Journal of Molecular Liquids 338 (2021) 116692



Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

TiO₂/Polyethersulphone films for photocatalytic degradation of acetaminophen in aqueous solution



Maureen O. Chijioke-Okere ^{a,b,d,*}, Zul Adlan Mohd Hir^e, Cynthia E. Ogukwe ^{a,d}, Paschal C. Njoku ^a, Abdul H. Abdullah ^{b,c}, Emeka E. Oguzie ^{a,d,*}

^a Department of Chemistry, School of Physical Sciences, Federal University of Technology Owerri, P.M.B 1526 Owerri, Imo State, Nigeria

^b Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

^c Materials Synthesis and Characterization Laboratory, Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

^d Africa Centre of Excellence in Future Energies and Electrochemical Systems (ACE-FUELS), Federal University of Technology Owerri, P.M.B 1526 Owerri, Imo State, Nigeria ^e Faculty of Applied Sciences, Universiti Teknologi Mara Pahang, 26400 Bandar Tun Abdul Razak Jengka, Pahang, Malaysia

Tutung of Applied Sciences, oniversiti Technologi Mara Funding, 20400 bundur Fun Abdur Kazak Jengka, Funding, Ma

ARTICLE INFO

Article history: Received 5 April 2021 Revised 30 May 2021 Accepted 7 June 2021 Available online 10 June 2021

Keywords: Photocatalysis Pharmaceutical residues Immobilized catalyst Polyethersulphone support Density functional theory

ABSTRACT

In this study, TiO₂-polyethersulfone films with different TiO₂ loadings, prepared by the phase inversion method were tested as photocatalysts for degradation of acetaminophen in aqueous solution. The prepared films were characterized by XRD, SEM-EDX, AFM, and XPS. The successful incorporation of the titanium dioxide nanoparticles was confirmed by the XRD and SEM-EDX. SEM images revealed a much smoother surface for the pristine PES as compared to the TiO₂-PES films, while EDX result confirmed the immobilization of titanium, as increasing amounts of titania were detected with increased loading of titanium dioxide. The SEM cross sectional images also show that the prepared films transformed into porous structures with tear-like pores and the porosity increased from 0.06%, for pristine PES, to 0.35% for the (14 wt%) TiO₂-PES photocatalyst film with 14 wt% content of TiO₂ exhibited 51% degradation efficiency for a film surface area of 80 cm², and a maximum efficiency of 80% at 320 cm² film surface area. However, an increased TiO₂ loading up to 17 wt% led to a decline in efficiency which is attributed to agglomeration and possible defective pore structure of the films. The reactivity of the acetaminophen molecule, modelled using the density functional theory (DFT), enabled identification of the acetamido group and the aromatic ring as the regions most prone to electrophilic and radical attack, respectively.

© 2021 Elsevier B.V. All rights reserved.

1. Introduction

The penetration of pharmaceutical residues into the environment has generated a lot of attention in recent years [1-3]. These compounds typically find their way into the environment via excreta in sewer systems, as the body metabolizes just a small percentage of ingested pharmaceuticals. Pharmaceutical industries and hospitals are also potent sources of such contaminants, which have been detected in their wastewater streams. These compounds are stable and non-biodegradable and therefore are not easily removed by conventional waste water treatment methods, which ab initio where mostly not designed with such category of contaminants in mind [4-6]. Acetaminophen, an over-the-counter medication, is amongst the most widely used and prescribed drugs for pain and fever relief the world over. It was ranked as one of the

* Corresponding authors. *E-mail address:* emeka.oguzie@futo.edu.ng (E.E. Oguzie).

top three drugs prescribed in England, and the mass of acetaminophen through prescription alone totalled more than 400 tons in the year 2000 [22]. Acetaminophen has been detected at concentrations up to 10 mg/L in wastewater treatment plant effluents [54], and in the range of 10–100 ng/L in surface water [55]. Likewise, Ternes et al., [56] reported acetaminophen concentrations up to 6 μ g/L in European STP effluents and up to 10 μ g/L in natural waters in USA. Acetaminophen has as well been detected in drinking water at concentrations ranging from 0.5 to 45 ng/L, and in freshwater reservoirs at concentrations ranging from 4.1 to 73 ng/L [57]. Indeed, the presence of trace amounts of acetaminophen and other xenobiotic compounds in drinking water raises pronounced public health concerns, particularly because there is insufficient information to enable prediction of the long-term effects when ingested by humans. Untreated acetaminophen is hardly biodegradable owing to its complex molecular structure and chemical persistence [22,54].

In a bid to curb the environmental accumulation of pharmaceutical residues and consequent toxicity to terrestrial and aquatic biodiversity, various novel wastewater treatment techniques have been developed to specifically target such emerging pollutants. One of such techniques is semiconductor photocatalysis using some metal oxides [7-9,47]. In this regard, TiO₂ is commonly employed in photocatalysis because of its photoactivity, nontoxicity, low cost and broad-spectrum efficacy on a wide range of organic contaminants [10–12]. TiO₂ is activated by UV light (with corresponding energy higher than the band gap of TiO_2 3.2 eV), causing excitation of electrons from the valence band to conduction band, thus generating electron-hole pairs (e^{-} and h^{+}). The holes have a high oxidation potential, and thus can oxidize acetaminophen adsorbed on the catalyst and/or react with 'OH and H₂O to produce OH which participates in the degradation process. The conduction band electrons can also by reductive reaction. create superoxide radical anions $(\cdot O_2^-)$ with sufficient reduction potential to degrade organic contaminants. The relevant reactions proceed as follows [40]:

$$hv + TiO_2 \rightarrow TiO_2 (h^+ e^-)$$
(1)

$$h^+ + OH^- \rightarrow OH$$
 (2)

$$h^+ + H_2 O \rightarrow \cdot OH + H^+ \tag{3}$$

$$e^{-} + O_2 \rightarrow O_2^{-} \tag{4}$$

$$h^+$$
 + Org \rightarrow products (5)

$$\cdot OH + Org \rightarrow products$$
 (6)

$$\cdot O_2^- + Org \rightarrow products$$
 (7)

The major setback associated with the use of titanium dioxide in slurry form is the post-treatment filtration, which is necessary to recover the photocatalyst, with associated humungous cost and time implications. Interestingly however, some technologies have in recent times been developed for immobilizing the photocatalyst on a suitable support, thereby circumventing the problematic filtration step [13,14]. Several photocatalyst support materials have been reported in literature, such as glass, silica materials, carbon, optical and woven cloth fibers as well as organic membranes [10,13–15]. Some organic membranes like polyacrylonitrile, polypropylene, polyvinylidene difluoride, cellulose acetate, polysulfone and polyethersulphone have also found use as support for photocatalysts [16]. The key physicochemical attributes of suitable support materials include good thermal stability and resistance to degradation by reactive oxidant species. In this regard, polyethersulphone is proving to be a membrane of choice [17,18]. Titanium dioxide and other metal oxides have as well been used to improve the antifouling performance of membranes used in water filtration. TiO2 also confers increased hydrophilicity and mechanical stability on membranes [19-21]. Such symbiotic interactions between PES membranes and TiO₂, have been usefully exploited in PES-supported TiO₂ photocatalysts [22,23].

In this report, we present what we consider to be the first attempt at photocatalytic degradation of acetaminophen (Fig. 1), in aqueous solution using a TiO₂-PES composite film photocatalyst. Operational parameters which play crucial role in the photodegradation of acetaminophen such as pH, concentration and scavengers have been considered. The kinetics of the acetaminophen removal is also reported. Quantum chemical computations were employed for identification of the potential sites on the acetaminophen molecule where electrophilic attack would be initiated.



Fig. 1. Molecular structure of acetaminophen.

2. Materials and methods

2.1. Chemicals and reagents material

 TiO_2 nanoparticles (>99% purity, primary particle size of 1– 150 nm), acetaminophen, polyethersulfone (PES Ultrason E6020P, M_w = 75,000 g/mol) and N-methyl-2-pyrrolidone were purchased from Sigma Aldrich, Guardian chemicals, Solvay Specialty Polymers and Merck, respectively. All chemicals were of analytical grade and were used as source without further purification. Distilled water was used for all solution preparations.

2.2. Synthesis of TiO₂-PES photocatalytic films

The TiO₂/PES photocatalysts were fabricated via phase inversion method [24]. Polyethersulphone (Fig. 2) was dissolved in N-methyl-2-pyrrolidone under stirring until the solution became clear. Requisite amounts of TiO₂ were added and the setup was maintained under constant stirring at room temperature for 24 h. The homogenous TiO₂-PES solution was then cast on a smooth glass plate measuring 10 cm \times 8 cm with an adjustable film applicator set at 100 μ m coating thickness [23]. The resulting membrane was soaked in distilled water for 24 h to make for complete phase separation and then air dried before use [25]. The compositions of the component casting membrane solutions used in this study are presented in Table 1.

2.3. Characterization of membranes

The morphology of the prepared membranes was studied with the aid of a scanning electron microscope coupled with an electron dispersive X-ray analyzer for the analysis of local chemical components (SEM-EDX, HITACHI TM3000). The surface topography was obtained with an atomic force microscope (Seiko SPI 3800N). Crystal structure investigation was carried out with X-ray diffractometer (PHILIPS PW 3040/60) with CuK α radiation λ = 1.540 Å, at a scanning speed of 2° per minute in 2 θ , from 20 to 60 °C. Identification of elements and chemical states of the membranes was done

 Table 1

 Compositions of TiO₂-PES casting solution.

PES wt%	TiO ₂ wt%	NMP wt%	
15	0	85	
15	8	77	
15	11	74	
15	14	71	
15	17	68	

with the aid of an X-Ray photoelectron spectrophotometer (Kratos Analytical Axis Ultra DLD).

2.4. Photocatalysis experiments

Batch photocatalysis experiments were conducted in an immersion well reactor as described previously by Hir et al [23]. Constant supply of oxygen was maintained by the means of an air pump. For each experiment, the photocatalytic film was used to encircle a specified surface area of the guartz tube. Thereafter, 1000 mL of the acetaminophen solution was introduced into the reactor and allowed to stand for 30 mins without radiation impingement, to enable attainment of adsorption-desorption equilibrium. The system was subsequently irradiated with a UV-A light source with wavelength and intensity of 365 nm and 30 W m⁻² respectively, for 420 mins. About 10 mL aliquot of the sample was withdrawn at 1 h intervals to determine residual concentration via absorbance measurements using a Perkin Elmer Lambda 35 UV-Vis spectrophotometer (at λ_{max} = 243 nm). Initial and residual concentration after irradiation were obtained based on the already determined calibration curve. The removal efficiency and amount degraded were obtained from equations (7) and (8) respectively.

Removal efficiency (R%) =
$$\frac{C_0 - C_t}{C_0} \times 100$$
 (7)

Amount of Ace degraded (mg/g)

$$=\frac{C_0 - C_t \binom{mg}{L} \times volume \ (L)}{Weight \ of \ TiO_2 - PES \ film \ (g)}$$
(8)

where C_o (mg/L) is the concentration of acetaminophen solution at initial time t = 0 (min) and C_t is the concentration of the acetaminophen at time (t), after adsorption–desorption treatment or irradiation with a light source.

The analyses of intermediates and identification of the chemical structures of reaction products from the photocatalytic degradation were carried out with a Thermo Scientific UHPLC-ESI-Q-Exactive Focus-MS/MS system. The chromatographic separation was achieved using Thermo Scientific Hypersil gold column (2.1 mm \times 100 mm \times 1.9 μ m) maintained at 25 °C. Gradient elution was carried out with 0.1% formic acid in water (A) and 0.1% formic acid in acetonitrile, delivered at a flow rate of 0.400 mL/min. The detection was carried out by an electrospray ionization source (ESI).

The ESI-MS analyses were conducted on Thermo Scientific Q Exactive Focus Orbitrap mass spectrometer with the following conditions: spray voltage values of 4 kV and -3.7 kV in positive and negative modes, respectively, capillary temperature was 300 °C. The sheath gas and auxillary gas were set at 80 and 40 arbitrary units, respectively. The Orbitrap analyzer scanned over a mass range of 50–500 *m*/*z* for full scan with a mass resolution of 70,000. Non data-dependent experiments were performed with collision-induced dissociation (CID) scan.

3. Results and discussion

3.1. XRD analysis

The X-ray diffraction patterns of the pristine PES and the TiO₂/ PES film photocatalysts with different TiO₂ loadings are shown in Fig. 3. Addition of TiO₂ to the polymer imparted corresponding peaks, characteristic of anatase TiO₂, with diffraction peaks located at $2\theta = 25.24^{\circ}$ (1 0 1), 37.84° (0 0 4), 48.13° (2 0 0), 53.88° (1 0 5), 55.02° (2 1 1) and 62.82° (2 0 4). A peak indexed to rutile TiO₂ with JCPDS No. 00-021-1276, located at $2\theta = 27.44^{\circ}$ (1 1 0) was observed for the TiO₂-PES film photocatalysts. No peaks were observed for



Fig. 2. Polyethersulphone polymer.

the pristine PES, suggesting product purity and proper immobilization of TiO_2 into the polymer network. Similar results were reported by Zanrosso et al. [48] in the photodegradation of methylene blue using TiO_2 immobilized on poly(vinylidene fluoride).

3.2. Photocatalyst morphology

Fig. 4 shows the SEM images of the pristine PES and the $TiO_2/$ PES film photocatalysts, in addition to their respective EDX profiles. The corresponding elemental compositions are outlined in Table 2. In comparison, the pristine PES showed a much smoother surface than the TiO₂-modified PES photocatalysts, which presented evidence of proper dispersal of the TiO₂ nanoparticles within the PES matrix. However, beyond 14 wt% TiO₂, we observed an increase in the viscosity of the casting solution and associated TiO₂ aggregation. Such aggregation has been reported to lead to reduced photocatalytic activity [23,26]. In-depth study of the photocatalyst morphology and surface roughness was achieved using AFM imaging. The surface roughness of the photocatalyst films was obtained via AFM visualization of 2 μ m imes 2 μ m samples (Fig. 5). The surface mean roughness can be seen to increase from 0.92 nm in the pristine PES, to 2.18 nm in TiO₂-PES 14% wt. These results show that addition of TiO₂ to the polymer matrix led to an increase in surface roughness and hence hydrophilicity, which invariably should increase the interaction of water, pollutant, and oxygen with the photocatalyst and is consistent with the findings of Hir et al [23].

The cross-sectional micrographs of the as prepared photocatalysts are shown in Fig. 6. The morphology of the polymer films is characterized by an almost regular array of macro voids. The volume and regularity of the macro voids increased clearly with TiO_2 loading up to 14%, beyond which the macro voids start becoming denatured and shunted [23,27,28]. This is further reinforced by the calculated porosity of the films; the pristine PES



Fig. 3. X-ray diffractograms of polyethersulfone (PES) with different wt % of $TiO_2\,(a)$ 0%, (b) 11%, (c) 14%, (d) 17%.

M.O. Chijioke-Okere, Z. Adlan Mohd Hir, C.E. Ogukwe et al.

Table 2

EDX analysis of TiO₂-PES film photocatalysts for different weight percent of TiO₂.

Element	(0%) Pristine PES		11% TiO ₂ -PES	11% TiO ₂ -PES		14% TiO ₂ -PES		17% TiO ₂ -PES	
	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	
Carbon	68.29	74.25	40.84	56.16	36.12	52.30	31.53	47.95	
Oxygen	31.38	25.62	32.22	33.26	32.06	34.84	32.44	37.04	
Sulphur	0.32	0.13	7.58	3.90	7.28	3.96	6.77	3.85	
Titanium	0.00	0.00	19.36	6.68	24.54	8.91	29.26	11.16	



Fig. 4. SEM-EDX analysis of TiO₂-PES film photocatalysts for different weight percent of TiO₂ (a-b) 0%, (c-d) 11%, (e-f) 14%, (g-h) 17%.



Fig. 5. Three-dimensional AFM images of the top layer of (a) Pristine PES and (b) TiO₂-PES 14%.

had initial porosity of 0.06%, which increased to 0.25% for TiO_2-PES of 14% wt but decreased to 0.21% for TiO_2-PES 17% wt.

The reason behind the slight decrease in porosity is attributed to an agglomeration of nanoparticles which can cause pore blockage, as seen clearly in the bottom segment of Fig. 6d. Other reasons include distortion of the polymer chain and ultimately, inhibition of movement which results in a less porous microstructure [25,28]. These observations are in agreement with the findings of Rajabi et al. [50].

3.3. Elemental state

Evaluation of the chemical states of the TiO₂-PES photocatalyst films was accomplished via XPS analysis (Fig. 7). The XPS of TiO₂-PES 14 wt% photocatalyst film shows the presence of Ti, C, S and O elements (Fig. 7a), in agreement with the EDX data. The C 1 s (Fig. 7b) showed two peaks with binding energies of 284.6 eV and 286.2 eV which are mainly assigned to adventitious carbon contamination species from XPS measurements and C—S groups in the polymer respectively [29,30]. The O 1 s spectrum was fitted into a total of four peaks (Fig. 7c). The peak at 529.5 eV corresponds to Ti—O—Ti (lattice O) species, while peaks 531.4 eV and 532.9 eV correspond to the O=S=O and C—O species of the PES film respectively, the peak at 533.6 eV was assigned to surface hydroxyl species (Ti—OH) or chemisorbed oxygen [31]. To investigate the state of the sulfur in the TiO₂-PES film photocatalyst, S 2p core levels were measured using XPS as shown in Fig. 7d. Two peaks are observed at binding energies 167.4 and 168.6 eV, which is in agreement with [23]. However, only the peak at 168.6 eV associated with the (O=S=O) species was observed by Liu et al. (2011) for pristine PES [32]. The peak identified at 167.4 eV could be attributed to hydrogen bonding interaction between superficial hydroxyl group (–OH) from TiO₂ and sulfone (O=S=O). The hydrogen bonding interaction could also be responsible for the proper dispersal of the TiO₂ on the PES as seen on the SEM images. Ti as shown in Fig. 7e had binding energies at Ti 2p_{3/2} and Ti 2p_{1/2} equivalent to 458.2 eV and 463.9 eV respectively. A splitting that is consistent with the standard value typical of TiO₂. This is indicative of the presence of Ti⁴⁺, a similar observation was made by Zhang and co-workers [33].

3.4. Photocatalytic degradation of acetaminophen by TiO₂-PES photocatalysts

The photocatalytic degradation of acetaminophen by TiO_2 -PES was monitored by absorbance measurements, using UV–vis spectroscopy. The obtained results are presented in Fig. 8(a–c). In the control experiment, photocatalytic degradation of acetaminophen by the pristine PES (without TiO₂ photocatalyst) was monitored for 30 mins initially and subsequently for 420 mins. The result showed that PES was unable to degrade acetaminophen, whereas



Fig. 6. Cross sectional SEM Images of TiO₂-PES film photocatalysts for different amounts of TiO₂ (a) 0%, (b) 11%, (c) 14%, (d) 17%.



Fig. 7. XPS analysis of the TiO₂-PES film photocatalyst containing 14 wt% TiO₂ (a = Survey, b = C 1 s, c = O 1 s, d = S 2p, e = Ti 2p).

addition of TiO_2 to the PES film yielded removal efficiencies that increased steadily with degradation time and with amounts of TiO_2 , up to 14 wt% (Fig. 8a and c). Enhanced values of the degradation efficiency with increasing TiO_2 content results from the increase in the population of active photocatalysis sites on the PES film. Further increase in amount of TiO_2 up to 17 wt% reduced the degradation efficiency, as anticipated from the observed slight decrease in porosity, due to agglomeration of nanoparticles.

The Langmuir-Hinshelwood (L-H) kinetic model (Eq. (9)) was used to model the photocatalytic degradation of acetaminophen by the TiO₂-PES film photocatalysts.

$$\mathbf{r} = -\frac{dC}{dt} = k_{obs}C_t \tag{9}$$

The integration of equation (9) gives a pseudo-first-order equation as follows:

$$\ln C_{\rm o}/C_{\rm t} = k_{obs}t \tag{10}$$

where k_{obs} represent the apparent pseudo-first-order rate constant (Fig. 8c) obtained from the slope of the plot of $\ln (C_o/C_t)$ against irradiation time t, C_o and C_t are the initial concentration and concentration at a specified time t, respectively. The linear plot of $\ln (C_o/C_t)$ vs. degradation time (Fig. 8b) shows that the experimental data for the degradation of acetaminophen by TiO₂–PES film photocatalyst followed the Langmuir-Hinshelwood kinetic model. immobilized up to 14 wt%. These results are consistent with the report of Zanrosso and co-workers in the study of the immobilization of different photocatalysts on PVF and subsequent degradation of methylene blue under ultraviolet and visible light [48].

3.5. Effect of initial pH

The initial pH of a contaminant in solution plays a key role in photocatalysis and significantly affects the rate of degradation. Accordingly, the influence of initial solution pH on the photocatalytic degradation of acetaminophen by TiO₂-PES film



Fig. 8. (a) Degradation profiles of acetaminophen by TiO₂-PES film photocatalysts with different amounts of TiO₂: (a) Time evolution of degradation efficiency (b) degradation kinetics (c) first order rate constant. Acetaminophen = 10 mg/L; pH = 7.8; T = 25 °C; TiO₂-PES film area = 160 cm².

photocatalysts was assessed by carrying out experiments within the pH range 4–10. The obtained results illustrated in Fig. 9 show a steady increase in degradation efficiency, going from pH 4 to pH 8, then decreased going from pH 8 to pH 10 [2]. The increasing trend of degradation efficiency with pH is related to the presence of more hydroxide ions on the TiO₂ surface, yielding increased amounts of OH species, which consequently enhances degradation rates of acetaminophen. The subsequent decrease in degradation



Fig. 9. Effect of initial pH on the degradation of acetaminophen by TiO_2 -PES film photocatalysts (a) pH dependence of degradation efficiency; (b) kinetics of removal Acetaminophen = 10 mg/L; pH = 7.8; T = 25 °C; TiO_2-PES film area = 160 cm².



Fig. 10. Effect of initial acetaminophen concentration on the degradation of acetaminophen by TiO₂-PES film photocatalysts (a) concentration dependence of degradation efficiency; (b) kinetics of the removal: pH = 7.8; T = 25 °C; TiO₂-PES film area = 160 cm².



Fig. 11. Effect of photocatalyst surface area on the degradation of acetaminophen by TiO₂-PES film photocatalysts (a) effect on degradation efficiency; (b) kinetics of removal Acetaminophen = 10 mg/L; pH = 7.8; T = 25 °C.



Fig. 12. Effect of radical scavengers on the acetaminophen degradation efficiency of by TiO₂-PES film photocatalysts Acetaminophen = 10 mg/L; pH = 7.8; T = 25 °C; TiO₂-PES film area = 160 cm².

efficiency at pH 10 is related to surface ionization of TiO₂. Indeed, TiO₂, with point of zero charge of 6.2, maintains a positive surface charge in acidic media (pH < 6.2), and negatively charged at alkaline conditions (pH > 6.2). Hence, increasing the pH (up to pH 10) increases the electrostatic repulsion between TiO₂ surface and acetaminophen with pka = 9.5, which is negatively charged at pH above 9.5 [34,53]. This finding is consistent with the findings of Shourong *et al.* [35] in studying dye photo removal in TiO₂ suspension .

Since polymeric films could become denatured and undergo deterioration under certain pH conditions, the stability of the

 TiO_2 -PES photocatalyst in the studied pH range was assessed by weighing the films before and after the photocatalytic experiments. Interestingly, the TiO_2 -PES film did not undergo any significant change in weight, which points towards the stability of the photocatalytic film in both acidic and basic medium, in agreement with a study by Adlan *et al.*, [23].

3.6. Effect of initial pollutant concentration

The effect of acetaminophen concentration (5–30 ppm) on degradation rate and degradation efficiency are presented in Fig. 10 (a,b). Both degradation rate and degradation efficiency decreased with increasing acetaminophen concentration. This could be due to possible occlusion of active catalyst sites by excess acetaminophen, a phenomenon that has been described as screening/ shielding effect [36,49]. Such shielding effect was reported by Lei and co-workers for the degradation of methyl orange by TiO₂ immobilized on PVA matrix [51]. There is as well the effect of reaction intermediates in the system, which compete with the contaminant for available active sites on the photocatalyst film [52]. Nonetheless, the amount of acetaminophen degraded (as computed from Eq. (8)) increased with concentration up to 25.68 mg/g at 25 ppm and then slightly decreased to 23.87 mg/g at 30 ppm acetaminophen.

3.7. Effect of catalyst film surface area

The effect of catalyst film surface area on acetaminophen degradation was investigated by altering the number of films as allowed by the reactor configuration, which can accommodate a maximum of four films of 80 cm² surface area. This configuration thus permits



Fig. 13. LC-MS spectra showing progress of the photocatalytic degradation of acetaminophen by PES-TiO₂/UV before (a) and after treatment (b).



Fig. 14. Proposed mechanism for the degradation of acetaminophen by TiO₂-PES/UV.

investigation of catalyst film surface areas of 80 cm² to 320 cm². Fig. 11 (a-b) show that the degradation efficiency and rate of degradation increased steadily as the surface areas of the catalyst film increased, up to a maximum of 80% at 320 cm², due essentially to increased availability of TiO₂ particles for the degradation of acetaminophen. The trend of the results shows clearly that increasing the catalyst film surface further would further increase the degradation efficiency. This is in sharp contrast to what obtains when TiO₂ is used in slurry form, wherein higher amounts of TiO₂ particles reduced light penetration, in addition to the prevalence of particle agglomeration, all of which reduce the degradation rate [9,37,38].

3.8. Photo catalysis mechanism

A radical scavenging test was done to determine the active species responsible for the observed degradation of acetaminophen and thus propose a mechanism for the TiO₂-PES degradation of acetaminophen. This was done using ethylenediaminetetraacetic acid (EDTA), as scavenger for holes (h⁺), *tert*butyl alcohol (*t*BuOH) as scavenger for hydroxyl radicals ('OH), and 1,4-benzoquinone (*p*-BQ) for superoxide radical anions (O_2^-) . In this investigation, 20 mL of 0.1 M of each scavenging agent was added into 1000 mL of 10 mg/L of acetaminophen solution and the system exposed for 420 mins under UV light. Fig. 12 compares the degradation efficiencies obtained without and with the scavenging agents and shows 42.05% reduction in degradation efficiency on addition of EDTA, while tertbutyl alcohol and 1,4-benzoquinone yielded reduction of 15.39% and 10.23% respectively. The implication is that holes (h⁺) exert the predominant influence on acetaminophen degradation and their elimination from the system notably hindered the degradation reaction. This is not unexpected since holes are involved directly in steps (2), (3) and (5) of the TiO_2 degradation.

It is important to note that, although many reactants in the system can indirectly degrade acetaminophen by contributing to 'OH, 'OH is the most dominant specie directly degrading acetaminophen [39,41].

3.9. Degradation pathway

The chemical structures of potential intermediates from the TiO₂-PES/UV degradation of acetaminophen were identified by UHPLC-ESI-O-ExactiveFocus-MS/MS, carried out in positive and negative modes. The LC-MS/MS data was analyzed by viewing the base peak chromatogram and the individual ions of interest using the extracted ion chromatogram. By comparing the chromatographic and spectrometric data from this study with data from databases and literature, it was possible to identify the degradation products. Fig. 13 shows the LC-MS spectra for the degradation of acetaminophen, for the spectrum in Fig. 13a was obtained prior to photocatalytic treatment of acetaminophen (at t = 0 min), while Fig. 13b was following photocatalytic treatment (at t = 420 min). The prominent peak with m/z 152 eluting at 1.70 min is attributed to protonated acetaminophen. The fact that this peak diminished in size after photocatalytic treatment, with a new peak eluting at 7.18 min, indicates breakdown of acetaminophen. The fragmentation of the $[1 + H]^+$ produced $[1 + H - CH_2CO]^+$ with a mass fragment ion of m/z 110, this is in agreement with [42]. The presence of other ions in the mass spectra obtained (spectra not included) in the photocatalytic run could be an indication of degradation products that were not verified, possibly due to very low concentration of such compounds.

Several studies have been carried out to investigate the intermediate products of acetaminophen degradation via UV/H_2O_2 [43], $O_3/H_2O_2/UV$ [44] and TiO_2/UV [2,42] and based on the structures of the aromatic compounds detected in the early studies, oxidative/hydroxylation pathways were proposed. The key reactions involve HO⁻ radical attack on the aromatic ring of acetaminophen with respect to the hydroxyl group.

Given the affinity of HO[•] for electron-rich aromatic compounds. it is expected that the breakdown proceeded via further hydroxylation and oxidation of phenolic compounds [43]. In monitoring the intermediate products of acetaminophen degradation by TiO₂/UV, Dalmázio et al., [42] proposed a mechanism similar to the latter which lends credence to the position that the reaction proceeds through in situ generation of HO[•] radicals. Based on the foregoing, a simplified pathway has been proposed. This involves the breakdown of acetaminophen via the hydroxylation of the benzene ring, thus, generating 3-hydroxyacetaminophen or hydroxylation and subsequent cleavage of the bond between nitrogen and carbon from the carbonyl group to form 4-aminophenol. The elimination of nitrogen followed by further hydroxylation would lead to hydroquinone and subsequently 1,4-benzoquinone. Similar trends were reported by [2]. However, further oxidation of the intermediates could lead to the breakdown of the aromatic structure, and subsequent conversion to acids and CO₂/H₂O. In this study, trace amounts of p-aminophenol and benzoquinone were detected as intermediate components. The electronic structures of acetaminophen and key intermediates like 1,4-benzoquinone, 3-hydroxyacetaminophen, 4-aminophenol, nitrophenol and hydroquinone were modeled to obtain their heats of formation, which is related to the stabilities of the intermediate products, wherein high negative values correspond to more stable compounds [45]. The experimental and computational results were thus taken into consideration in proposing the degradation pathway in Fig. 14.

Further elucidation of the acetaminophen degradation mechanism involved computational assessment of the reactivity of the different functional groups that make up the acetaminophen structure to identify their susceptibility to attack by electrophilic and radical species, and hence determine the sites where degradation is initiated [46]. From the values of the Fukui functions for electrophilic attack (F^-) and radical attack (F^\cdot) given in Table 3, it becomes clear that radical and electrophilic attack would be initiated at the carbonyl group, since the carbonyl oxygen has the highest values for both functions. Interestingly, the computational results support the degradation mechanism involving "hydroxylation and subsequent cleavage of the bond between nitrogen and carbon from the carbonyl group".

3.10. Reusability

The stability and reusability study of the photocatalyst film over the degradation of acetaminophen was ascertained by using 10 mg/L of acetaminophen at the natural pH of 7.8 for 420 mins of irradiation. The catalyst was washed with distilled water after each degradation run before a new acetaminophen solution was introduced into the reactor. Fig. 15 shows that the photocatalyst film was stable for 5 runs with comparable degradation efficiency before a slight drop in efficiency on the 6th run. This was so even as the weight of the film was not compromised, which serves as a confirmation of the strong attachment of the TiO_2 to the polymer via hydrogen bonding, thus, the films are germane for a possible process scale-up.

Table 3

Mulliken values of radical and electrophilic Fukui indices for acetaminophen.

No/Atom	Electrophilic Attack (F ⁻)	Radical Attack (F ⁰)
C (1)	0.039	0.020
C (2)	0.039	0.066
C (3)	0.035	0.071
C (4)	0.034	0.016
C (5)	0.032	0.053
C (6)	0.040	0.073
O (7)	0.104	0.074
N (8)	0.066	0.022
C (9)	0.008	0.018
C (1 0)	-0.011	-0.019
0 (1 1)	0.126	0.101
H (1 2)	0.074	0.085
H (1 3)	0.071	0.083
H (1 4)	0.061	0.074
H (1 5)	0.075	0.085
H (1 6)	0.043	0.038
H (17)	0.058	0.047
H (18)	0.042	0.035
H (19)	0.011	0.005
H (2 0)	0.054	0.053



Fig. 15. Reusability test: Acetaminophen = 10 mg/L; pH = 7.8; T = 25 °C; TiO₂-PES film area = 160 cm².

4. Conclusion

In this study, TiO₂-PES photocatalyst films prepared via phase inversion technique has been shown to degrade acetaminophen (10 mg/L), a stable and non-biodegradable active pharmaceutical ingredient. Due to reactor configuration, a maximum of four TiO2-PES 14 wt% photocatalyst films were used which gave the highest degradation efficiency of 80% at pH 7.8. Overall, pH plays an important role in the degradation process; a slightly basic pH was more favourable for the photocatalytic degradation. The main reactive oxidant species were found to be holes (h⁺) due to the considerable inhibition on the degradation of acetaminophen using EDTA, which may react with H₂O to form 'OH. LC-MS analysis result pointed to the formation of degradation products such as p-aminophenol, and benzoquinone. These compounds formed were suggestive of successive hydroxylation and consequent scission of the benzene ring of acetaminophen. This position was further reinforced by our quantum chemical computation results. The mechanism of the photocatalytic degradation of acetaminophen was proposed which involves in situ formation of highly active radical species as a result of the interaction of TiO₂-PES and UV light. The reusability study shows the photocatalyst films remained stable and only dipped at the sixth photocatalytic run.

CRediT authorship contribution statement

Maureen O. Chijioke-Okere: Conceptualization, Methodology, Data curation, Writing - original draft, Investigation, Formal analysis, Funding acquisition. Zul Adlan Mohd Hir: Methodology, Formal analysis. Cynthia E. Ogukwe: Project administration. Paschal C. Njoku: Project administration, Supervision. Abdul H. Abdullah: Conceptualization, Methodology, Supervision, Writing - review & editing. Emeka E. Oguzie: Conceptualization, Methodology, Funding acquisition, Writing - review & editing, Supervision.

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.

Acknowledgments

Maureen O. Chijioke-Okere gratefully acknowledges the support of the Organization for Women in Sciences (OWSD) and the Swedish International Development Cooperation Agency (SIDA) (Grant number: 3240291620). The authors are thankful to Universiti Putra Malaysia (UPM) for the facilities to carry out the research. Support from the World Bank funded Africa Centers of Excellence for Development Impact (ACE Impact) Project is gratefully acknowledged. J.C. Edoziem is acknowledged for assistance with computational modelling.

References

- [1] A.J. Ebele, M.A. Abdallah, S. Harrad, Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment, Emerging Contaminants 3 (2017) 1–16, https://doi.org/10.1016/j.emcon.2016.12.004.
- [2] E. Moctezuma, E. Leyva, C.A. Aguilar, R.A. Luna, P. Montalvo, Photocatalytic degradation of paracetamol: Intermediates and total reaction mechanism, J. Hazard. Mate. 243 (2012) 130–138, https://doi.org/10.1016/j. jhazmat.2012.10.010.
- [3] A.K. Sarkar, A. Pal, S. Ghorai, N.R. Mandre, S. Pal, Efficient removal of malachite green dye using biodegradable graft copolymer derived from amylopectin and poly(acrylic acid), Carbohydr. Polym. 111 (2014) 108–115, https://doi.org/ 10.1016/j.carbpol.2014.04.042.

- [4] W.C. Li, Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil, Environ. Pollut. 187 (2014) 193–201, https://doi.org/ 10.1016/j.envpol.2014.01.015.
- [5] M. Huerta-Fontela, M.T. Galceran, F. Ventura, Occurrence and removal of pharmaceuticals and hormones through drinking water treatment, Water Res. 45 (2011) 1432–1442, https://doi.org/10.1016/j.watres.2010.10.036.
- [6] L. Feng, E.D. van Hullebusch, M.A. Rodrigo, G. Esposito, M.A. Oturan, Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes, A review, Chem. Eng. J. 228 (2013) 944–964, https://doi.org/10.1016/j.cej.2013.05.061.
- [7] D. Kanakaraju, B.D. Glass, M. Oelgem, Green Materials for Energy, Products and Depollution, Springer, 2013, ISBN 978-94-007-6835-2.
- [8] C.B. Ong, L.Y. Ng, A.W. Mohammad, A review of ZnO nanoparticles as solar photocatalysts : Synthesis, mechanisms and applications, Renew. Sustain. Energy Rev. 81 (2018) 536–551, https://doi.org/10.1016/j.rser.2017. 08.020.
- [9] M.O. Chijioke-Okere, N.J. Okorocha, B.N. Anukam, E.E. Oguzie, Photocatalytic Degradation of a Basic Dye Using Zinc Oxide Nanocatalyst, Int. Lett. Chem. Phys. Astron. 81 (2019) 18–26, https://doi.org/10.18052/www.scipress.com/ ILCPA.81.18.
- [10] S. Singh, H. Mahalingam, P.K. Singh, Polymer-supported titanium dioxide photocatalysts for environmental remediation: A review, Appl. Catal. A 462– 463 (2013) 178–195, https://doi.org/10.1016/ji.apcata.2013.04.039.
- [11] C.L. de Dicastillo, C.P. Vidal, M.J. Galotto, J.L. Palma, D. Alburquenque, J. Escrig, Novel Antimicrobial Titanium Dioxide Nanotubes Obtained through a Combination of Atomic Layer Deposition and Electrospinning Technologies, Nanomaterials 8 (2018) 128, https://doi.org/10.3390/nano8020128.
- [12] A. Garg, T. Singhania, A. Singh, S. Sharma, S. Rani, A. Neogy, S.R. Yadav, V.K. Sangal, N. Garg, Photocatalytic Degradation of Bisphenol-A using N, Co Codoped TiO2 Catalyst under Solar Light, Sci. Rep. (2019) 1–13, https://doi.org/10.1038/2Fs41598-018-38358-w.
- [13] B. Srikanth, R. Goutham, R.B. Narayan, A. Ramprasath, K.P. Gopinath, A.R. Sankaranarayanan, Recent advancements in supporting materials for immobilised photocatalytic applications in waste water treatment, J. Environ. Manage. 200 (2017) 60–78, https://doi.org/10.1016/j.jenvman.2017. 05.063.
- [14] A.Y. Shan, T.I.M. Ghazi, S.A. Rashid, Immobilisation of titanium dioxide onto supporting materials in heterogeneous photocatalysis: A review, Appl. Catal. A 389 (2010) 1–8, https://doi.org/10.1016/j.apcata.2010.08.053.
- [15] M.E. Borges, D.M. García, T. Hernández, J.C. Ruiz-Morales, P. Esparza, Supported Photocatalyst for Removal of Emerging Contaminants from Wastewater in a Continuous Packed-Bed Photoreactor Configuration, Catalysts 5 (2015) 77–87, https://doi.org/10.3390/catal5010077.
- [16] K. Fischer, M. Kühnert, R. Glåser, A. Schulze, Photocatalytic degradation and toxicity evaluation of diclofenac by nanotubular titanium dioxide –PES membrane in a static and continuous setup, RSC Adv. 5 (2015) 16340– 16348, https://doi.org/10.1039/C4RA16219F.
- [17] S. Simone, F. Galiano, M. Faccini, M.E. Boerrigter, C. Chaumette, E. Drioli, A. Figoli, Preparation and Characterization of Polymeric-Hybrid PES/TiO₂ Hollow Fiber Membranes for Potential Applications in Water Treatment, Fibers 5 (2017) 14, https://doi.org/10.3390/fib5020014.
- [18] S. Mozia, D. Darowna, R. Wróbel, A.W. Morawski, A study on the stability of polyethersulfone ultrafiltration membranes in a photocatalytic membrane reactor, J. Membrane Sci. 495 (2015) 176–186, https://doi.org/10.1016/j. memsci.2015.08.024.
- [19] I. Kovács, S. Beszédes, S. Kertész, G. Veréb, C. Hodúr, I.Z. Papp, A. Kukovecz, Z. László, Investigation of titanium-dioxide coatings on membrane filtration properties, Stud. Univ. Babes-Bolyai, Chem. 62 (2017), https://doi.org/10.2166/wst.2017.610.
- [20] V. Vatanpour, S.S. Madaeni, R. Moradian, S. Zinadini, B. Astinchap, Novel antibifouling nanofiltration polyethersulfone membrane fabricated from embedding TiO₂ coated multiwalled carbon nanotubes, Sep. Purif. Technol. 90 (2012) 69–82, https://doi.org/10.1016/j.seppur.2012.02.014.
- [21] A. Razmjou, J. Mansouri, V. Chen, M. Lim, R. Amal, Titania nanocomposite polyethersulfone ultrafiltration membranes fabricated using a low temperature hydrothermal coating process, J. Membr. Sci. 380 (2011) 98– 113, https://doi.org/10.1016/j.memsci.2011.06.035.
- [22] N. Jallouli, K. Elghniji, H. Trabelsi, M. Ksibi, Photocatalytic degradation of paracetamol on TiO₂ nanoparticles and TiO₂/cellulosic fiber under UV and sunlight irradiation, Arabian J. Chem. 10 (2017) S3640–S3645, https://doi.org/ 10.1016/j.arabjc.2014.03.014.
- [23] Z.A.M. Hir, P. Moradihamedani, A.H. Abdullah, M.A. Mohamed, Immobilization of TiO₂ into polyethersulfone matrix as hybrid film photocatalyst for effective degradation of methyl orange dye, Mater. Sci. Semicond. Process. 57 (2017) 157–165, https://doi.org/10.1016/j.mssp.2016.10.009.
- [24] A.K. Hołda, I.F.J. Vankelecom, Understanding and guiding the phase inversion process for synthesis of solvent resistant nanofiltration membranes, J. Appl. Polym. Sci. 42130 (2015) 1–17, https://doi.org/ 10.1002/app.42130.
- [25] A. Idris, Z. Man, A.S. Maulud, M.S. Khan, Effects of phase separation behavior on morphology and performance of polycarbonate membranes, Membranes (2017) 7, https://doi.org/10.3390/membranes7020021.
- [26] M.R. Esfahani, J.L. Tyler, H.A. Stretz, M.J.M. Wells, Effects of a dual nanofiller, nano-TiO₂ and MWCNT, for polysulfone-based nanocomposite membranes for water purification, Desalination 372 (2015) 47–56, https://doi.org/10.1016/j. desal.2015.06.014.

- [27] C.A. Smolders, A.J. Reuvers, R.M. Boom, I.M. Wienk, Microstructures in phase inversion membranes.1. Formation of macrovoids, J. Membr. Sci. 73 (1992) 259–275, https://doi.org/10.1016/0376-7388(92)80134-6.
- [28] X. Li, X. Fang, R. Pang, J. Li, X. Sun, J. Shen, W. Han, L. Wang, Self-assembly of TiO₂ nanoparticles around the pores of PES ultrafiltration membrane for mitigating organic fouling, J. Membr. Sci. 467 (2014) 226–235, https://doi.org/ 10.1016/j.memsci.2014.05.036.
- [29] J.G. McEvoy, W. Cui, Z. Zhang, Degradative and disinfective properties of carbon-doped anatase – rutile TiO₂ mixtures under visible light irradiation, Catal. Today 207 (2013) 191–199, https://doi.org/10.1016/ j.cattod.2012.04.015.
- [30] D.S. Wavhal, E.R. Fisher, Membrane Surface Modification by Plasma-Induced Polymerization of Acrylamide for Improved Surface Properties and Reduced Protein Fouling, Langmuir (2003) 79–85, https://doi.org/10.1021/ la0206530.
- [31] N.M. Thuy, D.Q. Van, L.T.H. Hai, The Visible Light Activity of the TiO₂ and TiO₂: V4 + Photocatalyst, Nanomater. Nanotechnol. L (2012) 1–8, https://doi.org/ 10.5772/2F55318.
- [32] J.L. Zhao, G.G. Ying, B. Yang, S. Liu, L.J. Zhou, Z.F. Chen, H.J. Lai, Screening of multiple hormonal activities in surface water and sediment from the Pearl River system, South China, using effect-directed in vitro bioassays, Environ. Toxicol. Chem. 30 (2011) 2208–2215, https://doi.org/10.1002/etc.625.
- [33] P. Zhang, C. Shao, Z. Zhang, M. Zhang, J. Mu, Z. Guo, Y. Liu, Nanoscale TiO2 @ carbon core /shell nanofibers: Controllable preparation and enhanced visible photocatalytic activities, Nanoscale (2011) 2943–2949, https://doi.org/ 10.1039/C1NR10269A.
- [34] L. Yang, L.E. Yu, M.B. Ray, Degradation of paracetamol in aqueous solutions by TiO₂ photocatalysis, Water Res. 42 (2008) 3480–3488, https://doi.org/10.1016/ j.watres.2008.04.023.
- [35] Z. Shourong, H. Qingguo, Z. Jun, W. Bingkun, A study on dye photoremoval in TiO₂ suspension solution, J. Photochem. Photobiol. A: Chem. 108 (1997) 235– 238, https://doi.org/10.1016/S1010-6030(97)00014-2.
- [36] L. Zhang, M.S. Tse, O.K. Tan, Facile insitu synthesis of visible light-active Pt/C-TiO₂ nanoparticles for environmental remediation, J. Environ. Chem. Eng. 2 (2014) 1214–1220, https://doi.org/10.1016/j.jece.2014.05.006.
- [37] P. Lei, F. Wang, X. Gao, Y. Ding, S. Zhang, J. Zhao, S. Liu, M. Yang, Immobilization of TiO₂ nanoparticles in polymeric substrates by chemical bonding for multicycle photodegradation of organic pollutants, J. Hazard. Mater. 227–228 (2012) 185–194, https://doi.org/10.1016/j.jhazmat.2012.05.029.
- [38] M. Martín-Sómer, C. Pablos, R. van Grieken, J. Marugán, Influence of light distribution on the performance of photocatalytic reactors: LED vs mercury lamps, Appl. Catal. B 215 (2017) 1–7, https://doi.org/10.1016/j. apcatb.2017.05.048.
- [39] M. Pelaez, P. Falaras, V. Likodimos, K. O'Shea, A.A. de la Cruz, P.S.M. Dunlop, J.A. Byrne, D.D. Dionysiou, Chemical Use of selected scavengers for the determination of NF-TiO₂ reactive oxygen species during the degradation of microcystin-LR under visible light irradiation, J. Mol. Catal. A, Chem. 425 (2016) 183–189, https://doi.org/10.1016/j.molcata.2016.09.035.
- [40] C.M. Lee, B.A.A. Nurul Aiin, P. Palaniandy, S.S. Abu Amr, Performance of natural sunlight on paracetamol removal from synthetic pharmaceutical wastewater using heterogeneous TiO₂ photocatalyst, Desalin. Water Treat. 78 (2017) 341– 349, https://doi.org/10.5004/DWT.2017.20879.
- [41] L. Yang, L.E. Yu, M.B. Ray, Photocatalytic Oxidation of Paracetamol : Dominant Reactants, Intermediates, and Reaction Mechanisms, Environ. Sci. Technol. 43 (2009) 460–465, https://doi.org/10.1021/es8020099.

- [42] I. Dalmázio, T.M.A. Alves, R. Augusti, An Appraisal on the Degradation of Paracetamol by TiO₂ /UV System in Aqueous Medium. Product Identification by Gas Chromatography-Mass Spectrometry (GC-MS), J. Brazilian Chem. Soc. 19 (2008) 81–88, https://doi.org/10.1590/S0103-50532008000100013.
- [43] D. Vogna, R. Marotta, A. Napolitano, M. d'Ischia, Advanced Oxidation Chemistry of Paracetamol. UV/H₂O₂ -Induced Hydroxylation / Degradation Pathways and 15 N-Aided Inventory of Nitrogenous Breakdown Products, J. Organic Chem. (2002) 6143–6151, https://doi.org/10.1021/jo025604v.
- [44] R. Andreozzi, V. Caprio, R. Marotta, D. Vogna, Paracetamol oxidation from aqueous solutions by means of ozonation and H₂O₂/UV system, Water Res. (37) (2003) 993–1004, https://doi.org/10.1016/S0043-1354(02)00460-8.
- [45] K.L. Oguzie, M. Qiao, X. Zhao, E.E. Oguzie, V.O. Njoku, G.A. Obodo, Oxidative degradation of Bisphenol A in aqueous solution using cobalt ion-activated peroxymonosulfate, J. Mol. Liq. 313 (2020), https://doi.org/10.1016/j.molliq. 2020.113569 113569.
- [46] L.M. Mendoza-Huizar, C.H. Rios-Reyes, Chemical reactivity of Atrazine employing the fukui function, J. Mex. Chem. Soc. 55 (3) (2011) 142–147, https://doi.org/10.29356/jmcs.v55i3.812.
- [47] V.H. Thi, B. Lee, Effective photocatalytic degradation of paracetamol using Ladoped ZnO photocatalyst under visible light irradiation, Mater. Res. Bull. 96 (2017) 171–182, https://doi.org/10.1016/j.materresbull.2017.04.028.
- [48] C.D. Zanrosso, D. Piazza, M.A. Lansarin, Polymeric hybrid films with photocatalytic activity under visible light, J. Appl. Polym. Sci. 46367 (2018) 1-10, https://doi.org/10.1002/app.46367.
- [49] I.K. Konstantinou, T.A. Albanis, TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigation: A review, Appl. Catal. B 49 (2004) 1–14, https://doi.org/10.1016/j.apcatb.2003.11.010.
- [50] H. Rajabi, N. Ghaemi, S.S. Madaeni, P. Daraei, B. Astinchap, S. Zinadini, S.H. Razavizadeh, Nano-ZnO embedded mixed matrix polyethersulfone membrane: Influence of nanofiller shape on characterization and fouling resistance, Appl. Surf. Sci. 214 (2015) 1016, https://doi.org/10.1016/j.apsusc. 2015.04.214.
- [51] P. Lei, F. Wang, X. Gao, Y. Ding, S. Zhang, J. Zhao, Immobilization of TiO₂ nanoparticles into polymeric substrates by chemical bonding for multi-cycle photodegradation of organic pollutants, J. Hazard. Mater. 227–228 (2012) 185–194, https://doi.org/10.1016/j.jhazmat.2012.05.029.
- [52] A. Kumar, G. Pandey, A review on the factors affecting the photocatalytic degradation of hazardous materials, Mater. Sci. Eng. Int. J. 3 (2017) 106–114, https://doi.org/10.15406/mseij.2017.01.00018.
- [53] J.-C. Chou, L.P. Liao, Study on pH at the point of zero charge of TiO₂ pH ionsensitive field effect transistor made by the sputtering method, Thin Solid Films 476 (2005) 157–161, https://doi.org/10.1016/j.tsf.2004.09.061.
- [54] P.T. Lum, K.Y. Foo, N.A. Zakaria, Visible light driven photocatalytic degradation of paracetamol using incense ash supported ZnO nanocomposites, Malaysian J. Anal. Sci. 23 (2019) 771–780, https://doi.org/10.17576/mjas-2019-2305-02.
- [55] M. Magureanu, N.B. Mandache, V.I. Parvulescu, Degradation of pharmaceutical compounds in water by non-thermal plasma treatment, Water Res. 81 (2015) 124–136, https://doi.org/10.1016/j.watres.2015.05.037.
- [56] T.A. Ternes, Occurrence of drugs in German sewage treatment plants and rivers, Water Res. 32 (1998) 3245–3260, https://doi.org/10.1016/S0043-1354 (98)00099-2.
- [57] M. Gavrilescu, K. Demnerová, J. Aamand, S. Agathos, F. Fava, Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation, New Biotechnol. 32 (1) (2015) 147–156, https://doi.org/10.1016/j.nbt.2014.01.001.