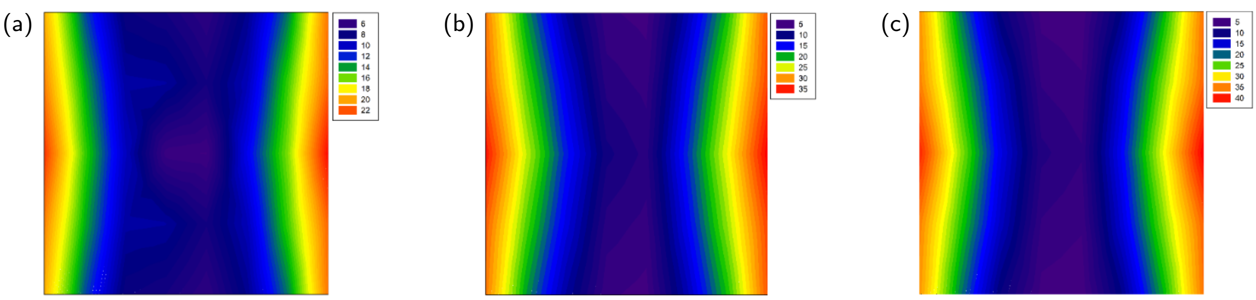

Figure 2. The contour pattern of the spatial distribution of the magnetic induction in the selected cross-section of the magnetically assisted photoreactor (MAP) for the frequency of the electrical current equal to a) 5 Hz; b) 25 Hz and c) 50 Hz.

Table 2. The changes in bacterial number during the water disinfection process assisted with the rotating magnetic field (without light).

| | | 0.5 Cu@HomoP25 | | | 2.0 Cu@HomoP25 | | | 5.0 Cu@HomoP25 | | | Positive control | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Time [h] | 0 | 1 | 3 | 0 | 1 | 3 | 0 | 1 | 3 | 0 | 1 | 3 |
| 5 Hz | | | | | | | | | | | | | |
| Bacterial number [logCFU × $mL^{-1}$] | *E. coli* | 2.49 | 1.51 | 1.26 | 2.49 | 0 | 0 | 2.49 | 0 | 0 | 2.49 | 2.43 | 2.35 |
| | | $\Delta = 1.3$ | | | $\Delta = 2.49$ | | | $\Delta = 2.49$ | | | $\Delta = 0.14$ | | |
| | *S. epidermidis* | 2.83 | 2.54 | 2.56 | 3.83 | 2.69 | 2.48 | 2.83 | 2.41 | 0 | 2.83 | 2.69 | 2.65 |
| | | $\Delta = 0.27$ | | | $\Delta = 1.35$ | | | $\Delta = 3.83$ | | | $\Delta = 0.18$ | | |
| 25 Hz | | | | | | | | | | | | | |
| Bacterial number [logCFU × $mL^{-1}$] | *E. coli* | 3.03 | 1.54 | 1.82 | 2.49 | 0 | 0 | 3.03 | 0 | 0 | 3.03 | 2.57 | 2.30 |
| | | $\Delta = 1.21$ | | | $\Delta = 2.49$ | | | $\Delta = 3.03$ | | | $\Delta = 0.73$ | | |
| | *S. epidermidis* | 2.91 | 2.55 | 2.17 | 2.91 | 0 | 0 | 2.84 | 0 | 0 | 2.91 | 2.91 | 2.85 |
| | | $\Delta = 0.74$ | | | $\Delta = 2.91$ | | | $\Delta = 2.84$ | | | $\Delta = 0.06$ | | |
| 50 Hz | | | | | | | | | | | | | |
| Bacterial number [logCFU × $mL^{-1}$] | *E. coli* | 2.84 | 0 | 0 | 2.84 | 1.6 | 0 | 2.84 | 0 | 0 | 2.84 | 2.48 | 2.43 |
| | | $\Delta = 2.84$ | | | $\Delta = 2.84$ | | | $\Delta = 2.84$ | | | $\Delta = 0.41$ | | |
| | *S. epidermidis* | 3.09 | 2.76 | 2.84 | 3.09 | 2.99 | 2.81 | 3.09 | 0 | 0 | 3.09 | 3.09 | 3.16 |
| | | $\Delta = 0.25$ | | | $\Delta = 0.28$ | | | $\Delta = 3.09$ | | | $\Delta = -0.07$ | | |

Table 3. The changes in the number of viable bacteria during the photocatalytic water disinfection process (without the rotating magnetic field).

| | | 0.5 Cu@HomoP25 | | | 2.0 Cu@HomoP25 | | | 5.0 Cu@HomoP25 | | | Positive control | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Time [h] | 0 | 1 | 3 | 0 | 1 | 3 | 0 | 1 | 3 | 0 | 1 | 3 |
| Bacterial number [logCFU × $mL^{-1}$] | *E. coli* | 2.49 | 2.16 | 1.86 | 2.49 | 1.30 | 0.00 | 2.49 | 0.00 | 0.00 | 2.49 | 2.46 | 2.43 |
| | | $\Delta = 0.63$ | | | $\Delta = 2.49$ | | | $\Delta = 2.49$ | | | $\Delta = 0.6$ | | |
| | *S. epidermidis* | 3.12 | 3.04 | 2.97 | 3.12 | 3.04 | 0.00 | 3.12 | 0.00 | 0.00 | 3.12 | 3.53 | 3.98 |
| | | $\Delta = 0.15$ | | | $\Delta = 3.12$ | | | $\Delta = 3.12$ | | | $\Delta = -0.86$ | | |

ing magnetic field with a frequency of 5 Hz caused complete disinfection of water after 1 h. The gram-negative bacteria *E. coli* were more susceptible to the disinfection process activated under RFM or LED light. It has been proven that 2.0 Cu@HomoP25 and 5.0 Cu@HomoP25 photocatalysts under magnetic field in the frequency range between 5 and 50 Hz were efficient to remove these bacteria from the water within 1 h (Table 2). In turn, the same efficiency against gram-positive bacteria *S. epidermidis* was obtained only for 2.0 Cu@HomoP25 and 5.0 Cu@HomoP25 photocatalysts activated by RMF with higher frequencies (25 or 50 Hz). Similar results have already been obtained for platinum-modified titania as described in previous report (Paszkiewicz et al., 2022). When only LED light was applied, the photocatalyst containing 5% of copper (5.0 Cu@HomoP25) caused complete inactivation of *E. coli* and *S. epidermidis* after 1 h (Table 3).

The effectiveness of the photocatalytic disinfection process with copper-modified photocatalysts conducted in a hybrid photoreactor (irradiation and rotating magnetic field) is presented in Figures 3–5.

Negative control experiments (without photocatalyst) showed that neither light nor RMF significantly altered the viability of bacteria (Figures 3–5). The photocatalyst 2.0 Cu@HomoP25 activation with LED light and a rotating magnetic field with frequency from 5 to 50 Hz resulted in complete disinfection of water after 1 h (Figures 3–5). The sole exception to this was *S. epidermidis* experiment conducted under frequency of 5 Hz (Figure 3b). The weakest bactericidal action exhibited photocatalyst with the lowest copper content (0.5 Cu@HomoP25), regardless of the field parameters used (Figures 3–5). These findings clearly indicate that copper has a positive impact on water disinfec-

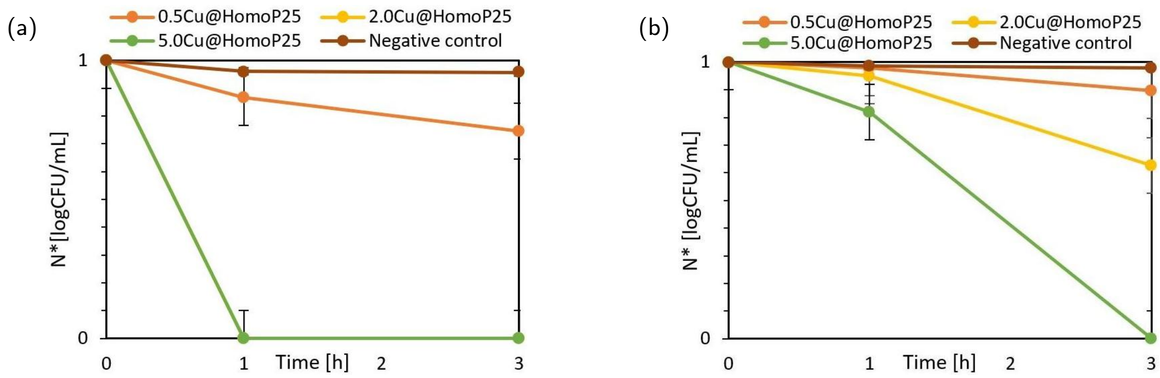


Figure 3. The influence of the copper-modified HomoP25 and RMF with the frequency of 5 Hz on the growth of *E. coli* (a) and *S. epidermidis* (b).

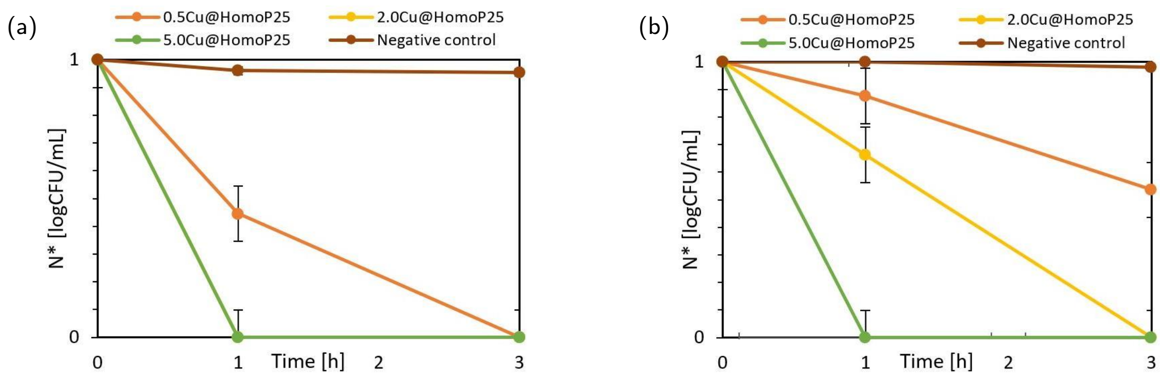


Figure 4. The influence of the copper-modified HomoP25 and RMF with the frequency of 25 Hz on the growth of *E. coli* (a) and *S. epidermidis* (b).

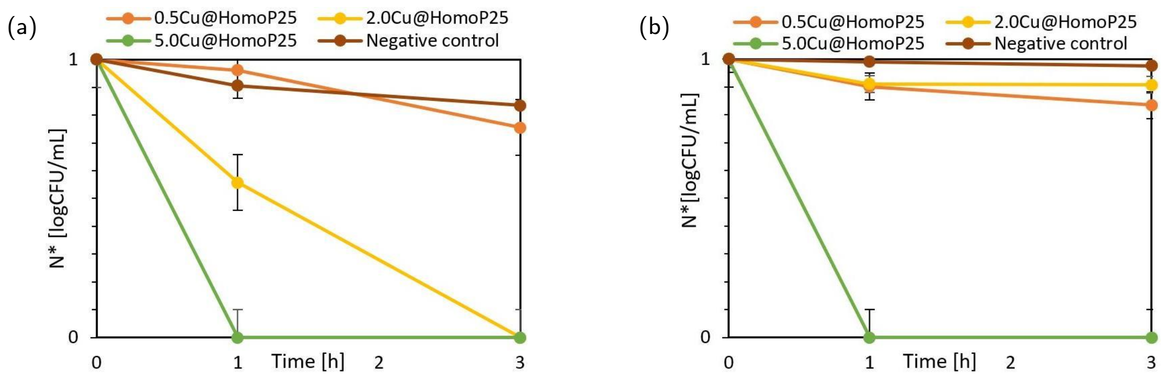


Figure 5. The influence of the copper-modified HomoP25 and RMF with the frequency of 50 Hz on the growth of *E. coli* (a) and *S. epidermidis* (b).

tion efficiency. Both metallic copper (e.g., released from the photocatalyst surface) and copper oxides might play a crucial role in killing bacteria. The mechanism of action has already been described in previous papers on copper-modified photocatalysts (e.g., Rychtowski et al., 2022; Wang et al., 2021). As shown by Rychtowski et al. (2022), total water disinfection is possible in less than 30 minutes for reduced $Cu–TiO_2$ under artificial solar irradiation. It is noteworthy that in that study, the high-power bulb was used (ULTRA-VITALUX 230V E27/ES, OSRAM 300W), whereas here low-intensity source (LED light; 7 $W\cdot m^{-2}$) was applied. Moreover, here the photocatalytic process is accelerated by the rotating magnetic field (RMF). It is thought that the design of photocatalytic reactor assisted with the rotating magnetic field for water disinfection should be economically viable (compared to photoreactors equipped with UV-A lamps). Indeed, the maximum cost energy for the applied RMF apparatus is equal to about 3 Euro for 24 h of operation time. The power requirements of 250 $m^3$ bioreactor are varied between 2–10 $kWh\cdot m^{-3}$ (Meyer et al., 2017). It should be noticed that the power consumption for the designed lab-scale reactor for water disinfection should be approximately equal. Economic analysis points out that each 1 USD, invested in drinking water sanitation, would yield a potential economic return of 74 USD (Noga and Wolbring, 2012). According to many authors, the application of this method allowed to reduce the cost of expensive analysis methods by minimalising many experiments (Kumari et al., 2019; Pandey et al., 2020).

Taking into account that complete photocatalytic disinfection of water in a hybrid reactor with a rotating magnetic field generator is possible after 1 h of the process, the optimization of process parameters, i.e., the copper content in the photocatalyst, the processing time and the frequency of the magnetic field, must be conducted.

The following quadratic equation might be considered as the ultimate model, resulting from statistical analysis in terms of coded factors of removal efficiency in magnetically-assisted photoreactor, as follows:

a) for *E. coli*

$$N^* = 1.480 - 0.467x_1 + 0.071x_1^2 - 0.737x_2 + 0.201x_2^2 - 0.040x_1x_2 \qquad (1)$$

b) for *S. epidermidis*

$$N^* = 1.229 - 0.035x_1 + 0.008x_1^2 - 0.321x_2 + 0.077x_2^2 - 0.051x_1x_2 \qquad (2)$$

where: $x_1$ – Cu content [%], $x_2$ – time [h], $x_3$ – frequency of magnetic field [Hz].

The empirical quadratic model for the response of the photocatalytic disinfection process, conducted in the hybrid photoreactor in terms of process variables was plotted in 3D diagrams (Figs. 6 and 7) to investigate the interaction between the variables and to determine the optimum combination of studied parameters for maximum removal of bacteria from contaminated water.

The quality of the models fitted was assessed with coefficients of correlation ($R^2$). The validity of the fitted model was evaluated through analysis of variance (ANOVA), and its statistical significance was controlled by $F$-test. The results of the analysis for the quadratic model are given in Tables 4 (*E. coli*) and 5 (*S. epidermidis*).

The results presented herein demonstrate a statistically significant reduction of *E. coli* and *S. epidermidis* from water, placed in the hybrid photoreactor assisted with the rotating magnetic field. The disinfection process appears to be related to multiple factors present in the experimental setting, namely: the type of photocatalyst (copper content), frequency of RMF, and time.

ANOVA analysis (Table 4 and Table 5) indicates that the model is statistically significant at 95% confidence level (Table 4, Table 5), with Fisher's test ($F$ value) and very low probability ($P$ value). The quadratic form of the model was chosen to explain the relationships between the studied independent factors, and the response (reduction of bacterial number) was found to satisfactorily represent the photocatalytic disinfection process.

Figures 6a and 7a show the effect of the most important parameters – Cu content and reaction time on the efficiency of bacteria removal (Tables 4 and 5), i.e., with an increase in Cu and extension of the process duration, the bacteria removal efficiency is increased. The reason could be an increase of

Table 4. ANOVA test for removal of *E. coli* from water (red – statistically important factors).

| Factor | Sum of Square | Degree of freedom | Mean Square | F-value | p-value |
|---|---|---|---|---|---|
| $x_1$ | 1.530778 | 1 | 1.530778 | 31.95194 | 0.000029 |
| $x_1^2$ | 0.592889 | 1 | 0.592889 | 12.37537 | 0.002640 |
| $x_2$ | 2.623159 | 1 | 2.623159 | 54.75320 | 0.000001 |
| $x_2^2$ | 0.936589 | 1 | 0.936589 | 19.54942 | 0.000374 |
| $x_3$ | 0.001864 | 1 | 0.001864 | 0.03890 | 0.845990 |
| $x_3^2$ | 0.010654 | 1 | 0.010654 | 0.22238 | 0.643229 |
| $x_1x_2$ | 0.240865 | 1 | 0.240865 | 5.02758 | 0.038572 |
| $x_1x_3$ | 0.001309 | 1 | 0.001309 | 0.02732 | 0.870665 |
| $x_2x_3$ | 0.002832 | 1 | 0.002832 | 0.05910 | 0.810830 |
| Error | 0.814449 | 17 | 0.047909 | | |
| Total SS | 5.716179 | 26 | | | |
| adjusted $R^2$ | 0.782 | | | | |
| predicted $R^2$ | 0. 85752 | | | | |

Table 5. ANOVA test for removal of *S. epidermidis* from water (red – statistically important factors).

| Factor | Sum of Square | Degree of freedom | Mean Square | F-value | p-value |
|---|---|---|---|---|---|
| $x_1$ | 1.170598 | 1 | 1.170598 | 24.31765 | 0.000127 |
| $x_1^2$ | 0.007588 | 1 | 0.007588 | 0.15763 | 0.696291 |
| $x_2$ | 1.625227 | 1 | 1.625227 | 33.76196 | 0.000021 |
| $x_2^2$ | 0.139499 | 1 | 0.139499 | 2.89791 | 0.106908 |
| $x_3$ | 0.044325 | 1 | 0.044325 | 0.92079 | 0.350717 |
| $x_3^2$ | 0.184855 | 1 | 0.184855 | 3.84012 | 0.066646 |
| $x_1x_2$ | 0.386752 | 1 | 0.386752 | 8.03427 | 0.011443 |
| $x_1x_3$ | 0.034373 | 1 | 0.034373 | 0.71406 | 0.409836 |
| $x_2x_3$ | 0.013808 | 1 | 0.013808 | 0.28685 | 0.599182 |
| Error | 0.818343 | 17 | 0.048138 | | |
| Total SS | 4.041363 | 26 | | | |
| adjusted $R^2$ | 0.690 | | | | |
| predicted $R^2$ | 0.795 | | | | |

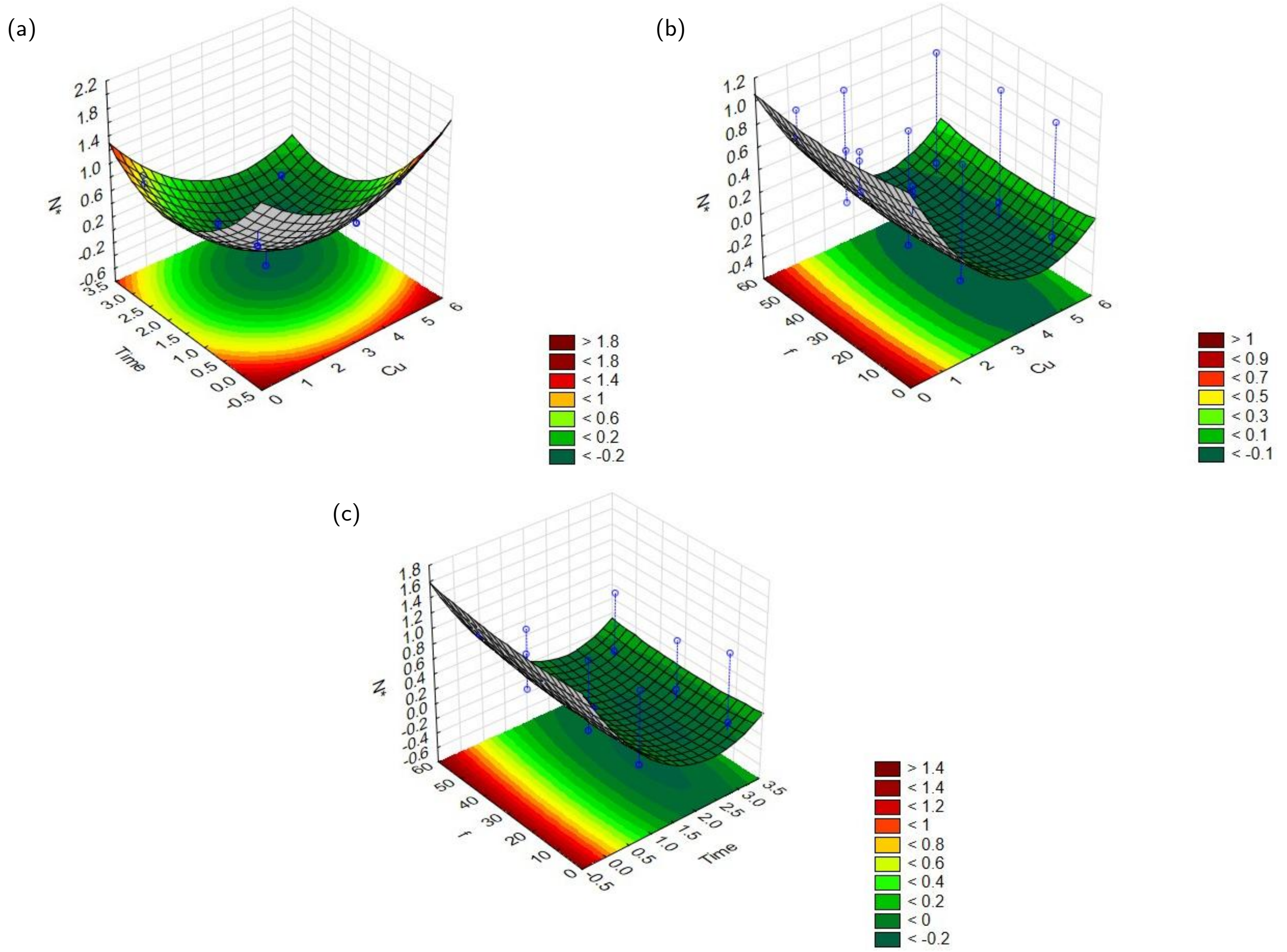

Figure 6. 3D plots of antibacterial potential of catalyst HomoP25 with the various Cu content [%], time of the process [h] and magnetic field frequency [Hz] against *E. coli*.

copper ions, released during the process, as well as enhanced generation of reactive oxygen species. With increasing processing time from 1 to 3 h, removal of bacteria increased and the maximum removal efficiency was obtained at 3 h. In fact, with increasing reaction time, reactive oxygen species from the photocatalytic process have more time to react with bacteria resulting in the increase of oxidative stress and killing efficacy.

In addition, the increase of RMF frequency over 30 Hz did not have a positive effect on water disinfection efficiency (Figures 6b, 7b). Figures 6b– 6c and 7b–7c analysis revealed that the effects of RMF frequency were less significant than copper concentration and process time. Interestingly, it has been reported that sufficient electric field intensity could increase electric conductivity and permeability of the cell membrane (Konopacki et al., 2019). However, in this study, the results of photocatalytic disinfection obtained for high (50 Hz) and low (5 Hz) frequencies of magnetic field were similar (Figs. 3–5). Accordingly, it might be concluded that there is no need to use expensive high-voltage generators (due to the high electrical current needed for their work).

Moreover, the optimization of the disinfection process enables to determine the optimum content of copper (in photocatalyst) and frequency of RMF to carry out the process in the shortest time. Accordingly, the optimum working conditions for *E. coli* bacteria are, as follows: $c = 5\%$; $t = 3$ h; $f = 50$ Hz, and for *S. epidermidis* $c = 2.5\%$; $t = 1.3$ h; $f = 26.6$ Hz, where $c$ – Cu content in HomoP25 [%], $f$ – frequency of rotating magnetic field [Hz], $t$ – time [h].

All photocatalysis reactions undergo via photoinduced intermolecular electron tranfer. It has been proposed by Wamser et al. (1981) that magnetic field might be useful in enhancing the separation of charge carriers, and thus enhancing the efficiency of photocatalytic reactions. However, it has also been reported that magnetic field could suppress the efficiency of photocatalysis reactions, e.g., when radical species diffuse to the catalyst surface, an applied magnetic field would interfere with the reactivity of the radical species, e.g., paramagnetic species responsible for the photocatalysis could become paired (Kiwi, 1983). Therefore, it is necessary to carry out further studies on the photocatalytic mechanism of bacterial degradation under rotating magnetic field.

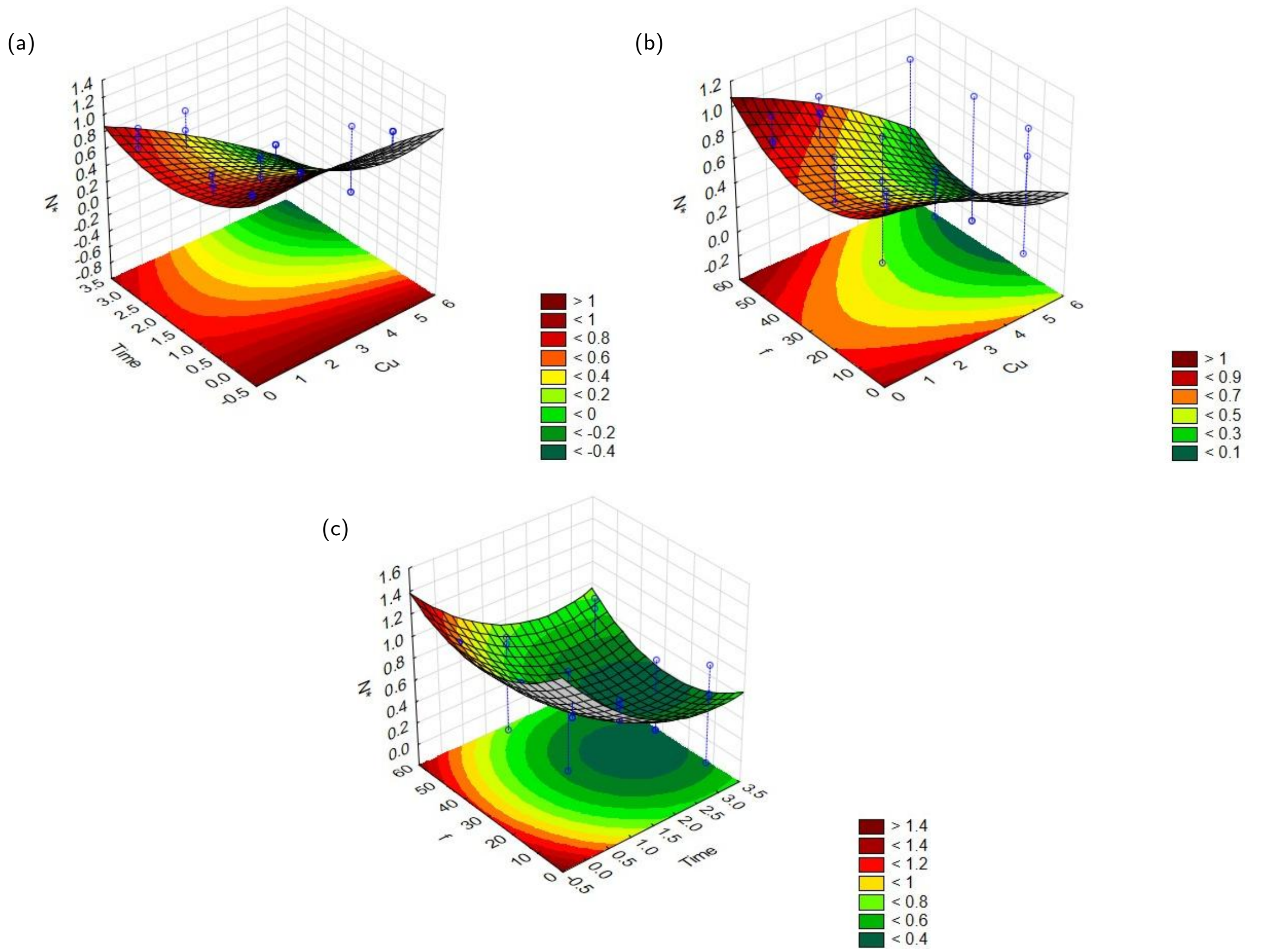


Figure 7. 3D plots of antibacterial potential of catalyst HomoP25 with the various Cu content [%], time of the process [h] and magnetic field frequency [Hz] against *S. epidermidis*.

## 4. CONCLUSIONS

The new magnetic-hybrid photoreactor assisted with the rotating magnetic field (RMF) has proven to be an excellent tool to carry out disinfection process. The copper-modified titania photocatalysts have shown high activity in removal of gram-negative bacteria *Escherichia coli* and *Staphylococcus epidermidis*. The disinfection efficiency of over 99.99% was achieved within only 1 h of low-intensity light irradiation (LED) when the copper content reached 5% (in respect to titania). Moreover, it has been shown that the optimization of process parameters, i.e., copper content [%], frequency of RMF [Hz] and time of disinfection process, is crucial for the design of cheap and efficient water purification systems.

An analysis of variance (ANOVA) test was employed for the optimization of the water disinfection process using copper-modifed titania in a hybrid photoreactor assisted with the rotating magnetic field. By using the regression analysis method, the main parameters, including copper content, duration of the process and frequency of magnetic field, were examined. This strategy exhibits the adequate performance in optimizing the formula. A second-order polynomial model was developed using multiple linear regression analysis. Statistical test (ANOVA) indicated a good agreement between experimental data and the developed model ($R^2$ from 0.69 for *S. epidermidis* and 0.86 for *E. coli*). The optimal operating conditions were determined using numerical optimization techniques. For this purpose, the maximum *Escherichia coli* and *Staphylococcus epidermidis* removal from the water was optimized for titania photocatalyst for *E. coli* bacteria $c = 5\%$; $t = 3$ h; $f = 50$ Hz, and for *S. epidermidis* $c = 2.5\%$; $t = 1.3$ h; $f = 26.6$ Hz.

It is believed that the further development of this method has the potential to eliminate pathogens responsible for waterborne diseases. The next study would focus on various pathogens (bacteria, viruses, and protozoa e.g. *Giardia lamblia*) and raw water (from lakes, rivers, or streams and many groundwater sources). Moreover, the mechanism study on this hybrid system should allow the rational design of water purification technology.

## ACKNOWLEDGMENTS

*The authors are grateful for the financial support from the National Science Center within the Preludium Grant (Grant No. 2021/41/N/ST8/00482).*

## SYMBOLS

| | |
|---|---|
| $c$ | content of Cu, % |
| $t$ | time of process, h |
| $f$ | frequency of magnetic field, Hz |
| $N^*$ | bacterial number, logCFU $\times$ mL$^{-1}$ |
| $R^2$ | coefficient of determination |
| *F-value* | value of Fisher's test |
| *p-value* | probability value |
| $x$ | factor for ANOVA analysis |

*Subscripts*

| | |
|---|---|
| *1, 2, 3* | factor number |

## REFERENCES

Burkett H.D., Faison J.H., Kohl H.H., Wheatley W.B., Worley S.D., Bodor N., 1981. A novel chloramine compound for water disinfection. *J. Am. Water Resour. Assoc.*, 17, 874–876. DOI: 10.1111/j.1752-1688.1981.tb01311.x.

Djurišić A.B., He Y., Ng A.M.C., 2020. Visible-light photocatalysts: Prospects and challenges. *APL Mater.*, 8, 030903. DOI: 10.1063/1.5140497.

Gkantzou E., Patila M., Stamatis H., 2018. Magnetic microreactors with immobilized enzymes – from assemblage to contemporary applications. *Catalysts*, 8, 282. DOI: 10.3390/catal8070282.

Gong M., Xiao S., Yu X., Dong C., Ji J., Zhang D., Xing M., 2019. Research progress of photocatalytic sterilization over semiconductors. *RSC Adv.*, 9, 19278–19284. DOI: 10.1039/c9ra01826c.

Habibi-Yangjeh A., Asadzadeh-Khaneghah S., Feizpoor S., Rouhi A., 2020. Review on heterogeneous photocatalytic disinfection of waterborne, airborne, and foodborne viruses: Can we win against pathogenic viruses? *J. Colloid Interface Sci.*, 580, 503–514. DOI: 10.1016/j.jcis.2020.07.047.

Jabłońska J., Dubrowska K., Gliźniewicz M., Paszkiewicz O., Augustyniak A., Grygorcewicz B., Konopacki M., Markowska-Szczupak A., Kordas M., Dołęgowska B., Rakoczy R., 2022. Chapter Two – The use of the electromagnetic field in microbial process bioengineering, In: Gadd G.M., Sariaslani S. (Eds.), *Advances in Applied Microbiology*. Academic Press, 121, 27–72. DOI: 10.1016/bs.aambs.2022.08.002.

Kiwi J., 1983. Magnetic field effects on photosensitized electron transfer reactions in the presence of titanium dioxide and cadmium sulfide-loaded particles. *J. Phys. Chem.*, 87, 2274–2276. DOI: 10.1021/j100236a005.

Konopacki M., Rakoczy R., 2019. The analysis of rotating magnetic field as a trigger of Gram-positive and Gram-negative bacteria growth. *Biochem. Eng. J.*, 141, 259–267. DOI: 10.1016/j.bej.2018.10.026.

Kumar A., Pandey G., 2017. A review on the factors affecting the photocatalytic degradation of hazardous materials. *Mater. Sci. Eng. Int. J.*, 1, 106–114. DOI: 10.15406/mseij.2017.01.00018.

Kumari M., Gupta S.K., 2019. Response surface methodological (RSM) approach for optimizing the removal of trihalomethanes (THMs) and its precursor's by surfactant modified magnetic nanoadsorbents (sMNP) – An endeavor to diminish probable cancer risk. *Sci. Rep.* 9, 18339. DOI: 10.1038/s41598-019-54902-8.

Li Q., Mahendra S., Lyon D.Y., Brunet L., Liga M.V., Li D., Alvarez P.J.J., 2008. Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and implications. *Water Res.*, 18, 4591–4602. DOI: 10.1016/j.watres.2008.08.015.

Lin L., Jiang W., Xu X., 2020. A critical review of the application of electromagnetic fields for scaling control in water systems: mechanisms, characterization, and operation. *NPJ Clean Water*, 3, 25. DOI: 10.1038/s41545-020-0071-9.

Maness P.C., Smolinski S., Blake D.M., Huang Z., Wolfrum E.J., Jacoby W.A., 1999. Bactericidal activity of photocatalytic $TiO_2$ reaction: toward an understanding of its killing mechanism. *Appl. Environ. Microbiol.*, 65, 4094–4098. DOI: 10.1128/AEM.65.9.4094-4098.1999.

Manimegalai S., Vickram S., Deena S.R., Rohini K., Thanigaivel S., Manikandan S., Subbaiya R., Karmegam N., Kim W., Govarthanan M., 2023. Carbon-based nanomaterial intervention and efficient removal of various contaminants from effluents – A review. *Chemosphere*, 312, 137319. DOI: 10.1016/j.chemosphere.2022.137319.

McMichael S., Fernández-Ibáñez P., Byrne J.A., 2021. A review of photoelectrocatalytic reactors for water and wastewater treatment. *Water*, 13, 1198. DOI: 10.3390/w13091198.

Meyer H.P., Minas W., Schmidhalter D., 2017. Industrial-scale fermentation, In: Wittmann C., Liao J.C. (Eds.), *Industrial biotechnology*. Wiley-VCH Verlag GmbH & Co. KGaA, New York, 1–53. DOI: 10.1002/9783527807833.ch1.

Noga J., Wolbring G., 2012. The economic and social benefits and the barriers of providing people with disabilities accessible clean water and sanitation. *Sustainability*, 4, 3023–3041. DOI: 10.3390/su4113023.

Pandey N., Thakur C., 2020. Statistical comparison of response surface methodology – based central composite design and hybrid central composite design for paper mill wastewater treatment by electrocoagulation. *Process Integr. Optim. Sustain.*, 4, 343–359. DOI: 10.1007/s41660-020-00123-w.

Paszkiewicz O., Wang K., Rakoczy R., Kordas M., Leniec G., Kowalska E., Markowska-Szczupak A., 2022. Antimicrobial properties of pristine and Pt-modified titania P25 in rotating magnetic field conditions. *Chem. Eng. Process. Process Intensif.*, 178, 109010. DOI: 10.1016/j.cep.2022.109010.

Rakoczy R., Kordas M., Markowska-Szczupak A., Konopacki M., Augustyniak A., Jabłońska J., Paszkiewicz O., Dubrowska K., Story G., Story A., Ziętarska K., Sołoducha D., Borowski T., Roszak M., Grygorcewicz B., Dołęgowska B., 2021. Studies of a mixing process induced by a rotating magneticfield with the application of magnetic particles. *Chem. Process Eng.*, 42, 157–172. DOI: 10.24425/cpe.2021.138922.

Rakoczy R., Masiuk S., 2011. Studies of a mixing process induced by a transverse rotating magnetic field. *Chem. Eng. Sci.*, 66, 2298–2308. DOI: 10.1016/j.ces.2011.02.021.

Rychtowski, P., Paszkiewicz, O., Román-Martínez M.C., Lillo-Ródenas M.Á., Markowska-Szczupak A., Tryba B., 2022. Impact of $TiO_2$ Reduction and Cu doping on bacteria inactivation under artificial solar light irradiation. *Molecules*, 27, 9032. DOI: 10.3390/molecules27249032.

Srivastav A.L., Patel N., Chaudhary V.K., 2020. Disinfection by-products in drinking water: Occurrence, toxicity and abatement. *Environ. Pollut.*, 267, 115474. DOI: 10.1016/j.envpol.2020.115474.

Sun Y., O'Connell D.W., 2022. Application of visible light active photocatalysis for water contaminants: A review. *Water Environ. Res.*, 94, e220781. DOI: 10.1002/wer.10781.

Upadhyaya A., Rincón G., 2019. Visible-light-active noble-metal photocatalysts for water disinfection: A review. *J. Water Resour. Prot.*, 11, 1207–1232. DOI: 10.4236/jwarp.2019.1110070.

Vaskina I., Roi I., Plyatsuk L., Vaskin R., Yakhnenko O., 2020. Study of the magnetic water treatment mechanism. *J. Ecol. Eng.*, 21, 251–260. DOI: 10.12911/22998993/116341.

Wamser C.C., Otvos J.W., Calvin M., 1981. *Magnetic field effects on photosentisitized electron transfer reactions*. Lawrence Berkeley National Laboratory. LBNL Report #: LBL-12361. Retrieved from: https://escholarship.org/uc/item/8vt6s4hz.

Wang K., Bielan Z., Endo-Kimura M., Janczarek M., Zhang D., Kowalski D., Zielińska-Jurek A., Markowska-Szczupak A., Ohtani B., Kowalska E., 2021. On the mechanism of photocatalytic reactions on $Cu_xO@TiO_2$ core–shell photocatalysts. *J. Mater. Chem. A*, 9, 10135–10145. DOI: 10.1039/D0TA12472A.

Wang K., Wei Z., Ohtani B., Kowalska E., 2018. Interparticle electron transfer in methanol dehydrogenation on platinum-loaded titania particles prepared from P25. *Catal. Today*, 303, 327–333. DOI: 10.1016/j.cattod.2017.08.046.