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Antimicrobial properties of pristine and Pt-modified titania P25 in rotating magnetic field conditions

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ABSTRACT

Effective and cheap water purification is one of the most important tasks facing humanity. Among various methods of water treatment, heterogeneous photocatalysis is probably most recommended. However, the application of artificial sources of irradiation results in high investment and operating costs. Accordingly, either vis-responsive photocatalysts or different ways of photocatalyst activation should be developed. In the present study, rotating magnetic field (RMF) has been tested to inactivate gram-positive (*Staphylococcus epidermidis*) and gram-negative (*Escherichia coli*) bacteria in the presence of pristine and Pt-modified titania P25 photocatalyst. Liquid cultures of the bacteria have been exposed to the titania and RMF (RMF frequency of 1–50 Hz, RMF magnetic induction of ca. 19.92 mT, 180 min exposure time, temperature of incubation at 37 °C). It has been found that highly active titania photocatalyst might also work in the absence of photoirradiation but under RMF. Moreover, its modification with platinum besides highly improved photocatalytic activity (tested for two model reactions of oxidative decomposition of acetic acid and anaerobic dehydrogenation of methanol under UV/vis irradiation) results in significant enhancement of antimicrobial effect under RMF. Additionally, photocatalysts with larger content of oxidized forms of platinum show higher antimicrobial activity, and thus it is proposed that platinum oxides are more active than zero-valent platinum under RMF. This study provides evidence of antimicrobial effect of titania without photoirradiation, indicating that RMF might efficiently activate photocatalyst.

1. Introduction

One of the major challenges facing humanity is water pollution that has not only environmental impact, but also a major effect on human health. Lack of sanitation, safe water facilities and services, and poor hygiene are significant contributors to the high rates of waterborne diseases - an illness caused by pathogenic microorganisms that most commonly are transmitted in contaminated fresh water. This includes amebiasis (caused by protozoan *Entamoeba histolytica*), cholera (Gram-negative bacteria *Vibrio cholerea*), dysentery (a genus *Shigella* sp., *Salmonella* sp.), serious and fatal infections evoked by multiple drug-resistant bacteria AMR (Anti-Microbial Resistance), e.g., methicillin-resistant *Staphylococcus aureus* (MRSA), multidrug-resistant Gram-negative rods (MDR), e.g., *Escherichia coli, Klebsiella pneumoniae, Pseudomonas aeruginosa* etc., or viruses poliomyelitis (polio virus), virial hepatitis (*Hepatitis A and B*) and popular in recent times SARS (e.g. SARS-CoV-2) [1,2]. It is widely recognized that microbiological risk is considered as a top priority in drinking water management, and the microbiological quality of water should never be compromised. For that reason, particular attention should be paid to the development of an efficient method for water disinfection. Moreover, the focus is needed on new sanitation technologies involving low investment and operational costs of the treatment systems. One of the promising methods that can meet above mentioned requirements is photocatalysis, which is defined as light-initiated chemical reactions begun on the surface of irradiated photocatalysts [3]. Due to high stability, high activity, chemical inertness, fine optical properties and market availability, titanium(IV) oxide (TiO_2; titania; titanium dioxide) is one of the most investigated and used at present. However, the energy needed for titania excitation is quite high, reaching 3.2 eV for anatase and 3.02 eV for rutile (two most known

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titania polymorphs) that corresponds to 385 and 400 nm, respectively [4]. The wavelength of radiation in the range of 315–400 nm is defined as UVA, which comprises below 4 – 5% of solar terrestrial radiation since most of it is removed by stratospheric ozone. Accordingly, the low performance of titania under sunlight limits its broad commercialization [5,6]. In this regard, many ways of titania modification have been widely investigated, e.g., surface modification with noble metals (e.g., Au, Ag, Pt), heterojunction formation with metal oxides (e.g., ZnO, WO_3, Cu_2O/CuO, SiO, CrO) and doping with nonmetals (e.g., S, C, N [7–11]) and metals (e.g., Rh, Fe, Er [12–15]).

Additionally, it should be mentioned that from an economic point of view, photocatalytic process under artificial UVA light seems to be very expensive option for water disinfection, considering the costs of UV lamps, their part replacement and the overall energy consumption, as well as the post-separation of particulate photocatalyst after wastewater treatment, e.g., by expensive ultrafiltration. Considering these arguments, the magnetic nanomaterials seem to be the promising solution because of their target specificity, easy separation, high adsorption per unit area, as well as low maintenance [16]. Interestingly, the similarities between photocatalytic reactions and the nature of the magnetic field were shown by Kiwi in 1983 [17]. However, there are only several studies on the influence of a magnetic field on the heterogeneous photocatalysis. It is known that the magnetic fields might affect the recombination of cation and anion radicals and favor the separation of photogenerated holes and electrons during photocatalysis process, which causes the improvement of quantum yields of photocatalytic reactions [18]. However, there is a lack of knowledge concerning the influence of the magnetic field, especially rotating one, on the photocatalytic disinfection of water. Moreover, research on the influence of magnetic field on the microorganisms is very limited [18]. The biological effects depend critically on the physical characteristics of the magnetic signal, in particular the wave shape. For example, pulsed electric fields (PEF), applied for the nonthermal disinfection of water, provokes negative adjustment, e.g., reduction in bacteria vitality. Several different mechanisms of bacteria death have been proposed, such as damaging the cell membrane of the bacteria and affecting the cell transport mechanism or disruption of proteins and DNA [19,20]. Taking into account the contradictory results on bacteria inactivation, and also little understanding on the influence of magnetic fields on the photocatalytic process, this study on the disinfection assisted with rotating magnetic field (RMF) in the presence or absence of photocatalysts has been carried out. The RMF is a special case of the electromagnetic field that is created due to an interaction between the force vectors of the electromagnetic fields generated by the coils situated in the circle every 120°. The position of the magnetic field in the generator core is constant, nevertheless, the direction of the magnetic force changes, depending on the phase of the current propelling the windings [18]. Based on literature reports and own experience, it might be concluded that RMF influences and improves various processes [20–24]. However, the lack of knowledge about the impact of the external interactions, including the RMF and the synergistic effect of RMF and photocatalyst, on the wastewater processes has motivated us to perform the present study. Accordingly, this paper focuses on the examination of the effect of RMF on the antibacterial properties of pristine and Pt-modified titania photocatalysts.

2. Experimental details

2.1. Materials and reagents

Pristine and Pt-modified titania P25 (from Nippon Aerosil; known also as P25 from Evonik/Degussa) have been used in the present study as highly active photocatalysts. Titania P25 is probably the most known photocatalyst, because of very high photocatalytic activity in various reactions systems, and thus being commonly used as a reference. Besides its famousness, it is also highly nonuniform, i.e., with different ratio of anatase/rutile/noncrystalline component, and thus P25 sample was homogenized first by suspending it into water and freeze drying (HomoP25), as reported elsewhere [25]. Then, HomoP25 was modified with platinum (0.5 and 2.0 wt%) by photodeposition method. In brief, titania (500 mg) was suspended in aqueous methanol (50 vol%, 25 mL) to which aqueous solution of chloroplatinic acid (H_2PtCl_6) was added under continuous stirring. Then, air from the tube (55 mL pyrex glass) was purged by argon (Ar; anaerobic condition) or oxygen (O_2; aerobiotic condition) bubbling (ca. 15 min), the tube was sealed with a rubber septum, and irradiated (400 W high-pressure mercury arc, $\lambda > 290$ nm) under continuous stirring (1000 rpm) at constant temperature of 298 K in a thermostated water bath for 2 h. After irradiation, the samples were centrifuged, washed with methanol (3 times) and water (5 times), and freeze dried. Samples were named accordingly to the content of platinum (0.5Pt or 2.0Pt) and photodeposition conditions (Ar or O_2), e.g., 2.0Pt-HomoP25-Ar means that 2.0 wt% of platinum (in respect to titania) was photodeposited on HomoP25 under anaerobic conditions. The composition of pristine and Pt-modified P25 samples is shown in Table 1.

Samples were characterized by various methods, such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), diffuse reflectance spectroscopy (DRS) and scanning transmission electron microscopy (STEM), as follows:

XRD was used for measuring the crystalline size and crystalline composition of samples. The crystallinity was estimated by the internal standard method, with a highly crystalline nickel oxide (NiO) as the standard. In brief, 40 mg NiO (20.0 wt%) was mixed thoroughly with a 160 mg titania sample (80.0 wt%) by grinding in an agate mortar. XRD analysis was performed using a Rigaku intelligent X-ray diffraction system SmartLab, equipped with a sealed tube X-ray generator (a copper target; operated at 40 kV and 30 mA), a D/teX high-speed position sensitive detector system and an ASC-10 automatic sample changer. XRD analysis was performed for 2Θ range of 10–90°, scan speed of 1.0° min^{-1} and scan step of 0.008°. The obtained XRD patterns were analyzed by Rigaku PDXL, a crystal structure analysis package including, Rietveld analysis, installed in a computer controlling the diffractometer. To characterize the photoabsorption properties of titania samples, diffuse reflectance spectra (DRS) were recorded. The measurements were carried out on Jasco V-670 spectrophotometer equipped with a PIN-757 integrating sphere. The baseline was recorded using $BaSO_4$ as a reference. The morphology of samples was analyzed by scanning transmission electron microscopy (STEM, HITACHI HD-2000). STEM images were acquired at a wide range of magnifications (1500–1500000), for 200 kV accelerating voltage and 20-A emission current. X-ray photoelectron spectroscopy (XPS; JEOL JPC-9010MC) was used for studying the surface composition and oxidation states of elements. Usually, 50 scans were carried out and average data were used for analysis. Considering low content of Pt, 100 scans were performed. During the measurements, the main chamber pressure was kept below 5.0×10^{-6} Pa.

2.2. Photocatalytic activity test for chemical compounds

Bare and Pt-modified P25 samples were first tested under UV/vis irradiation for standard photocatalytic reactions, i.e., (1) oxidative decomposition of acetic acid under aerobic conditions (CO_2 system), and (2) dehydrogenation of methanol under anaerobic conditions (H_2 system).

In the case of oxidative decomposition of acetic acid, photocatalytic activity was examined by measuring an amount of evolved carbon dioxide (CO_2) from continuously stirred suspensions of a sample (50 mg) in aqueous solution of acetic acid (5.0 mL, 5.0 vol%) under UV/vis irradiation for every 20 min by gas chromatography (TCD-GC, Shimadzu GC-8A-IT). The photocatalytic activities in H_2 system were examined by measuring an amount of evolved H_2 from continuously stirred (1000 rpm) suspensions of a sample (50 mg) from a deaerated (15-min Ar pre-

Table 1
Crystalline properties of samples.

Sample	Composition (wt%)					Crystallite size (nm)			
	anatase	rutile	NC	Pt	PtO_x	anatase	rutile	Pt	PtO_x
HomoP25	77.0	13.8	9.2	-	-	25.3	39.6	-	-
2.0Pt-HomoP25-Ar	73.9	13.2	8.8	1.6	2.5	21.6	37.6	12.3	6.7
0.5Pt-HomoP25-O_2	75.6	13.6	9.0	0.3	1.5	21.7	39.5	1.0	8.5
2.0Pt-HomoP25- O_2	73.8	13.2	8.8	2.5	1.7	22.5	41.3	5.2	3.9

NC – non-crystalline content

bubbling) aqueous methanol solution (5.0 mL, 50 vol%).

2.3. Experimental set-up for disinfection in RMF

All measurements were performed using the experimental set-up shown in Fig. 1. The novel construction of the magnetically assisted reactor was applied for this study.

The magnetically assisted reactor consists of the housing (1), in which the RMF generator (2) is mounted. The cylindrical conduct (3) is centrally located in the housing (1) and the RMF generator (2). In the case of these investigations, the RMF is generated by means of the stator of three-phase induction motor. The cylindrical conduct (3) has a bottom (4) in which pipe-in-pipe inlet (5) and outlet (6) of reactor chamber are mounted. The cylindrical baffle (7) is mounted above the bottom (4). The diameter of this baffle is smaller than the internal diameter of the cylindrical conduct (3). The gap between the conduct and the baffle allows to flow the liquid to thermostat the process chamber (In the present study, demineralized water has been used.). The outlet (6) is connected to inlet (5) by the coil (9) that is placed in the thermostat (10). The circulating pump (8) is used to flow the liquid through the coil (9). The cooling system keeps the constant temperature inside the reactor chamber at 37±0.5°C. The housing (1) is equipped with inlet (11) and outlet (12) for liquid coolant. The heat exchanger (13) and circulating pump (14) are placed between the stubs (11) and (12). The dielectric oil is used as the coolant of the RMF generator (2). The application of this circuit allows to remove the excess heat produced by the RMF generator. Probes (15) with the rack (16) are placed inside the reactor chamber.

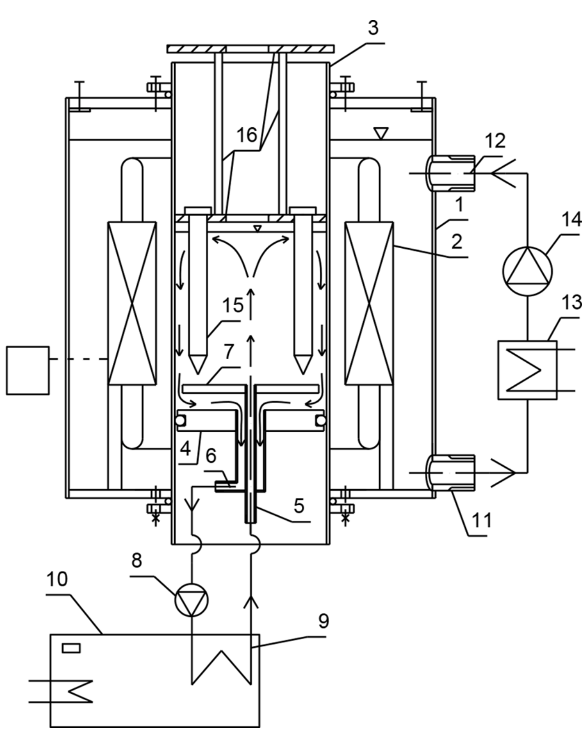

Fig. 1. Sketch of experimental set-up: 1 – housing; 2 – generator of RMF; 3 – cylindrical conduct; 4 – bottom; 5 – reactor chamber inlet; 6 – reactor chamber outlet; 7 – baffle; 8 - circulating pump; 9 – coil; 10 – thermostat; 11 – tank outlet; 12 – tank inlet; 13 – heat exchanger; 14 – circulating pump; 15 – probe; 16 – probe rack.

The applied RMF was characterized by the measurements of magnetic induction. The experiments were performed according to the procedure of Rakoczy and Masiuk [24]. The dependence of the magnetic induction on the frequency of RMF is shown in Fig. 2. It was found that the scatter of averaged values of magnetic induction as a function of RMF frequency can be defined as follows

In the case of this study, the RMF with the frequency equal to 50 Hz has been applied, and thus based on data shown in Fig. 2, the averaged value of the magnetic induction for this frequency is equal to about 19.92 mT.

2.4. Antibacterial tests

Two reference strains of bacteria: Gram-negative *Escherichia coli* K12 (ATCC 29425) and Gram-positive *Staphyloccocus epidermidis* (ATCC 49461) were used to determine antibacterial properties of photocatalysts under magnetic field condition. Two types of liquid media were used to cultivate tested microorganisms – nutrient broth (NB, BioMaxima S.A., Poland) for *E. coli* and Brain-Heart Infusion BHI (BioMaxima S.A., Poland) for *S. epidermidis*, in which bacteria were incubated for 24 h at 37 °C. Centrifuged test culture was diluted using 0.85% sodium chloride buffer (for *E. coli*) and phosphate-buffered saline (for *S. epidermidis*) to the final concentration of 0.5 in McFarland standard, ca. 1×10^8 CFU/mL.

2 mL bacterial suspension was added to the bottle with 198 mL of NaCl solution (for *E. coli*) or PBS solution (for *S. epidermidis*), and 5 mL of bacterial suspension was added to the bottle with 495 mL of TiO_2 suspension (0.1 g/L), to obtain a hundred-fold dilution. 5 mL of prepared bacterial suspension with TiO_2 and control sample only with bacteria were placed in 20 plastic tubes and inserted in two reactors (10 under magnetic field and 10 without magnetic field). Both reactors were thermostated to maintain the temperature at 37 °C. The magnetic field frequency was 50 Hz. Tubes that were placed in the reactor with magnetic field also contained metal balls to mix bacterial suspensions.

Each experiment lasted for 5 h, and samples were taken every hour, when a series of decimal dilutions were made (0.5 mL of working dilution with 4.5 mL of NaCl and PBS for *E. coli* and *S. epidermidis*, respectively). 0.25 mL diluted solutions were plated on appropriate solid media, i.e., Standard Plate Count Agar (PCA, BioMaxima S.A., Poland) for *E. coli* and Brain-Heart Infusion Agar (BHI, BioMaxima S.A., Poland) for *S. epidermidis*. The inculcated plates were incubated at 37 °C for 24 h. Then, visible colonies were counted and shown as logCFU/mL.

3. Results and discussion

3.1. Characterization of photocatalysts

Pristine titania is white, whereas its modification with platinum has caused the color change to grey for 0.5 wt% of Pt and black for larger content of metal, as shown in Fig. 3a. The photoabsorption properties of samples correlate with their color, as evident by DRS spectra in Fig. 3b.

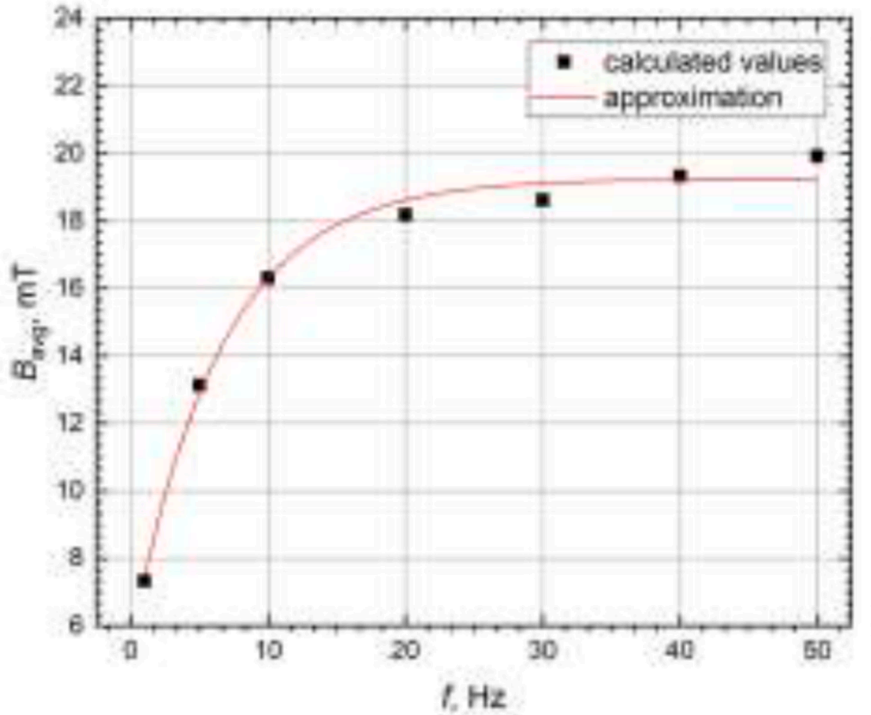

Fig. 2. Relation between the averaged values of magnetic induction (calculated values) and the RMF frequency.

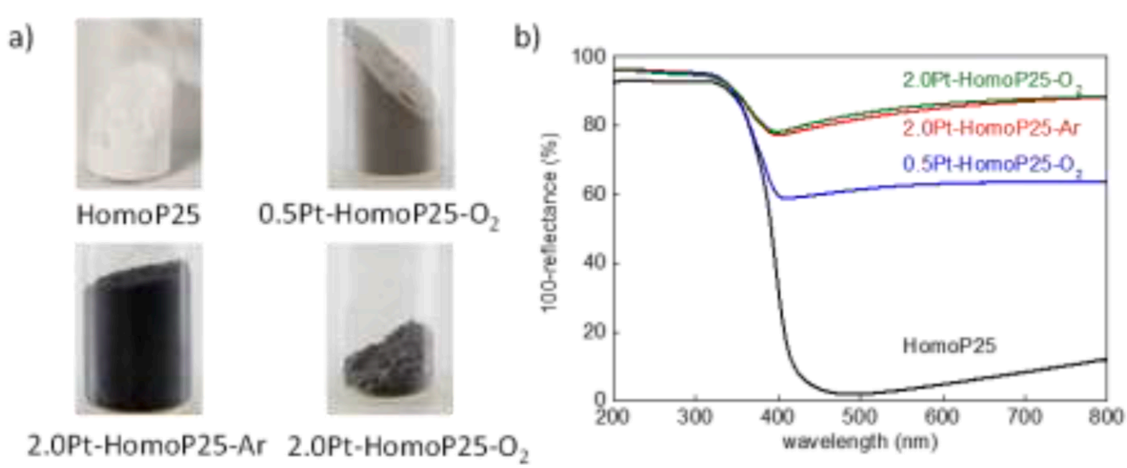

Fig. 3. Photoabsorption properties of samples: (a) the photographs, and (b) DRS spectra.

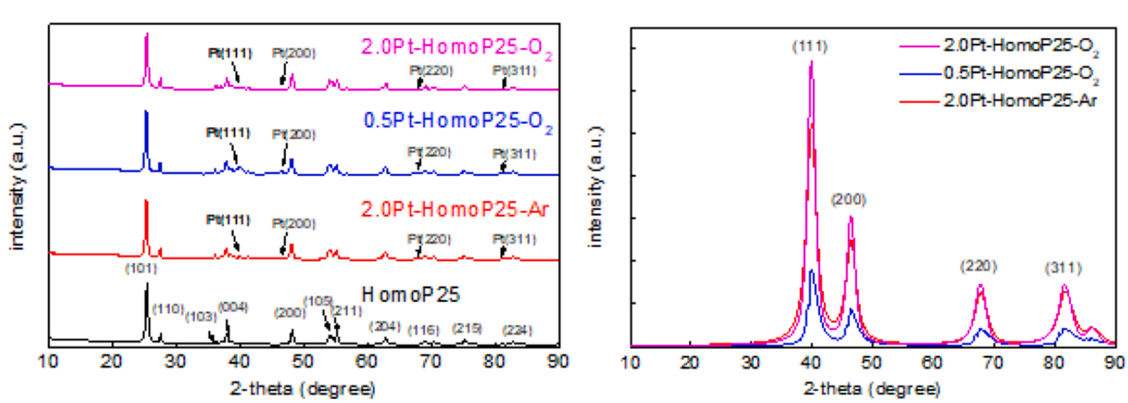

Fig. 4. XRD patterns of pristine and Pt-modified HomoP25 samples: (a) original patterns, (b) patterns after subtraction of titania.

Modification of titania with platinum has resulted in significant improvement of the photoabsorption at visible region. Interestingly, samples containing same content of platinum (2 wt%) but prepared in different conditions (under Ar or O_2) have shown almost same photoabsorption properties. The slight stronger photoabsorption at shorter wavelengths (450–700 nm) by the sample prepared in the presence of oxygen indicates the smaller sizes of Pt NPs.

XRD data have confirmed that P25 consists of two polymorphic forms of titania: anatase and rutile (Fig. 4), with their characteristic peaks, e.g., most intensive at 25.31° and 27.63° for (101) and (110) facets, respectively (Fig. 4a). As expected, the surface modification with platinum has not changed the crystalline properties of titania, and practically same patters could be observed for all samples. The slight differences could be only noticed at the angels characterized for platinum, but since the content of platinum is very low, titania peaks have been subtracted to observe clear platinum peaks, as shown in Fig. 4b. Indeed, five characteristics peaks could be seen at ca. 39.8°, 46.2°, 67.5°, 81.3° and 85.7°, corresponding to (111), (200), (220), (311) and (222) lattice planes of platinum (fcc). It is clear that with an increase in platinum content the intensities of platinum peaks increase. Similar to DRS data, the samples with 2 wt% of Pt have shown very similar properties. However, detailed analysis has indicated some differences between samples, considering the size of platinum deposits and chemical composition, i.e., zero-valent and oxidized form of platinum, as summarized in Table 1. As expected, smaller sizes of platinum have been obtained for its smaller content and for samples prepared under aerobic conditions, as oxygen competes with platinum cations for photogenerated electrons, and thus slowing down platinum deposition, which inhibits NPs' aggregation [26].

Two samples containing same content of platinum (2 wt%) but prepared at different conditions (aerobic/anaerobic) has been observed by three modes of STEM, i.e., SE - secondary electron image (corresponding to SEM), ZC - Z contrast image and TE - phase contrast image (corresponding to TEM). The observed morphology of samples (SE) confirms that P25 is composed of irregular titania particles of various sizes ranging from ca. 10 nm to > 100 nm (Fig. 5 a,d). It has been reported that anatase has formed smaller particles than rutile in P25, and Pt is preferably deposited on rutile phase [25]. The presence of platinum has been confirmed in both samples (white and black areas in ZE- and TE-images, respectively), as seen in Fig. 5 b, c, e, f. Although the aggregation of fine nanocrystals (1–3 nm) of platinum has been observed in both samples, it seems that platinum has been slightly better distributed on titania surface in the case of the sample prepared in the presence of oxygen, due to much slower photodeposition rate (as discussed above).

As presented above, modification of HomoP25 with 2wt% of platinum has resulted in preparation of the samples with very similar properties, independently on the preparation conditions, i.e., with almost same photoabsorption properties and platinum distribution. However, obtained photocatalytic and RMF activities have differed significantly (as discussed in the next section). Therefore, XPS analysis has been performed, as oxidation state of platinum could be responsible for these differences. Indeed, samples prepared in the presence of oxygen contain much larger content of oxidized form of platinum, as shown in Fig. 6 and Table 2.

3.2. Photocatalytic activity tests

Photocatalytic activity of pristine and Pt-modified HomoP25 have been tested for two reaction systems: oxidative decomposition of acetic acid (aerobic) and dehydrogenation of methanol (anaerobic), and obtained data are shown in Fig. 7. As well-known for many years noble metals are efficient scavengers of photo-generated electrons, preventing charge-carriers' recombination [27–31]. Indeed, platinized HomoP25 exhibits much higher activity than pristine sample. Although in the case of CO_2 system, Pt works mainly as an electron scavenger, resulting in 6-10-fold activity increase (white bars in Fig. 7), in the case of H_2 system, main reaction takes place on platinum deposits, as bare titania is practically inactive for hydrogen evolution. Therefore, few orders increase in activity is not surprising after titania modification with platinum. Interestingly, best performance has been obtained for 2.0Pt-homoP25-O_2 sample for both reactions. In the case of hydrogen evolution, it has been reported that there is an optimum content of platinum above which a slight decrease in activity could be observed due to shielding effect [25]. Anyway, HomoP25 sample modified with 2 wt% of platinum by photodeposition showed best performance [25].

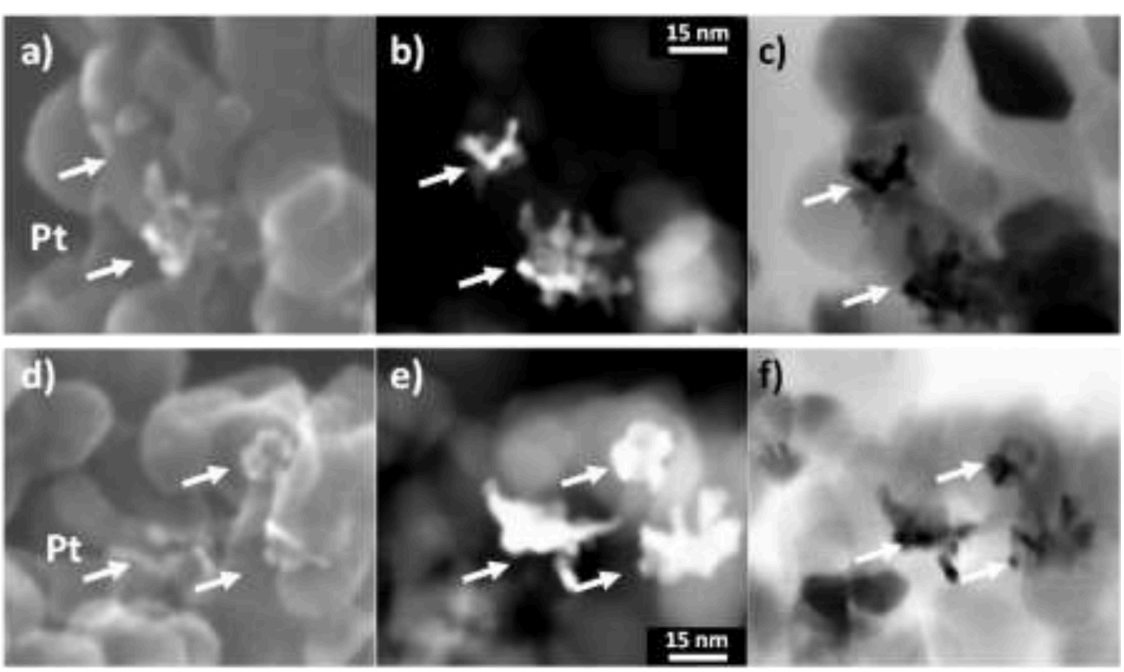

Fig. 5. STEM images for 2.0Pt-HomoP25-Ar (a-c) and 2.0Pt-HomoP25-O_2 (d-f) samples; same area of samples observed in three modes: SE (a and d), ZC (b and d) and TE (c and f).

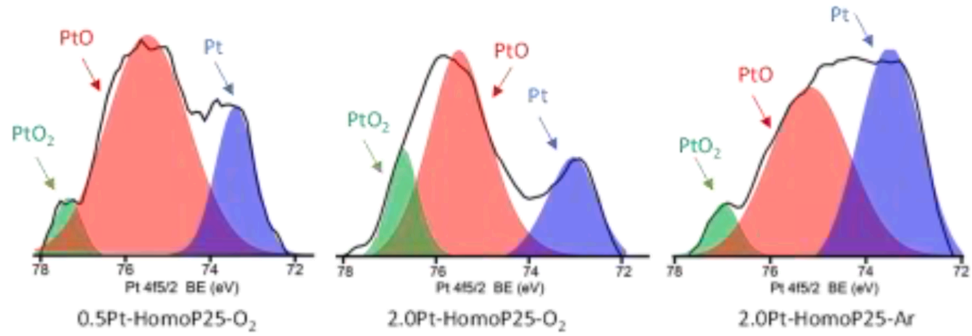

Fig. 6. XPS spectra for Pt $4f_{5/2}$ of Pt-modified samples.

Table 2
Surface distribution of platinum forms after deconvolution of Pt $4f_{5/2}$ peaks (at %).

Sample	PtO_2	PtO	Pt
2.0Pt-HomoP25-Ar	5.8	49.0	45.1
0.5Pt-HomoP25-O_2	6.3	70.7	23.0
2.0Pt-HomoP25- O_2	16.5	63.3	20.2

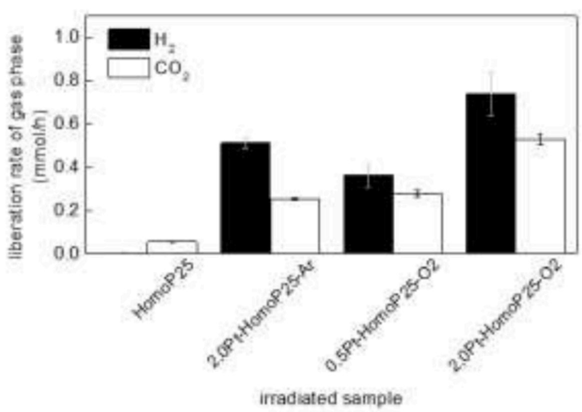

Fig. 7. Photocatalytic activities of pristine and Pt-modified HomoP25 samples in H_2 and CO_2 systems.

Interestingly in the present study, the sample prepared in the presence of oxygen has exhibited much higher activity than that prepared under argon. It should be pointed out that under activity testing (H_2 system) highly reductive conditions are provided (lack of oxygen and methanol as a hole scavenger), and thus it is expected that though three forms of oxidation state of platinum have been detected (XPS data), under activity testing platinum is re-reduced (same as during photodeposition) and zero-valent platinum is its predominant form in all samples. Accordingly, it is proposed that probably better (more uniform) distribution of platinum in the samples prepared under oxygen conditions is responsible for their better performance. This could be also supported by data obtained in CO_2 system, as same activity is obtained for four times less content of platinum for the sample prepared in the presence of oxygen.

3.3. Antimicrobial tests in RMF

The liquid cultures of bacteria *E. coli* and *S. epidermidis* were exposed to the RMF of indicated frequencies of 50 Hz (B = 22–34 mT) during 5-h incubation at 37 °C, and mean values of bacterial number (log CFU/mL) are presented in Fig. 8a. The growth curve in appropriate sterile buffers at the same time and under identical temperature conditions are shown in Fig. 8b. The results indicate that RMF does not cause any statistically significant differences. Moreover, both bacterial species present similar behavior during exposition to RMF, i.e., ca. 1 log reduction of bacteria number (Fig. 8a). Therefore, these data are in accordance with available literature data. Static magnetic field (SMF) as well as electromagnetic fields (EMFs) do not show any effects or point to inhibitory influences on the proliferation, cell metabolic activity and biofilm formation by bacteria [32–35].

In contrast, addition of photocatalyst has reduced the growth rate of bacteria significantly, as clearly shown in Figs. 9 and 10. In the case of bare HomoP25, bacteria are only inactivated in the case of both photocatalysts and RMF (Fig. 9). Interestingly, both bacteria species exhibit quite different behavior, i.e., the number of *E. coli* has not been significantly changed after 1 h of exposition (Fig. 9a), whereas a decrease in the number of *S. epidermidis* has been continued during RMF, reaching zero for 5-h duration (Fig. 9b).

It is worth to notice that platinum presence has resulted in significant

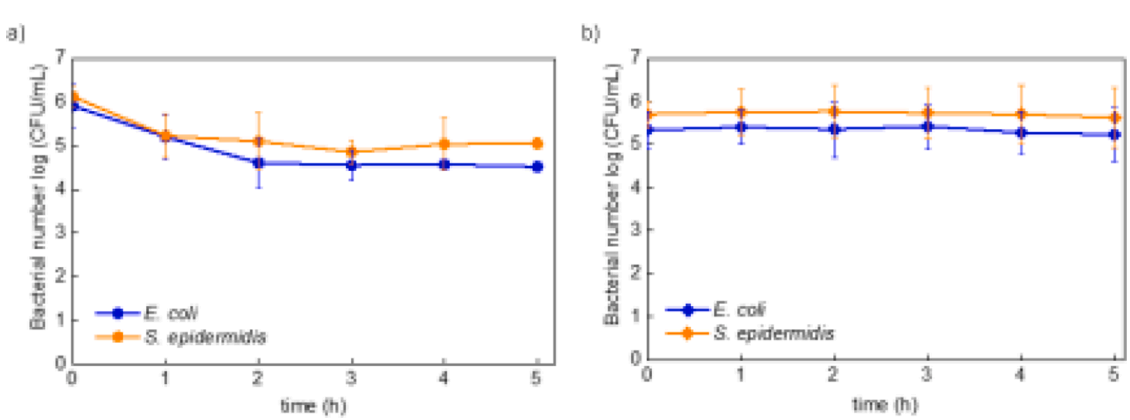

Fig. 8. The growth of *E. coli* and *S. epidermidis* in the presence (a) and absence (b) of RMF with indicated frequencies.

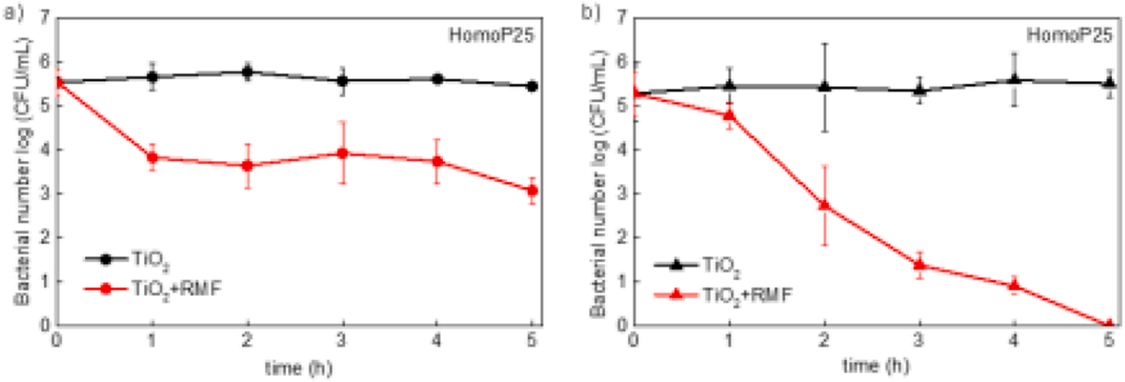

Fig. 9. The influence of the HomoP25 and RMF with indicated frequencies on the growth of *E. coli* (a) and *S. epidermidis* (b).

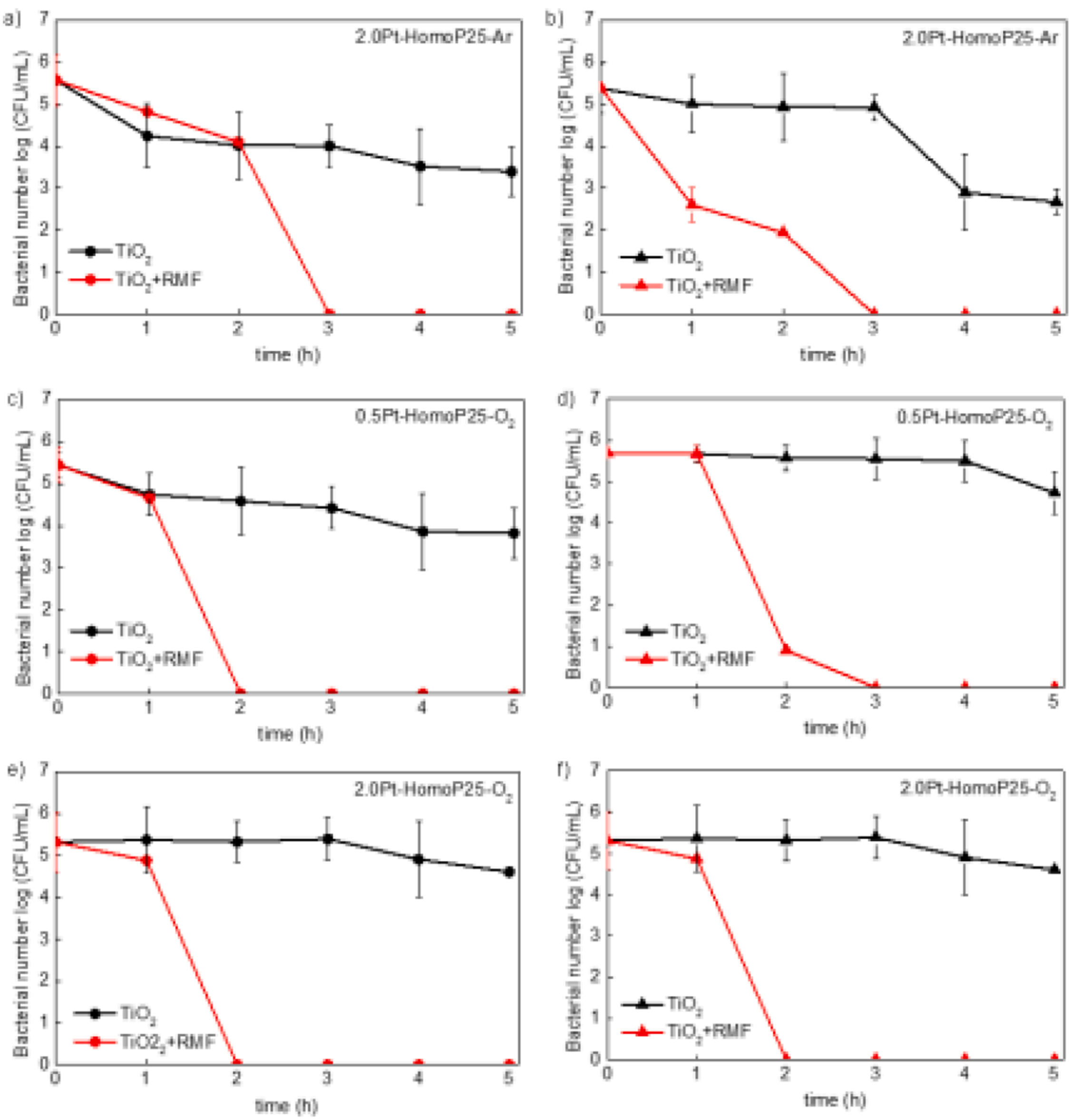

Fig. 10. The influence of the platinum-modified HomoP25 and RMF with indicated frequencies on the growth of *E. coli* (b, d, f) and *S. epidermidis* (b, e, f): 2.0Pt-HomoP25-Ar (a-b), 0.5Pt-HomoP25-O_2 (c-d), 2.0Pt-HomoP25-O_2 (e-f).

increase in bacterial inactivation, especially under RMF exposition, as shown in Fig. 10. In contrast to experiments for pristine titania, it has been found that Gram-negative bacteria is more sensitive to all tested photocatalyst, which could result from electrostatic attractions between positively charged platinum (XPS data) and negatively-charge bacteria. Indeed, two samples prepared in the presence of oxygen (0.5Pt-

HomoP25-O_2 and 2.0Pt-HomoP25-O_2) and thus with larger content of positively charged platinum has caused complete reduction of *E.coli* during 2-h RMF exposition, whereas longer time has been necessary (3 h) for 2.0Pt-HomoP25-Ar (with lower content of positively charged Pt).

The decay growth rate of Gram-positive bacteria *S. epidermidis* is much lower. Under the same conditions, complete inactivation of live *S. epidermidis* has been observed after 3 h for 2.0Pt-HomoP25-Ar and 0.5Pt-HomoP25-O_2, and after 1-h longer duration (4 h) for 2.0Pt-HomoP25-O_2 with RMF. Interestingly, only for sample prepared under argon (2.0Pt-HomoP25-Ar) significant reduction (3 log) of *S. epidermidis* has been noted without application of RMF (Fig. 10b). Therefore, it might be concluded that zero-valent platinum exhibits anti-bacterial activity against Gram-positive bacteria.

The disinfection kinetics of tested bacterial suspensions have been calculated, considering four models, as follows: Chick model, used for photo-disinfection, is based on traditional disinfection, where the reaction rate is characterized as the first order reaction, and is expressed by the equation [36]:

$$r = -kN \quad (2)$$

According to this model, photo-disinfection is a two-molecular chemical reaction, in which microorganisms are treated as chemical molecules. Although, this model is simplified, it has found application in the assessment of antimicrobial activity of chemicals (e.g., chlorine, ozone, hydrogen peroxide, chloroamine) used in disinfection. It has been used in the studies on the rate of photocatalytic deactivation of model *E. coli* [36, 37].

Chick-Watson model is more frequently used for photo-disinfection tests [39]:

$$\frac{N}{N_0} = e^{-k' t} \quad (3)$$

where N is the bacteria concentration [CFU/mL] at time t [min], N_0 – is the initial bacteria concentration [CFU/mL], and k represents the photocatalytic destruction kinetic rate constant;

$$k' = -k[c]^n \quad (4)$$

where c, n – constants

In this model, the reaction rate is defined as a linear function of the number of microorganisms and the charge of the photocatalyst. This is a primary reaction, and the “c” and “n” constants are not physically significant. However, in most experimental studies, there is no linear correlation for bacterial deactivation, which limits the use of these models. Finally, a modified Chick-Watson model, which uses the delay parameter to estimate the integrated kinetic parameter, has found practical use [38]. This model is based on the relation between the dose of the photocatalyst and the irradiation time needed to achieve complete inactivation.

Empirical modification of the Chick-Watson model was developed by Hom, who used it for testing of cyanobacteria removal from water [36]. Deactivation of the examined microorganisms occurred in a logarithmic way depending on the dose of disinfectant. The Hom model can only be used for photo-disinfection with up to two different non-linear areas as it is a two-parameter model:

$$\log \frac{N}{N_0} = -kC^n T^m \quad (5)$$

where: log N bacterial reduction unit; N is the bacterial population at time t; C_0 is the initial bacterial population; k - experimental reaction rate, N - concentration of photocatalyst used, t is the applied irradiation time, n, m – empirical parameters.

To take into account three different deactivation characteristics, the Hom model was modified:

$$\log \frac{N}{N_0} = -k_1 [1 - \exp(-k_2 t)]^{k_3} \quad (6)$$

where: k_1, k_2 and k_3 are the empirical constants for the modified Hom model. Taken into account the calculated parameters (Table 3), all disinfection curves agree with Hom model.

Photocatalytic active TiO_2 shows antimicrobial properties against a wide spectrum of microorganisms, such as Gram-negative and Gram-positive bacteria, yeast, mold fungi and as well as viruses, prions and bacterial toxins [26,40–47]. It has been proposed that the antimicrobial activity of titania is multifactorial and involves the generation of reactive oxygen species, which induce oxidative injuries to bacterial DNA and cell wall or damage of enzymes structure. All mechanisms work together, ultimately leading to cell death. The final product of bacterial cell mineralization is carbon dioxide and water [47–50]. As was mentioned in the introduction, there are some similarities between photocatalysis and applied magnetic field [17]. At the beginning of the 19th century Maxwell described light as an oscillation of an electromagnetic field that attracted keen interest of scientists. The present study has been conducted to appraise the influence of titania photocatalyst and RMF at electric frequencies of 50 Hz and the mean values of magnetic induction B = 34 mT on disinfection process against model Gram-positive and Gram-negative bacteria. The effects of magnetic field treatment are low (approx. 1 log reduction of bacteria), whereas platinum-modified titania supported by RMF have led to full disinfection after 2–4 h, depending on the photocatalyst type. As shown by Kiwi, the photocatalytic process supported by the action of magnetic field might influence the recombination process of cationic and anionic radicals and promote the separation of photo-generated holes and electrons during the photocatalytic process, which improves the efficiency of light energy and material conversion. It was reported that magnetic field of 1.5 T intensity caused 10% increase in photocatalytic oxidation of tert-butyl alcohol to acetone with ultrafine colloidal TiO_2 particles under UV irradiation [22]. It should be taken into consideration that the cell wall of Gram-positive and Gram-negative bacteria has a varied structure, which essentially influences the rate of the transport of vital elements for nutrients’ growth. All of them are electrically charged, therefore transport mechanisms might be affected by the external electromagnetic field. It was demonstrated that electric field has caused the punch-through effect or dielectrical breakdown of the membrane, what leads to their extensive damage [51]. Therefore, Gram-negative bacteria with thick layer of peptidoglycan (7 to 8 nm) are more sensitive than Gram-positive microorganisms. In view of the above, a mechanism of action for titania supported by RFM has been proposed, as follows: By exposure to RMF, bacterial membranes become transiently permeable (pores are formed) to titania particles. It is accompanied by outflow of cytoplasm. Particles of platinum might interfere with DNA inside the bacteria cells, preventing the replication and transcription of the genetic material or inhibit enzymes and nutrient assimilation [52]. Therefore, pristine titania HomoP25 exhibits low antimicrobial activity, whereas platinum has predominant effect. Moreover, titania modified by different method or characterized by vary content of platinum not exposed to RMF exhibits only slight germ destroying potential. This may

Table 3
The calculated parameters in the modified Hom model.

	Parameter			
	K		R^2	
Photocatalysts	*E. coli*	*S. epidermidis*	*E. coli*	*S. epidermidis*
HomoP25	4.78	3.27	0.806	0.976
2.0Pt-HomoP25-Ar	14.55	3.07	0.995	0.990
0.5Pt-HomoP25-O_2	15.81	14.28	1.000	1.000
2.0Pt-HomoP25- O_2	16.33	2.41	1.000	0.999

K- constant of destruction kinetic rate constant, R – regression coefficient.

indicate that the effect resulting from the leached metal ions was not significant. It has been demonstrated that environmental conditions (e.g. water matrix or organic matter content) play an important role in metal leaching [53]. It is obvious that the way of titania modification (in O_2 or Ar atmosphere) and the properties of deposited platinum (oxidation state) influence the disinfection efficacy. It is though that though in the absence of RMF, zero-valent platinum is more effective, especially against Gram-positive bacteria, the synergistic effect is observed for positively charge platinum and RMF for both types of bacteria.

The most interesting finding of this research is that antimicrobial activity in the presence of RMF correlates with photocatalytic activity for decomposition of organic compounds. It is clear that acetic acid decomposition depends on the photocatalyst type, similarly as RMF-initiated *E.coli* inactivation, i.e., the most active and the less active are 2.0Pt-HomoP25-O_2 and 2.0Pt-HomoP25-Ar, respectively. However, in the case of *S. epidermidis* the most active is the sample with the lowest content of platinum (0.5 wt%). Therefore, it is proposed that in the case of Gram-positive bacteria, optimal content of platinum should be estimated first, as it might cause the electrostatic repulsions between bacteria and photocatalyst.

4. Conclusions

Titania P25, known as highly active mixed-phase photocatalyst, has also shown activity in the absence of irradiation but under rotating magnetic field (RMF) against bacteria. It has been found that modification with platinum besides significant enhancement of photocatalytic activity for oxidative decomposition of acetic acid and dehydrogenation of methanol has also improved the antimicrobial effect. The most active sample contains 2 wt% of platinum and has been prepared in the presence of oxygen, and thus its surface is mainly composed of oxidized forms of platinum. Accordingly, it is proposed that platinum oxides are more active than zero-valent platinum under RMF.

Finally, it might be concluded that magnetic field technology is highly suitable for water disinfection. Application of magnetic field instead of expensive UV lamps, used as an irradiation source for photocatalyst excitation, might result in minimizing the costs of water purification. It is believed that this area of study will be further explored.

CRediT authorship contribution statement

Oliwia Paszkiewicz: Investigation, Methodology, Writing – original draft. **Kunlei Wang:** Resources, Visualization. **Rafał Rakoczy:** Conceptualization, Supervision. **Marian Kordas:** Software. **Grzegorz Leniec:** Resources, Visualization. **Ewa Kowalska:** Resources, Supervision, Writing – original draft. **Agata Markowska-Szczupak:** Methodology, Investigation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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