UV-light photocatalytic degradation of non-ionic surfactants using ZnO nanoparticles

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Abstract

The aim of this study was to evaluate the performance of zinc oxide nanoparticles as a photocatalyst for photodegradation of two model non-ionic surfactants (Triton X-100 and C₁₂E₁₀). The first part of the investigation was focused on the synthesis and characterization of ZnO nanoparticles, since its crystalline structure strongly impacts its photocatalytic properties. Based on the results of the XRD analysis, it was concluded that the obtained material occurred in the form of hexagonal wurtzite with a polycrystalline structure. FT-IR and XPS analyses were used to elucidate and confirm the nanomaterial structure, whereas investigation of N₂ adsorption/desorption and SEM/TEM imaging allowed to establish that the synthesized ZnO was characterized as a mesoporous material with uniform, spherical shape and particle size fluctuating between 90 and 130 nm. The second part of the study included spectrophotometric assessment of the photodegradation process. The use of the obtained ZnO nanoparticles allowed to achieve efficient photodegradation of both C₁₂E₁₀ (92%) and Triton X-100 (82%) after 1 h of UV irradiation. The Langmuir–Hinshelwood mechanism was used to describe the reaction kinetics. Subsequent LC-MS/MS analysis of the residues indicated that the degradation mechanism is most likely based on both central fission of the surfactant molecules with further terminal oxidation of poly(ethylene glycol) and terminal oxidation leading to carboxylic derivatives of surfactants.

Keywords Photodegradation · Nanomaterials · Zinc oxide · Surfactants · C₁₂E₁₀ · Triton X-100 · Central fission

Introduction

Surface active agents (surfactants) are among the most commonly used products in the chemical industry and possess a broad spectrum of practical applications (Rosen and Kunjappu 2012). The versatility of surfactants results from their specific structure and properties, which allow for emulsification, micellization, wetting and reduction of surface tension (Rosen and Kunjappu 2012). Surfactants are usually classified based on the nature of their hydrophilic group as:

anionic, cationic, zwitterionic and non-ionic (Rosen and Kunjappu 2012). Analysis of global production in terms of surfactant structure indicates that the industrial synthesis is dominated by anionic and non-ionic surfactants. Surfactants are present in such diverse products as motor oils, pharmaceuticals, detergents, drilling muds used in prospecting for petroleum, and flotation agents used in mineral processing (Rosen and Kunjappu 2012; Pattanaik and Venugopal 2019). The last decades have shown the practical utility of surfactants in more sophisticated technologies including synthesis of nanomaterials (Deng et al. 2018), production of advanced electronic devices (Deng et al. 2018; Li et al. 2018; Kim et al. 2018), biotechnology (Janoska et al. 2018), cell imaging (Komatsu et al. 2018) and many others. Future outlook for the global surfactants market forecasts that the market will grow to 16.60 million tons by 2022. The growing spectrum of surfactant applications also results in an increased quantity of surfactants released to the terrestrial and aquatic environments (Liwarska-Bizukojc et al. 2005). Uncontrolled releases of industrial wastewater with high concentration of surfactants are particularly hazardous,

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especially in developing countries (Babayemi et al. 2017; Huszla et al. 2018). It has been reported that surfactants and the products of their biodegradation are harmful for a variety of organisms (Giger et al. 1984; Könnecker et al. 2011; Lechuga et al. 2016; Rios et al. 2018; Shukla and Trivedi 2018), including humans (Cserati et al. 2002; Khunt et al. 1993) reported that surfactants alter soil chemistry and soil biology even at low concentrations and, as a result, significantly suppress the development of plant roots. Very recently, it has been reported that detergents present in irrigation water affect maize (*Zea mays L.*) at higher concentrations by impairing its light-harvesting pigments and cell viability (Uzma et al. 2018). Several studies regarding the aquatic toxicity of surfactants indicate that these compounds induce oxidative stress and tend to bioaccumulate in fish (Shukla and Trivedi 2018), which act as an exposure gateway to the human consumers (Tan et al. 2010).

The environmental risk caused by surfactants mostly depends on the final concentration reached in the aquatic medium, but it also varies based on their chemical structure. Nevertheless, successful elimination of surfactant contamination from wastewater is of critical importance (Jardak et al. 2016). Various physical, chemical and biological methods of surfactant detoxification are reported (Noorimotlagh 2019, Rebello et al. 2014). Biodegradation is one of the cheapest and most commonly applied methods for neutralization of surfactant-polluted wastewater. Nevertheless, uncontrolled biodegradation may lead to the formation of stable degradation products, which are even more harmful than the initial surfactants (Giger et al. 1984). Additionally, high surfactant load may result in incomplete biodegradation and cause the wastewater treatment plants to discharge considerable amounts of surfactant degradation products into the environment (Chen et al. 2005, Wyrwas et al. 2013). Therefore, the search for alternative, highly effective methods for neutralization of surfactants is still of high importance. Heterogeneous photocatalysis is one of the promising modern methods of eliminating hazardous organic pollutants, which received great attention (Byrne et al. 2015; Fox and Dulay 1993; Kabra et al. 2004; Noorimotlagh et al. 2019). In photocatalysis, semiconductors are irradiated by UV or near-UV light. When the photon energy ($h\nu$) is equal to or exceeds the band gap of the semiconductor/photocatalyst, a photon is absorbed and this excites an electron from the valence band to the conduction band, simultaneously leaving positive charge holes in the valence band. The electron and hole pairs then migrate to the surface of the applied photocatalyst and participate in a series of redox reactions forming reactive oxygen species (Fox and Dulay 1993; Imbhadon and Fitzpatrick et al. 2013; Kabra et al. 2004). Thus, due to the strong oxidizing ability, photocatalysis is an efficient method to decompose organic contaminants in

water, especially in heavy contaminated industrial waste waters, which are not suitable for biological processing due to their toxicity to microorganisms (Imbhadon and Fitzpatrick et al. 2013). Photocatalytic degradation of various organic pollutants including dyes (Sałata et al. 2019, Siwińska-Ciesielczyk et al. 2020), phenol (Shet and Shetty 2015, Norman et al. 2018), antibiotics and pharmaceuticals (Liu et al. 2018; Sabouni and Gomaa 2019; Jia et al. 2020) with the use of broad variety of photocatalysts is comprehensively studied and well described. However, there is a considerable lack of reports regarding photocatalytic degradation of surfactants. Taking into account the recent progress in the design and modification of photocatalysts, it is surprising that photocatalytic degradation of surfactants was realized mostly by utilization of commercial TiO_2 as a photocatalyst (Hidaka and Zhao et al. 1992; Hidaka et al. 1986; 1989; 1992a, b; Rao and Dube 1995; Zhao et al. 1993). Only recently, Noorimotlagh et al. (2019) reported the application of TiO_2 modified with graphite for the treatment of surfactants and Rahimpour et al. (2020) reported application of ZnO/FeVO_4 in photo-Fenton-like process in SDS removal. Nevertheless, there is still a broad field for research regarding the photodegradation of surfactants with modern sensitized photocatalysts or alternatives to TiO_2 . In the framework of this study, for the first time, we report the application of ZnO nanoparticles as an effective catalyst for the photocatalytic degradation of non-ionic surfactants. The aim of this study was to evaluate the performance of zinc oxide nanoparticles as a photocatalyst for photodegradation of two model non-ionic surfactants (Triton X-100 and $\text{C}_{12}\text{E}_{10}$).

Materials and methods

Reagents and chemicals

The non-ionic surfactants dodecyl alcohol ethoxylate ($\text{C}_{12}\text{E}_{10}$) and octylphenol ethoxylate (Triton X-100) were obtained from Sigma-Aldrich (Saint Louis, MO, USA). All reagents used in spectrophotometric analysis (bismuth(III) nitrate, glacial acetic acid, potassium iodide, barium chloride, anhydrous sodium phosphate, thiourea, nitric acid) were obtained from Avantor Performance Materials Poland S.A. (Gliwice, Poland). Zinc acetate dihydrate used in synthesis of ZnO nanoparticles was obtained from Sigma-Aldrich (Saint Louis, MO, USA). LC/MS-grade methanol and ammonium acetate were purchased from Sigma-Aldrich (Saint Louis, MO, USA). HPLC-grade water was prepared by reverse osmosis in a Demiwa system from Watek (Ledec and Sazavou, The Czech Republic) followed by double distillation from a quartz apparatus.

Synthesis of ZnO nanoparticles

The preparation of ZnO was performed according to the method published previously by Tian et al. (2012) with a slight modification. The crucible containing 25 g of solid zinc acetate dihydrate was placed in the furnace P320 MB1 (Nabertherm GmbH, Germany) and annealed to 600 °C with a heating rate of 5 °C/min in the air atmosphere and kept at the maximum temperature for 120 min. Afterward, the sample was naturally cooled down to ambient temperature and 9 g of the gray precipitate was collected and used for further studies.

Physicochemical characterization of ZnO nanoparticles

The XRD analysis was performed with a D8 Advance diffractometer (Bruker, Germany) equipped with an X-ray tube with Cu K α radiation ($\alpha=1.5418$ Å). The patterns were obtained in a step-scanning mode ($\Delta 2\theta=0.05^\circ$) over an angular range of 10–80°. The average crystallite size has been calculated with the Scherrer equation (1) by using the full width at half maximum (FWHM) values of the (101) peak line.

$$D = K\lambda/(\beta \cos \Theta) \quad (1)$$

where D is the mean crystallite size, K is the Scherrer constant, β is the full width at half maximum (FWHM) of the diffraction line, Θ is the diffraction angle, and λ is the wavelength of the X-ray radiation.

The FT-IR spectra were recorded using a VERTEX 70 Fourier transform infrared spectrophotometer (BrukerOptik GmbH, Germany). The spectrometer was equipped with a multireflection variable angle horizontal ATR accessory (Platinum ATR – BrukerOptik GmbH, Germany). Data processing was carried out with the Opus 7.5 software package (BrukerOptik GmbH, Germany). The X-ray photoelectron spectroscopy (XPS) experiments were recorded on Specs UHV spectrometer (SPECS, Germany) with a charge neutralizer. The C 1s peak at 284.8 eV was used as a reference to rectify the binding energies. The microstructure of the obtained photocatalyst was visualized using an EVO40 scanning electron microscope. Before testing, samples were coated with gold for 45 s using a Balzers PV205 P sputter (Zeiss, Germany). Additionally, to get a better insight into the nanostructural features, the obtained material was analyzed using a Jeol 1200 EX II transmission electron microscope (TEM, Jeol, Peabody, MA, USA) at an accelerating voltage of 100 kV. The textural properties of the synthesized ZnO nanoparticles were determined by N₂ adsorption/desorption isotherm measurements at –196 °C using an ASAP

2020 physisorption analyzer (Micromeritics Instrument Co., Norcross, CA, USA). The Brunauer–Emmett–Teller (BET) model was used to calculate the specific surface area of obtained photocatalyst. The pore size and the total volume of pores were calculated by the Barrett–Joyner–Halenda (BJH) method, using the Halsey equation. Prior to the measurement, the sample was degassed at 120 °C for 24 h.

Photocatalytic degradation experiment

Photoactivity tests were performed in a UV-RS2 laboratory reactor (Heraeus, Hanau, Germany) equipped with a 150-W medium-pressure mercury lamp as a UV light source, surrounded by a water cooling quartz jacket, at room temperature. In the experiment, the photocatalyst (200 mg) was suspended in 200 mL of selected surfactant solution at an initial concentration of 10 mg/L. The catalyst concentration was experimentally selected as most effective, (see SI). First, the surfactant solution and photocatalyst were magnetically stirred using an R05 IKAMAG magnetic stirrer (IKA Werke GmbH, Staufenim Breisgau, Germany) in darkness for 30 min to reach the adsorption/desorption equilibrium prior to UV–Vis irradiation. After equilibrium was reached, the concentration of surfactants was measured and the radiation was then turned on to initiate the photocatalytic reaction. In the next step, the irradiated mixtures (8 mL) were collected from the reactor at intervals (1, 5, 10, 20, 30, 40, 50, 60 min) and centrifuged at 12,000 rpm (MPW-352, MPW MED. Instruments, Warsaw, Poland) to remove the photocatalyst nanoparticles.

Spectrophotometric analysis

The concentration of non-ionic surfactants after adsorption and UV irradiation was analyzed by means of the iodobismuthate method with final measurement of absorbance of the bismuth-thiourea complex (BiAS-thio), based on the precipitation of oxyethylate with Dragendorff's reagent (Cierniak et al. 2020). The precipitate dissolved with the simultaneous formation of the bismuth-thiourea complex, the absorbance of which was proportional to the surfactant content of the sample tested. The modified Dragendorff's solution (iodide bismuth(III) complex in the presence of barium ions) was prepared by dissolving in a 1000 mL volumetric flask 1.2 g basic bismuth(III) nitrate, 150 mL glacial acetic acid, 50 g potassium iodide, 100 g barium chloride and 5 g of anhydrous sodium phosphate in approx. 300 mL of demineralized water. After the solids had dissolved, the flask was filled to volume with demineralized water. Before use, the solution was filtered through a medium filtration paper filter. A complexing-dissolution solution (100 mL) was prepared by dissolving 15 g of thiourea and 6.9 mL of concentrated nitric acid (65%) in water (15% thiourea in

1 M HNO_3). 1 mL of modified Dragendorff's reagent was added to an 8 mL centrifuge tube containing 0.1 mL of test sample. Then, after precipitation of oxyethylates, the precipitate was centrifuged for 5 min in a high-speed centrifuge at 12,000 rpm (MPW-352, MPW MED. Instruments, Warsaw, Poland), the supernatant was drained as waste, and the remaining precipitate was washed with glacial acetic acid (3×1 mL) to wash away the residual Dragendorff's reagent. Next, 2 mL of the complexing solution was added to the isolated precipitate of oxyethylate with Dragendorff's reagent. Then, the absorbance of the solution at $\lambda = 468$ nm was measured using a UV–Vis spectrophotometer (V-530, Jasco, Hachioji City, Japan) using water as a reference. Based on the obtained results, the efficiency of surfactant degradation was determined (percentage removal of analyte from the solution) using formula (2):

$$\text{Degradation}(\%) = [(C_0 - C_t) / C_0] \cdot 100\% \quad (2)$$

where C_0 is the surfactant concentration before the degradation process, mg/L, and C_t is the surfactant concentration in samples collected during the degradation process, mg/L.

Liquid chromatography–mass spectrometry

Identification of degradation products was performed using the UltiMate 3000 HPLC from Dionex (Sunnyvale, CA, USA) connected with the 4000 QTRAP mass spectrometer from ABSciex (Foster City, CA, USA). Exactly 5 μL samples were injected into a Gemini-NX C18 column (100 mm $\times$ 2.0 mm I.D.; 3 μm) from Phenomenex (Torrance, CA, USA) maintained at 35°C. The mobile phase consisted of 5 mM ammonium acetate in water and methanol at a flow rate of 0.3 mL min^{-1} in a gradient from 70 to 95% methanol in 3 minutes and then 3 minutes in isocratic conditions. The electrospray (ESI) ion source operated in a positive mode. Nitrogen was used in both the source and the mass spectrometer. The following parameters of the ESI source and mass spectrometer were used: curtain gas pressure 20 psi, nebulization gas pressure 40 psi, auxiliary gas pressure 40 psi, source temperature 350 °C, ESI voltage 4500 V, declustering potential 50 V, entrance potential 10 V. Chromatograms were collected in the Q1 mass spectra mode in a 100–1200 m/z range.

Results and discussion

Characterization of synthesized ZnO

Zinc oxide nanoparticles have received substantial attention in a wide range of practical applications due to their exceptional properties. One of them is application as an

alternative photocatalyst to TiO_2 (Kołodziejczak-Radzimska and Jesionowski 2014). Zinc oxide possess the same band gap energy (3.37 eV) as TiO_2 , while its absorption efficiency across a large fraction of the solar spectrum is higher (Ong et al. 2018; Özgür et al. 2018). Furthermore, according to the literature reports (Kołodziejczak-Radzimska and Jesionowski 2014; Ong et al. 2018), the production costs of ZnO are ca. 75% lower than in case of TiO_2 . The photocatalytic properties of ZnO are closely associated with its crystal structure. Zinc oxide is a compound that possesses a tetrahedral bonding configuration corresponding to the sp^3 covalent bonding (Ong et al. 2018; Özgür et al. 2018), but this material also exhibits a substantial ionic character that tends to increase the bandgap beyond the expected from the covalent bonding (Özgür et al. 2018). ZnO can form crystals in three different forms: hexagonal wurtzite, cubic zinc blende and rock salt (Özgür et al. 2018). The phase and crystal parameters of the obtained zinc oxide nanoparticles were investigated by X-ray diffraction pattern presented in Fig. 1a. The registered diffractogram corresponds with the lines of ZnO wurtzite (hexagonal) matching with the database JCPDS card No. 36-1451 in line with the previously reported data (Dimapilis et al. 2018, van Heerden and Swanepoel 1997). The sharpness and strong intensity of recorded diffractions indicate that the synthesized ZnO sample is well crystallized and has a polycrystalline structure, with a (101) preferred orientation. The calculated average size of the obtained ZnO crystallites was 40.5 nm. It should be noted that the crystallite size is assumed to be the size of a coherently diffracting domain and it is not reflecting the particle size (Bindu&Thomas 2014). Therefore, further observations with SEM and TEM were necessary and will be discussed in the next paragraphs.

Figure 1b presents the FT-IR spectrum of as-obtained ZnO nanoparticles. The broad absorption bands at 3438 cm^{-1} and ~ 1630 cm^{-1} are assigned to the vibration of the hydroxyl groups, most likely resulting from the re-absorption of water molecules from ambient atmosphere (Krishnakumar et al. 2009). The band registered at 1558 cm^{-1} corresponds to the asymmetric stretching of the carboxyl group, resulting from small amounts of residual, unreacted zinc acetate. The sharp peak located at 530 cm^{-1} is atypical band of the wurtzite hexagonal phase of pure ZnO (Krishnakumar et al. 2009).

XPS is an effective tool for analyzing the chemical states of constituent elements. Therefore, the ZnO nanoparticles were also analyzed by X-ray photoelectron spectroscopy (XPS). The Zn 2p core-level (Fig. 2a) of the prepared ZnO nanoparticles has four fitting peaks. The peaks located at approx. 1044.2 and 1021.1 eV are attributed to Zn 2p_{1/2} and Zn 2p_{3/2}, respectively. Symmetrical shape of the Zn 2p spectra and their small half-width values (1.58 and 1.53 eV, respectively) indicate that Zn^{2+} ions

Fig. 1 **a** X-ray diffraction pattern of the prepared zinc oxide nanoparticles; **b** FT-IR spectrum of the prepared zinc oxide nanoparticles

are in a tetrahedral oxygen environment and the chemical Zn–O bonds are dominant in the studied nanoparticles (Al-Gashani et al. 2013). Higher binding energy at Zn 2p (peaks located at about 1045.5 and 1022.3 eV) is associated with the presence of Zn–OH groups on the sample surface. The O 1s core-level spectrum (Fig. 2b) of ZnO nanoparticles shows three different forms of oxygen. Two fitting Gaussians peaks located at 529.8 and 531.2 eV can be attributed to O^{2-} ions in the Zn–O bonding of the wurtzite structure of ZnO and to the Zn–OH bonding, respectively (Al-Gashani et al. 2013). The peak located at 530.5 eV is characteristic for the presence of C=O groups most likely associated with the presence of adventitious carbon, which is usually found on the surface of most air

exposed samples. The presence of adventitious carbon is also confirmed by the C 1s core-level spectrum (Fig. 2c).

The SEM and TEM observations (Fig. 3 a,b) were necessary to determine the structure; morphology and particle size of obtained ZnO nanoparticles. Both SEM and TEM images of obtained synthesized photocatalyst confirm that it exhibits a uniform, spherical shape with the particle size fluctuating between 90 and 130 nm and possesses a tendency for aggregation and formation of larger conglomerates. To further confirm the chemical composition of the ZnO nanoparticles, an EDS analysis shown in Fig. 3c was carried out, which revealed only the presence of Zn and O elements. As a less sensitive technique than XPS, it strongly confirms that the carbon detected by XPS is adventitious.

Fig. 2 XPS spectra of Zn 2p **a**; O 1s **b** and C 1s **c** registered for synthesized ZnO nanoparticles

To assess the parameters of the porous structure of the ZnO photocatalyst, the N_2 adsorption/desorption was recorded (Fig. 4). In accordance with the IUPAC classification, the registered isotherm is classified as type IV isotherm with an H3 type hysteresis loop $p/p_0=0.45-0.99$. This means that the sample has a mesoporous texture, tendency to aggregate and slit-shaped pores (Cychosz&Thommes 2018). The specific surface area calculated by the BET method is equal to $9.64 \text{ m}^2/\text{g}$, while the total pore volume is $0.55 \text{ cm}^3/\text{g}$ and average pore diameter is equal to 21.27 nm . The obtained ZnO characteristics correspond with the previous studies by Tian et al. (2012) and Pourrahimi et al. (2016).

Degradation of surfactants

The removal efficiency of selected surfactants under UV irradiation (150 W) with and without the presence of ZnO nanoparticles is presented in Fig. 5. The calculated non-catalytic removal efficiency of octylphenol ethoxylate (Triton X-100) was equal to 18%, 7% of which was caused by adsorption of this compound on the photoreactor surface. Correspondingly, low removal efficiency (equal to 10%, 4% of which was adsorbed on the photoreactor surface) was calculated for dodecyl alcohol ethoxylate ($C_{12}E_{10}$). Addition of 200 mg of ZnO nanoparticles significantly improved the removal efficiency for both tested surfactants. The maximal removal efficiencies, achieved after only 1h of UV irradiation, were equal to 82% and 92%, for Triton X-100 and $C_{12}E_{10}$, respectively. Removal of surfactants from the aqueous environment during photodegradation is based on several indirect processes: (i) diffusion of surfactants from the solution to the zinc oxide surface (external mass transport), (ii) their diffusion between or inside the catalyst particles to its active surface (internal mass transport); (iii) adsorption of surfactants on photon-activated zinc oxide surface, photodegradation reaction of the adsorbed phase on the zinc oxide surface, desorption of intermediate products from the ZnO surface and transfer of primary photodegradation products from the interface to the liquid phase. Results presented in Fig. 5a indicate that the removal of Triton X-100 from the aqueous solutions is mainly caused by the adsorption of this compound on the catalyst surface (60% of the removal efficiency) with slight effect of photocatalytic oxidation (22%). In contrast, adsorption of dodecyl alcohol ethoxylate ($C_{12}E_{10}$) was equal to 20%, while photodegradation process reached 72%, which contributes to a total removal efficiency of 92% (Fig. 5b).

Fig. 3 SEM **a**; TEM **b** images and EDS spectrum **c** of synthesized ZnO nanoparticles

Fig. 4 N_2 adsorption/desorption isotherms of ZnO nanoparticles

Fig. 5 Removal efficiency of **a** octylphenol ethoxylate (Triton X-100) and **b** dodecyl alcohol ethoxylate ($C_{12}E_{10}$) under UV irradiation with (violet, squares) and without ZnO (orange, circles).

The number of catalyst active sites occupied by the substrate is expressed by fractional occupancy of the adsorption sites θ which is defined as the ratio of the amount of substrate adsorbed on the catalyst to the maximum number of molecules that can be adsorbed on a given mass of ZnO catalyst. In mathematical terms, it is defined by the use of initial substrate concentrations C_{init} , the equilibrium concentrations C_{equil} and the amount of catalyst per unit amount of solution C_{cat} (3). The θ depends on the concentration of the substrate in the region of catalyst reaction. It can be defined

by the Langmuir adsorption isotherm at a constant temperature by taking into account the following assumptions: the catalyst adsorption sites on the surface are evenly distributed and their number is limited, adsorption site has the ability to adsorb only one molecule, the adsorption takes place in catalyst monolayer only adsorbed particles do not interact each other.

$$\theta = \frac{C_{init} - C_{equil}}{C_{cat}} \quad (3)$$

In order to estimate the kinetic constants of the Langmuir–Hinshelwood kinetic model (4), K -Langmuir adsorption constant, and k_r -rate of the adsorption constant, the least squares method was used. This is the classic approach in regression analysis to bring the model closer to the value of the experiment by minimizing the sum of the squares of the residuals calculated for each measurement. For this purpose, the differential kinetic equation is embedded in the method of minimizing the least squares.

$$r = -\frac{dC}{dt} = \frac{k_r K \cdot C}{1 + K \cdot C} = k_r \theta \quad (4)$$

The least squares method requires multiple, iterative calculations of the fitting function (4), at points corresponding to the positions of the experimental values. For this purpose, numerical integration of the above differential kinetic equation is carried out using the classic Adams–Bashforth method in the range between the initial integration time 0 to the time corresponding to the given experimental value. The residual sum minimization algorithm can then calculate the square of the distance for a given point and consequently the sum of all squares. The sum defined in this way is then minimized by the Levenberg–Marquardt algorithm by successive stepwise adjustments of the searched parameters k_r and K .

The comparative study for the reaction without catalyst follows typical equilibrium reaction path. With the assumption of equimolar reaction, the kinetic equation for equilibrium system reads:

$$r = -\frac{dC}{dt} = -k_1 C + \frac{k_1}{K_{eq}} (C_{init} - C) \quad (5)$$

The algorithm of estimating the rate constant k_1 and equilibrium constant K is exactly the same as for the adsorption case discussed earlier in the text.

The results obtained for all $C_{12}E_{10}$ and Triton X-100 cases clearly indicate correctness of the applied assumptions. For reactions without ZnO catalyst, the reactions exhibit equilibrium type (5), while the photodegradation catalyzed with ZnO follows the Langmuir–Hinshelwood model (2). The table below shows the individual results obtained for the respective constants for the above-mentioned reactions. The statistical quality of the fit is measured with the minimized value of the residual sums R . The obtained R -values, which are small compared to the square of the absolute values, indicate that the obtained models are of good quality and correctly reflect the analyzed photodegradation processes.

The models fit to the experimental results are presented on two figures for catalyzed and non-catalyzed reactions. The relative fractional occupancy of the adsorption sites θ is presented on separate graphs (Fig. 6ab) for clarity of presentation. It is visible that the coverage decreases during

the process which corresponds to the decreasing substrate concentrations.

Comparative analysis of the kinetic parameters of photodegradation process for both surfactants revealed that the photodegradation rate in the case of $C_{12}E_{10}$ increases significantly, in comparison with Triton X-100 (Tables 1 and 2).

The observed difference in photodegradation rate may be due to the branched hydrocarbon chain, which increases the resistance to photocatalytic oxidation. On the other hand, dodecyl alcohol ethoxylate ($C_{12}E_{10}$) possesses a straight hydrocarbon chain, which undergoes efficient photodegradation (Figs. 5, 7). Similar behavior is observed for the completely different biodegradation processes using microorganisms, in case of which the biological oxidation processes of non-ionic surfactants usually shorten the oxyethylene chain by 2–3 units with the formation of a homologue series. Further metabolism is associated with the degradation of the alkyl group and finally with ring cleavage (Ding et al. 1996; Staples et al. 2001).

The LC-MS/MS analysis was carried out to obtain information regarding compounds formed during the photodegradation of both non-ionic surfactants. Figure 8 presents the spectra of two surfactants subjected to the tests and products resulting from their photodegradation. Spectra of Triton X-100 and its degradation products are presented on the left side of Fig. 8, whereas spectra of dodecyl alcohol ethoxylate ($C_{12}E_{10}$) on the right side. The degradation products were studied after 30 and 60 minutes. Similar products have been identified in all tests although at different intensities. Triton X-100 contains homologues which include from $n = 2$ (m/z 312) to $n = 21$ (m/z 1060) ethoxy groups in the molecule, as can be seen in the spectrum (Fig. 8a), while $C_{12}E_{10}$ contains homologues which include from $n = 3$ (m/z 336) to $n = 21$ (m/z 1128) ethoxy groups (Fig. 8b). The peaks differ from each other by 44 Da, which indicates the difference of a single ethoxy unit. The peak series in each homologue can be identified as the NH_4 adducts. The next sections in Fig. 8 present the spectra of products formed during photodegradation. Triton X-100 and $C_{12}E_{10}$ oxidized to their carboxylic acid derivatives are presented in Fig. 8b, f, respectively. Series of homologues from m/z 370 ($n = 3$) to m/z 810 ($n = 13$) and from m/z 350 ($n = 3$) to m/z 966 ($n = 17$) were found for oxidized Triton X-100 and $C_{12}E_{10}$, respectively. The last four spectra (Fig. 8c, d, g, h) indicate the presence of polyethylene glycol and its oxidized form with the carboxylic group on one side of the chain. The presence of polyethylene glycol among photodegradation products suggests that the parent molecules (both octylphenol ethoxylate and dodecyl alcohol ethoxylate) were possibly cleaved into the hydrophobic and hydrophilic part, as was the case described in the report of Zhang and Wan (2014) regarding the photodegradation of Triton X-100 using TiO_2 .

Fig. 6 Coverage fraction of catalyst θ for the case with **a** Triton X-100 and **b** $C_{12}E_{10}$.

Table 1 Results for the reaction catalyzed with ZnO according to Langmuir–Hinshelwood model

Substance	k_r	K	R
$C_{12}E_{10}$	1.348	$6.061 \cdot 10^{-2}$	2.994
Triton X-100	$7.411 \cdot 10^{-1}$	$2.814 \cdot 10^{-2}$	$8.35 \cdot 10^{-1}$

Table 2 Results for the non-catalyzed, comparative reaction according to equilibrium model

Substance	k_1	K	R
$C_{12}E_{10}$	$2.243 \cdot 10^{-3}$	$9.377 \cdot 10^{-2}$	$1.251 \cdot 10^{-2}$
Triton X-100	$2.248 \cdot 10^{-2}$	$1.15 \cdot 10^{-1}$	$1.43 \cdot 10^{-2}$

Fig. 7 Langmuir–Hinshelwood model for catalyzed and comparative non-catalyzed model for photodegradation of **a** Triton X-100 and **b** C₁₂E₁₀

Photocatalytic degradation of non-ionic surfactants can proceed in three main stages: (i) adsorption of surfactant molecules on the ZnO surface, (ii) fast photoinduced steps (electron–hole pairs formation, generation of reactive oxygen species), (iii) slow dynamic steps (gradual transformation of organic molecules to simpler forms and their final mineralization) (Hoffmann et al. 1995; Hidaka et al. 1992a, b). As it is shown in Fig. 9 ZnO photocatalyst absorbs UV light with energy above band gap of 3.37 eV. The absorption of photon excites an electron to the conduction band

(e_{CB}^-) and simultaneously generates a positive hole in the valence band (h_{VB}^+) (eq. 6). Another consequence of the second stage is the migration of charge carriers to the photocatalyst surface to initiate redox reactions with adsorbate molecules (Hoffmann et al. 1995; Hoffmann et al. 1994; Pelaez et al. 2012). Holes (h_{VB}^+) can oxidize H₂O or OH⁻ to produce hydroxyl radicals with high redox potential (2.8 V) (eq. 7, 8). Electrons (e_{CB}^-) located in the conduction band can be rapidly trapped by oxygen adsorbed on ZnO surface and its reduction to superoxide radical anion ($O_2^{\bullet-}$)

Fig. 8 Mass spectra of Triton X-100 and its degradation products (left side) as well as dodecyl alcohol ethoxylate ($C_{12}E_{10}$) and its degradation products (right side) obtained after 60 min of degradation. Raw surfactants at (a) and (e), carboxy-terminated surfactants at (b) and (f), poly(ethylene glycols) at (c) and (g) and one-side carboxy-terminated poly(ethylene glycols) at (d) and (h)

Fig. 9 Schematic diagram of energy band for ZnO with proposed mechanism of photocatalytic generation of reactive oxygen species participating in surfactant degradation

occurs (eq. 9). This reactive oxygen specimen can further react with H^+ to form hydroperoxyl radicals (eq. 10) which can then be transformed to H_2O_2 (eq. 11). Furthermore, H_2O_2 can also react with trapped electrons and superoxide radical anions to form $\bullet OH$ (eq. 12, 13) (Schneider et al. 2014, Giah et al. 2012). The resulting reactive oxygen species (primarily hydroxyl radicals) can further react (in the third slower stage) with adsorbed surfactant molecules. In the literature, there are available ESR studies about the experimental proof of photoinduced $\bullet OH$ generation from ZnO nanoparticles (Yang et al. 2016).

In the third (slow dynamic) stage, reactive oxygen species (mainly hydroxyl radicals) participate in oxidation reactions of organic compounds. After addition of $\bullet OH$ radicals to aromatic groups, the hydroxylated ring is opened and the transformation through hydroxyl intermediates, aldehydes and carboxylic acids, and finally to CO_2 can be observed. In the case of alkyl chain, hydroxyl radicals can attack carbon in the α - or β -position to form peroxides, aldehydes and carboxylic acid derivatives, and then also to cause a final mineralization (Hidaka et al. 1992a, b).

Conclusion

The experimental data presented in this study confirm that the nanocrystalline, hexagonal ZnO nanoparticles can be used as a photocatalyst for effective removal of selected non-ionic surfactants from the aqueous environment with removal efficiency 82% and 92% for Triton X-100 and $C_{12}E_{10}$, respectively. The obtained results clearly show that dodecyl alcohol ethoxylate ($C_{12}E_{10}$) is more susceptible to photocatalytic degradation than octylphenol ethoxylate (Triton X-100) due to linear molecular structure. The kinetic behavior for photocatalytic degradation of $C_{12}E_{10}$ and Triton X-100 on ZnO nanoparticles can be described in terms of the Langmuir–Hinshelwood model. Identification of photo-degradation products by the LC-MS/MS method indicated the mechanism of central fission terminal oxidation, which results in the removal of the hydrophilic part of the surfactant molecule form of poly(ethylene glycols). Such a course of biodegradation has also been found for numerous consortia of microorganisms present in surface waters, sewage and soil. The polydispersity of the non-ionic surfactants used in the study, the structure of the alkyl chain or the length of the oxyethylene chain, did not affect the mechanism of photo-degradation, although it did affect their kinetics. This allows to establish that ZnO nanoparticles can be efficiently applied as an alternative to TiO_2 .

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Compliance with ethical standards

Conflict of interest None.

Consent to participate All of the co-workers have agreed to participate.

Consent for publication All of the co-workers have agreed to participate.

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