Understanding the photodegradation of amoxicillin antibiotic using visible light sensitized poly(methyl methacrylate)/TiO_2 nanocomposite

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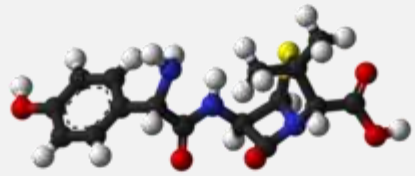
Abstract

The present study aimed to investigate the feasibility of using the novel type of PMMA/TiO_2 nanocomposite film as a highly efficient visible light photocatalyst for photocatalytic degradation of amoxicillin (AMOX) as a model pollutant from aqueous solution and determining its removal efficiency. The PMMA/TiO_2 nanocomposite which was prepared by ionic liquid based microemulsion with (0.01 wt.%) of TiO_2 content exhibited high photocatalytic activity due to increase in the generated hydroxyl radicals during the mineralization under visible light illumination. The effect of pH as an operating factor was evaluated and it was found that the pH of 7 is optimal pH to achieve the high photocatalytic efficiency. Also, we tried to understand the reasons behind this performance of nanocomposites by means of generated hydroxyl radicals. Finally, we introduced a survey mechanism of the behaviour of this novel PMMA/TiO_2 nanocomposite with low loading amount of TiO_2 nanoparticles.

1. Introduction

Recently, the fate of medicines into the aquatic environment and related risks is an interesting concern in water detoxification and has become an environmental issue of ever-increasing importance worldwide [1-5]. Mainly focus on the antibiotics parent compound removal and mineralization has been developing because of their potential role in the improvement of antibiotic resistant bacteria and continuous input into the ecosystem. One of the most extensively used antibiotics is amoxicillin (AMOX, (2S, 5R, 6R)-6-{[(2R)-2-amino-2-(4-hydroxyphenyl)-acetyl]amino}-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0] heptane-2-carboxylic acid, see Tab. 1) as a semi-syntethic and a moderate-spectrum bacteriolytic β lactam antibiotic [1, 6-10]. It has been widely utilized in humans and food-producing animals to treat several diseases for a long time, making livestock agriculture a major source of antibiotic pollution. Consequently, it can be chosen as the model contamination [11-14].

Table 1. Chemical structure and characteristics of AMOX as a pollutant model.

Characteristics	
Structure	
IUPAC name	(2*S*,5*R*,6*R*)-6-[(*R*)-(-)-2-amino-2-(*p*-hydroxyphenyl)acetamido]-3,3-dimethyl-7-oxo-4thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid
Molecular formula	$C_{16}H_{19}N_3O_5S$
Molecular weight	365.4 g/mol
Bioavailability	95% oral
Half-life	61.3 minutes

Up to now, many efforts were directed for AMOX degradation and also, a variety paper reported based on the photocatalysis systems toward extending TiO_2 nanoparticles response to visible light region and also enhancing the photocatalytic activity of TiO_2 nanoparticles in wastewater treatment applications [15]. Although TiO_2 nanoparticles is one of the most efficient nanoparticles in photocatalysis wastewater treatment system, with the highest stability and simple preparation methods with the lowest cost, there are drawbacks that hinder its practical applications like its release and environmental risks and need of costly post-treatment separation processes [16]. To head off these limitations, immobilized visible light sensitized TiO_2 nanoparticles in polymer matrix received considerable attention due to their role in accelerating the transfer charge carriers and also due to the simple recovery which decreases the photocatalytic activity. In our recent reported literatures, the photodegradation of methylene blue (MB) and trypan blue dye [17-19], photoreduction of 4-nitrophenol to 4-aminophenol [20], MTBE [21] as a pollutant model, antibacterial activity against a variety of bacteria including of (*Escherichia coli* and *Bacillus*) as Gram negative and (*Staphylococcus arouse* and *kelebsiella*) as Gram positive bacteria [20,22] and also photoinduced hydrophilicity [23] were evaluated by a novel type of polymer nanocomposite as visible light active PMMA-TiO_2 photocatalyst prepared by ionic liquid based microemulsion system. The main purpose of microemulsion system based on the micelles is to control the particle growth, size, morphology and monodispersity of nanoparticles in polymer matrix and hence, increase the surface area of nanofillers and also increase the photocatalytic activity [24-33]. In continuing, the elucidation of the AMOX degradation reaction makes the novelty of the present research based on photocatalytic activity using PMMA-supported TiO_2 nanocomposite film. Then the mechanism of action of PMMA-supported TiO_2 nanocomposite film during the visible light degradation of AMOX is presented. This study is expected to explore the applicability of visible light induced heterogeneous PMMA/TiO_2 photocatalyst process.

2. Experimental

2.1. Materials

Hydrophilic ionic liquid, ([bmim][BF_4]), the nonionic surfactant of Triton X-100 and the amoxicillin (AMOX) as a pollutant model were purchased from Sigma-Aldrich. The titanium dioxide TiO_2 nanoparticles used in this study was Degussa P25 (ca. 80% anatase, 20% rutile, with a BET surface area of 50 m^2/g and particle size of less than 15 nm). All chemicals used in this study were analytical grade and purchased from Merck. Aqueous solutions were prepared with deionized water (0.055 μΩ) which was produced in our lab with PKA (Smart two pure) instrument.

2.2. Preparation of the visible light sensitized PMMA/TiO_2 nanocomposite film

The modified PMMA/TiO_2 nanocomposite film was prepared by the controlled TiO_2/IL nanosphere in polymer matrix using IL based microemulsion system as a soft template which this procedure is described elsewhere [17]. For marking purposes, the resultant transparent modified nanocomposite films of PMMA/TiO_2 were labeled as S1, S2 and S3 indicating to the amounts of TiO_2 nanoparticles corresponding to 0.008, 0.01and 0.012 *wt.*%. No apparent visible phase separation was observed during polymerization process for all samples. Techniques such as UV-Vis diffuse reflectance spectra (DRS), TEM, FT-IR and TGA were used to characterize the resulting modified nanocomposite and reported in our previous paper [17]. The scanning electron microscopy (SEM) was also used to characterize the fabricated nanocomposite film.

2.3. Characterization

Nanostructural characterization of the fractured surface of the PMMA/TiO_2 (S2) as a representation sample was performed on a scanning electron microscopy (SEM) Philips XL30 instrument. Prior to analysis the S2 nanocomposite sample was coated with gold thin layer in order to prevent charging of the surface, to promote the emission of secondary electrons so that the specimen conducts evenly, and to provide a homogeneous surface for analysis and imaging.

2.4. Photocatalytic activity

The photocatalytic degradation of the AMOX using the produced nanocomposites at different loading of TiO_2 in nanocomposites was evaluated according to their photodegradation efficiency of AMOX in aqueous solution. In a typical experiment, thermostatted at 21 ˚C 50-ml batch reactor with inner diameter 100 mm, was used in photocatalytic degradation experiments and the desired amount of the nanocomposite samples heterogeneously placed into reactor and was called ‘‘active’’ and the other containing no nanocomposite was called ‘‘blank’’. In the experiments, the initial concentration of AMOX was fixed at 100 μg/ml. Amoxicillin Standard Solution (100 $\mu g.ml^{-1}$) was prepared as follows: 0.01 g of is dissolved in 1 ml 0.1 M sodium hydroxide solution then the mixture is diluted to 100 ml in a volumetric flask with doubled distilled water. Working solutions were freshly prepared by subsequent dilutions. Each of reactors was exposed to the identical experimental conditions. The samples from the active reactor were compared to the reference samples to confirm the photocatalytic activity of prepared nanocomposites under visible light illumination. The nanocomposite as a highly visible light photocatalyst in photocatalytic assessment was irradiated with a xenon lamp (300 W) doubly covered with a UV cut filter. The illuminance of the applied lamp was measured using TES 1332 luxmeter (TES Inc., Taiwan), which corresponds to the irradiance of 0.3 mW/cm^2.

In this study, all the experiments were carried out for at most three times under identical experimental conditions. It must be noted that the average deviation of data in parallel experiments did not exceed 6%.

AMOX concentration in aqueous phase was determined using a UV-Visible spectrophotometer (UV2550, Shimadzu, Japan) by a 1-cm quartz cell with the AMO preconstructed calibration curves. It was noted that the UV-absorbance spectra of photocatalytic-treated solutions did not exhibit a change in shape of the UV-absorbance spectra, showing no new peaks or a wavelength shift in maximum absorbance. Chemical oxygen demand (COD) was determined by a standard dichromate method, using HACH kits LCK 314 (15–150 mg O/l) and LCK 414 (5–60 mg O/l). Waters Model high performance liquid chromatography (HPLC) (Waters YL9100HPLC SYSTEM, USA) system with C_{18} column (CP-SIL 5 CB column model, 250*4.6 mm, 5 μm) was also used to AMOX concentration detection which was calibrated and tested prior to injection of the photodegraded samples. The mobile phase was included methanol and water. The volume ratio of methanol to water was optimized at 30/70 and flow rate of 0.5 ml/min was optimized, respectively. A UV absorbance detector at 230 nanometer wavelengths was used to detect AMOX in the samples. The AMOX photodegradation efficiency, E is calculated according to the following equation:

$$E = \frac{\Delta c \times V \times 1000}{I \times S \times t} \quad (1)$$

where E, AMOX photodegradation efficiency, mg/(W.h); Δc, the decrease in the AMOX concentration, mg/l, or COD, mg O/l; V, the volume of the sample to be treated, l; I, irradiance, mW/cm^2; S, irradiated area, cm^2; t, treatment time, h. The photodegraded products were identified on HPLC-MS spectra (LCQ-Advantage, USA) equipped with an ODS C_{18} column (150 mm × 2.1 mm, 3.5 μm). The detection limit for the sample was 1nanogram/ l.

3. 3. Results and Discussion

3.1. Characterization of PMMA/TiO_2 nanocomposite

3.1.1. SEM analysis of PMMA/TiO_2 nanocomposite

The SEM image of PMMA/TiO_2 (S2) as a typical sample (0.01 wt.% of TiO_2 in nanocomposite) is shown in Fig. 1. It can be confirmed that the morphology of the sensitization of TiO_2 nanoparticles with hydrophilic ionic liquid TiO_2 in nanocomposite dos not much from that original TiO_2 which was used to prepare the novel type of PMMA/TiO_2 nanocomposite. The sensitization of TiO_2 does not significantly change the size of TiO_2 nanoparticles and are slightly dispersed in polymer matrix accordance with the TEM result [17]. The average particle size of TiO_2 nanoparticles in polymer matrix was detected to be 11 nm.

3.1.2. Measurement of Hydroxyl Radical

Fig. 2 shows the hydroxyl radical with different TiO_2 content as a comparative study. This work concerns recent research work on the measurement of generated hydroxyl radical during the photon irradiation to nanocomposite film [17]. This is because of an excellent role of the hydroxyl radical as a powerful oxidizing species with potential oxidation of approximately 2.8 volt (versus NHE). It is clear that the photocatalytic activity is a positive correlation to the formation rate of *OH radicals and this phenomenon lead to complete photomineralization of water pollutants.

salicylic acid as a probe molecule was used to test the effect of different TiO_2 loading in polymer nanocomposites including (0.008, 0.01 and 0.012 wt.%) on the amount of produced hydroxyl radical [36,37]. The amount of hydroxyl radicals increases as the TiO_2 content in polymer matrix increases up to 0.01 wt.% nanofiller and then decreases. As can be seen from Fig. 2, the amount of generated hydroxyl radical of 0.012 wt.% TiO_2 is very low, hence the sample has a high recombination rate of photoinduced charge carriers in contrast of 0.01 wt.% as one of the major drawbacks of TiO_2 mediated photocatalysis.

Based on the previous report [18], due to the reaction of salicylic acid with the hydroxyl radicals during 60 min, the 2,3-dihydroxybenzoic acid formed and the amounts of hydroxyl radicals absorbed by the solution at the wavelength of 510 nm were measured. In this investigation, first, a control experiment was run before adding the nanocomposite and no change is observed in the absorbance of solution, indicating that there was no photolysis reaction in salicylic acid under visible light illumination.

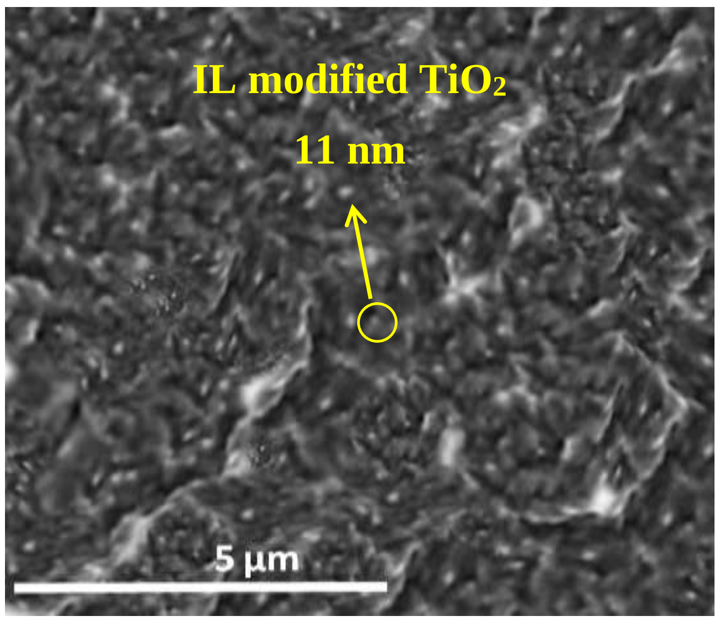


Fig. 1. SEM image showing surface morphology of modified PMMA/TiO_2 (S2) nanocomposite

3.2. Photocatalytic activity results

3.2.1. The effect of TiO_2 dosage in nanocomposite on AMOX photodegradation efficiency

The results of AMOX photodegradation using PMMA/TiO_2 is illustrated in Fig. 3. The obtained results revealed that photocatalytic activity that was calculated with Eq. 1, regularly increased with increasing content of TiO_2 up to 0.01 wt.% and then decreased with increasing of TiO_2 dosage (0.012 wt.%). The enhancement of photocatalytic activity of (S2) sample of PMMA/TiO_2 nanocomposite film could be assigned to the fact that the IL based microemulsion is an excellent method to produce PMMA/TiO_2 nanocomposite as a highly efficient visible light photocatalyst. As shown in Fig. 3, the highest treatment efficiency occurred at its natural pH of AMOX solution. As per our previous literature survey, it was evident that high amount of generated hydroxyl radicals during the photocatalysis mechanism leads to an increase in photocatalytic degradation efficiency.

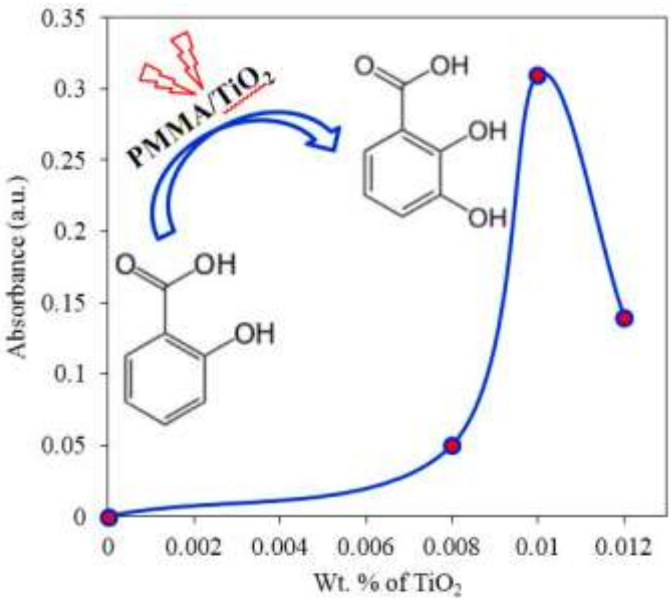


Fig. 2. Hydroxyl radical amounts obtained using modified PMMA/TiO_2 nanocomposite at different TiO_2 content under visible light irradiation for 60 min

3.2.2 The effect of pH on AMOX photodegradation efficiency

The variations of pH on the photodegradation efficiency of AMOX by visible light photocatalysis process over the S2 sample of PMMA/TiO_2 nanocomposite at initial concentration of the AMOX antibiotic (C_0=100 µg/ml) was shown in Fig 4. Data regarding the effect of pH shows that as pH increased from 5 to 7, the photocatalytic efficiency increased and then decreased with increasing pH (Fig. 4). Based on the data obtained in the present study, pH of 7 is optimal pH for photodegradation of AMOX under visible light irradiation and AMOX can be facilely on the surface of nanocomposite. The photocatalytic efficiency of 52.56 % was calculated by Eq. (1) in this case after 8 h of visible light irradiation. The superior photodegradation efficiency of prepared nanocomposite could be attributed to high amount of obtained hydroxyl radicals at natural pH on the surface of nanocomposite. Moreover, the hydrophilic effect of carbonyl group and conjugation effect of phenyl ring reduce the alkalinity of amino groups, which induced the surface of nanocomposite and hence the adsorptive capacity of nanocomposite for photodegradation of AMOX increase at pH of 7.

As the reduction of chemical oxygen demand (COD) reflects the extent of degradation, the change of COD concentration in the photodegradation of AMOX was investigated under visible light for 8 h. The initial COD of AMOX solution was obtained 218.46 mg/L. After visible light irradiation for 8h, the COD concentration was decreased to 45.1 mg/L over S2 nanocomposite sample at pH of 7. The reductions of COD further verify that AMOX pollutant was successfully photodegraded by the nanocomposite film at the optimal pH. Fig. 4-(b) described the % COD/COD_0 *vs*. time (h) over S2 sample at pH of 7.

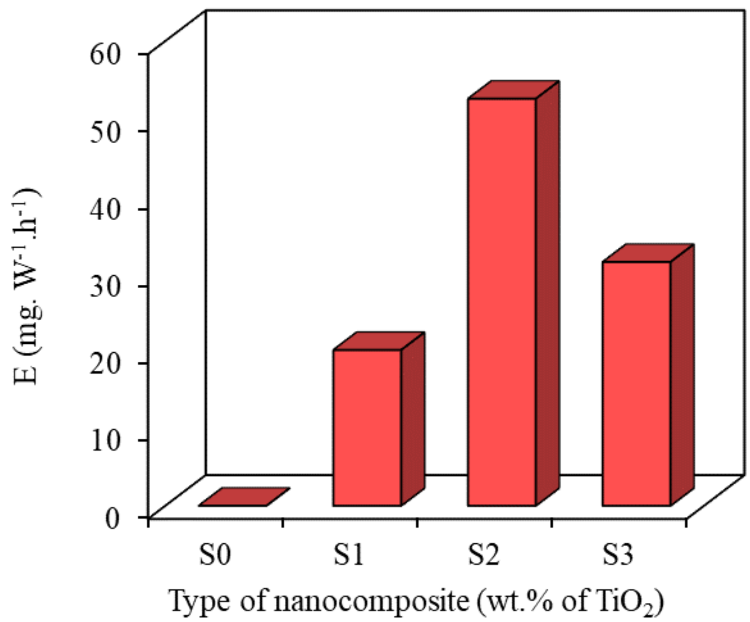


Fig. 3. The dependence of AMOX photocatalytic degradation efficiency (E) *vs*. type of nanocomposite at 21 ˚C after 8 h visible light irradiated

3.2.3. Photodegraded products of AMOX

The photodegraded products of AMOX after 8h visible light irradiated over S2 sample of nanocomposite were separated by HPLC at the retention time of 1.98, 3.25, and 16.52 min (Fig. 5), and each peak was characterized by its mass measurements (*m*/*z*) attributed to amoxicillin penicilloic acid (*m/z* 383), amoxicillin penicilloic acid (*m/z* 325) and amoxicillin penicilloic acid (*m/z* 284), respectively.

3.2.4. Proposed mechanism for photodegradation of AMOX

An important highlight of this work based on our previous works is that the ionic liquid to form ionic liquid-in-oil microemulsion acts as the sensitizer agent showed an extended light sensitivity to visible light range (400-700 nm) with an absorption edge up to 400 nm which was significantly greater that original TiO_2 without the recombination of charge carries from sensitized TiO_2. Overall, taking previous research the photo-generated electrons may easily transfer from excited ionic liquid to TiO_2, but not to recombine with the photo-generated holes on the surface of TiO_2 immediately [17]. A schematic representation of the photocatalytic mechanism under visible light irradiation is shown in Fig. 6.

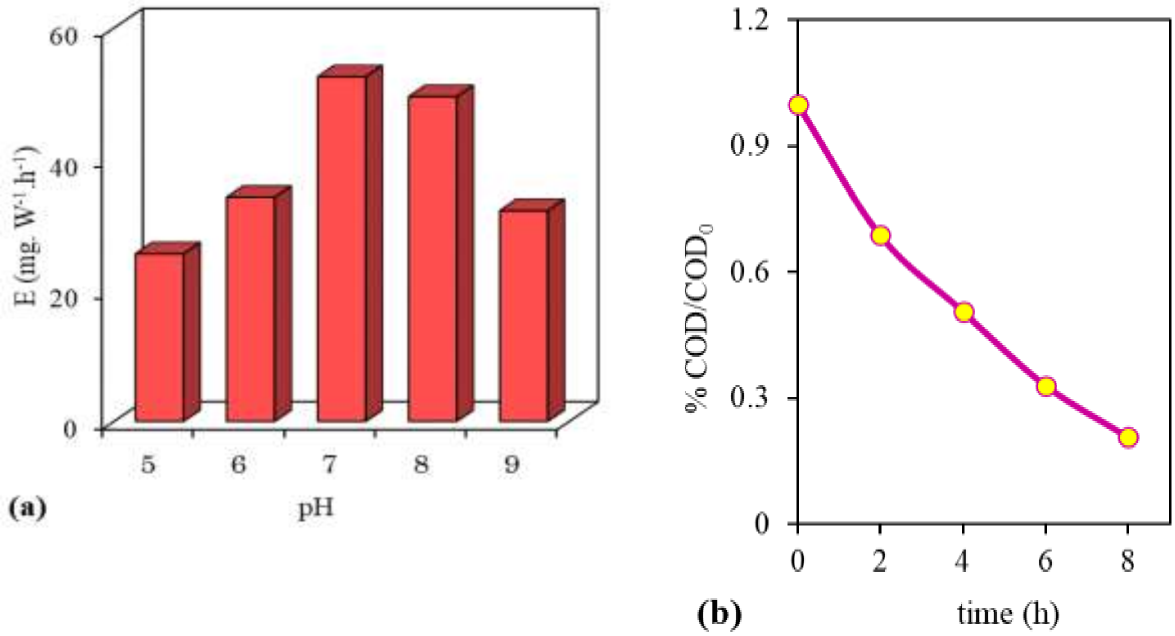


Fig. 4. (a) The dependence of AMOX photocatalytic degradation efficiency (E) *vs*. pH values at 21 ˚C after 8 h visible light irradiated and (b) % COD/COD$_0$ *vs*. time (h) over S2 sample at pH of 7.

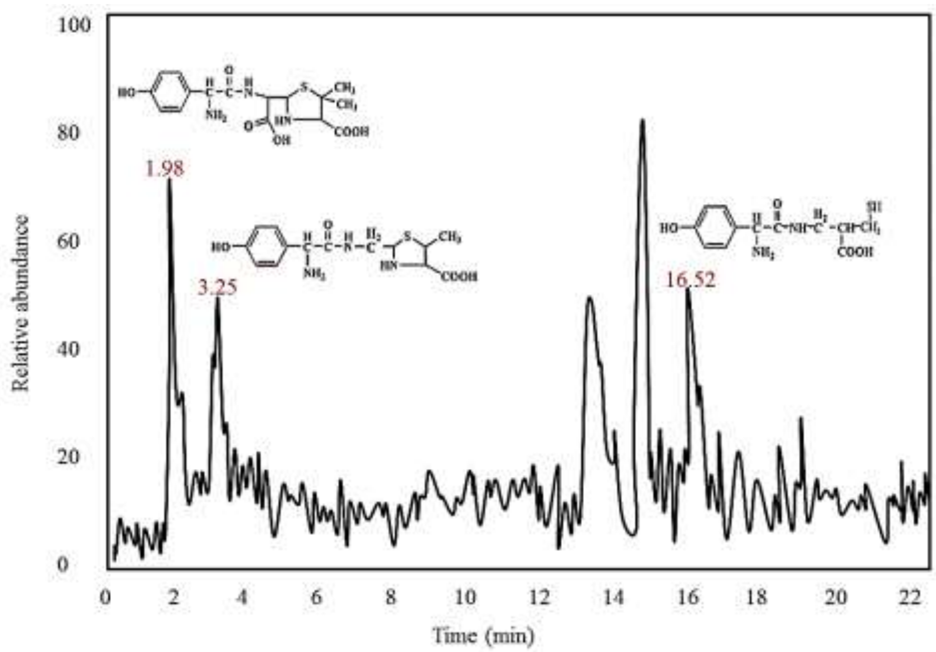


Fig. 5. HPLC chromatogram of the photodegraded AMOX over S2 sample at pH=7 after 8h of visible light irradiation

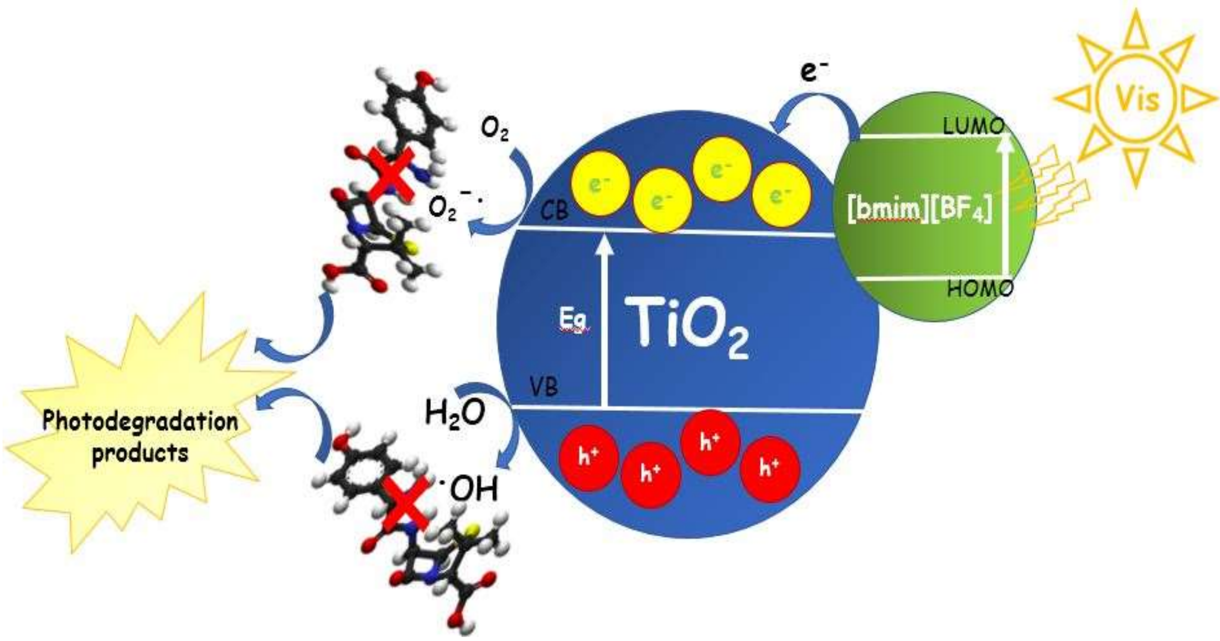


Fig. 6. Mechanism of the photoinduced charge transfer on the modified PMMA/TiO_2 nanocomposite that harvest visible light for photodegradation of AMOX pollutant. CB, Conduction band; VB, Valence band; $^{\bullet}OH$, Hydroxyl radical; $O_2^{\bullet -}$, Superoxide anion radical; E_g, Band gap energy, LUMO, Lowest unoccupied molecular orbital; HOMO, Highest occupied molecular orbital.

4. Conclusions

In this work, a novel photocatalytic decomposition process of visible light responsive PMMA/TiO_2 nanocomposite films have been investigated for the degradation of amoxicillin at its natural pH, resulting in appreciable treatment efficiency. As can be seen, it was found that PMMA/TiO_2 nanocomposite with 0.01 wt.% of TiO_2 content has a best photocatalytic activity under visible light for 8 h. The results further revealed that the pH=7 acted as a key factor to achieve the high photodegradation efficiency. Hence, the prepared nanocomposite film with low dosage of TiO_2 content construct an efficient, reproducible and stable visible light active photocatalysis system for the elimination of organic pollutants and also microorganisms, which offers potential for medical application and is crucial to industrial wastewater treatment.

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References

[1] D. Klauson, J. Babkina, K. Stepanova, M. Krichevskaya, S. Preis, Aqueous photocatalytic oxidation of amoxicillin, Catal. Today 151 (2010) 39–45. https://doi.org/10.1016/j.cattod.2010.01.015

[2] A. Al-Ahmad, F.D. Daschner, K. Ku¨mmerer, Biodegradability of cefotiam, ciprofloxacin, meropenem, penicillin G, and sulfamethoxazole and inhibition of wastewater bacteria, Arch. Environ. Contam. Toxicol. 37 (1999) 158–163. https://doi.org/10.1007/s002449900501
[3] T. Fotiou, T.M. Triantis, T. Kaloudis, A. Hiskia, Evaluation of the photocatalytic activity of TiO_2 based catalysts for the degradation and mineralization of cyanobacterial toxins and water off-odor compounds under UV-A, solar and visible light, Chem. Eng. J. 261 (2015) 17–26. https://doi.org/10.1016/j.cej.2014.03.095
[4] K. Kummerer, A. Al-Ahmad, V. Mersch-Sundermann, Biodegradability of some antibiotics, elimination of their genotoxicity and affection of wastewater bacteria in a simple test, Chemosphere 40 (2000) 701–710. https://doi.org/10.1016/s0045-6535(99)00439-7
[5] R. Alexy, T. Ku¨ mpel, K. Ku¨ mmerer, Assessment of degradation of 18 antibiotics in the closed bottle test, Chemosphere 57 (2004) 505–512. https://doi.org/10.1016/j.chemosphere.2004.06.024
[6] T. Herberer, Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, Toxicol. Lett. 131 (2002) 5–17. https://doi.org/10.1016/s0378-4274(02)00041-3
[7] M.N. Abellan, B. Bayarri, G. Gimenez, J. Costa, Photocatalytic degradation of sulfamethoxazole in aqueous suspension of TiO_2, Appl. Catal. B 74 (2007) 233–241. https://doi.org/10.1016/j.apcatb.2007.02.017
[8] B. Halling-Sorensen, S. Nors Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Holten Lu¨ tzhoft, S.E. Jorgensen, Occurrence, fate and effects of pharmaceutical substances in the environment—a review, Chemosphere 36 (1998) 357–393. https://doi.org/10.1016/s0045-6535(97)00354-8
[9] C. Hartig, T. Storm, M. Jekel, Detection and identification of sulphonamide drugs in municipal waste water by liquid chromatography coupled with electrospray ionisation mass spectrometry, J. Chromatography. A, 845 (1999) 163–173. https://doi.org/10.1016/s0021-9673(99)00378-7
[10] S. Kim, P. Eichhorn, J.N. Jensen, A.S. Weber, D.S. Aga, Removal of antibiotics in wastewater: effect of hydraulic and solid retention times on the fate of tetracycline in the activated sludge process, Environ. Sci. Technol. 39 (2005) 5816–5823. https://doi.org/10.1021/es050006u
[11] W. Baran, J. Sochacka, W. Wardas, Toxicity and biodegradability of sulfonamides and products of their photocatalytic degradation in aqueous solutions, Chemosphere 65 (2006) 1295–1299. https://doi.org/10.1016/j.chemosphere.2006.04.040
[12] H. Sorum, in: F.M. Aarestrup (Ed.), Antimicrobial resistance in bacteria of animal origin, American Society for Microbiology Press, Washington, DC, 2006.
[13] A. Chatzikakis, C. Berberidou, I. Paspaltsis, G. Kyriakou, T. Sklaviadis, I. Poulios, Photocatalytic degradation and drug activity reduction of Chloramphenicol, Water Res. 42 (2008) 386–394. https://doi.org/10.1016/j.watres.2007.07.030
[14] E.S. Emolla, M. Chaudhuri, Degradation of the antibiotics amoxicillin, ampicillin and cloxacillin in aqueous solutions by the photo-Fenton process, J. Hazard. Mater. 172 (2009) 1476–1481.
[15] S. Singh, H. Mahalingam and P. Kumar Sing, Polymer-supported titanium dioxide photocatalysts for environmental remediation: A review, Appl. Catal., A, 462 (2013) 178-195. http://dx.doi.org/10.1016/j.apcata.2013.04.039
[16] M. Ratova, A. Mills, Antibacterial titania-based photocatalytic extruded plastic films, J. Photochem. Photobiol., A, 299 (2015) 159. https://doi.org/10.1016/j.jphotochem.2014.11.014
[17] F. Mirhoseini, A. Salabat, Ionic liquid based microemulsion method for fabrication of poly(methyl methacrylate)–TiO_2 nanocomposite as highly efficient visible light photocatalyst, RSC Adv. 5 (2015) 12536–12545. https://doi.org/10.1039/c4ra14612c
[18] F. Mirhoseini, Alireza Salabat, Investigation of operational parameters on the photocatalytic activity of a new type of poly(methyl methacrylate)/ionic liquid-TiO_2 nanocomposite, Iranian J. Chem. Chem. Eng., 38 (2019) 101-114. https://doi.org/10.30492/IJCCE.2019.37613
[19] F. Mirhoseini, Alireza Salabat, Photocatalytic filter, United States patent 10828629.
[20] A. Salabat, F. Mirhoseini, Applications of a new type of poly(methyl methacrylate)/TiO_2 nanocomposite as an antibacterial agent and a reducing photocatalyst. Photochem. Photobiol. Sci., 14(9) (2015) 1637–1643. https://doi.org/10.1039/c5pp00065c
[21] F. Mirhoseini, Alireza Salabat, Removal of methyl tert -butyl ether as a water pollutant by photodegradation over a new type of poly(methyl methacrylate)/TiO_2 nanocomposite. Polymer Composites, 39(4) (2018) 1248–1254. https://doi.org/10.1002/pc.24059
[22] F. Mirhoseini, A. Salabat, Antibactrial activity based poly(methyl methacrylate) supported TiO_2 photocatalyst film nanocomposite, Tech. J. Eng. Appl. Sci. 5 (2015)115-118.
[23] A. Salabat, F. Mirhoseini, Photo-induced hydrophilicity study of poly(methyl methacrylate)/TiO_2 nanocomposite prepared in ionic liquid based microemulsion system. Current Appl. Polym. Sci., 2(2), (2018) 112–120. https://doi.org/10.2174/2452271602666180803141554

[24] A. Salabat, F. Mirhoseini, Polymer-based nanocomposites fabricated by microemulsion method, Polym. Compos. 43 (2022) 1282–94. https://doi.org/10.1002/pc.26504

[25] A. Salabat, F. Mirhoseini, M. Mahdieh, H. Saydi, A novel nanotube-shaped polypyrrole-Pd composite prepared using reverse microemulsion polymerization and its evaluation as an antibacterial agent, New J. Chem. 39 (5) (2015) 4109–4114. https://doi.org/10.1039/c5nj00175g

[26] A. Salabat, F. Mirhoseini, M. Arjomandzadegan, E. Jiryaei, A novel methodology for fabrication of Ag-polypyrrole core-shell nanosphere using microemulsion system and evaluation of its antibacterial application, New J. Chem. 41 (21) (2017) 12892–12900. https://doi.org/10.1039/c7nj00678k

[27] A. Salabat, F. Mirhoseini, R. Valirasti, Engineering poly(methyl methacrylate)/Fe_2O_3 hollow nanospheres composite prepared in microemulsion system as a recyclable adsorbent for removal of benzothiophene, Ind. Eng. Chem. Research 58 (2019) 17850-1785. https://doi.org/10.1021/acs.iecr.9b04322

[28] F. Kamali, K. Faghihi, F. Mirhoseini, High antibacterial activity of new eco-friendly and biocompatible polyurethane nanocomposites based on Fe_3O_4/Ag and starch moieties. Polym. Eng. Sci., 62(5) (2022) 1444-1462.https://doi.org/10.1002/pen.25934

[29] A. Salabat, F. Mirhoseini, F.H. Nouri, Microemulsion strategy for preparation of TiO_2–Ag/poly(methyl methacrylate) nanocomposite and its photodegradation application. J. Iranian Chem. Soc. 20 (2022) 599–608. https://doi.org/10.1007/s13738-022-02693-7.

[30] A. Salabat, F. Mirhoseini, K. Abdoli, A microemulsion route to fabrication of mono and bimetallic Cu/Zn/γ-Al_2O_3 nanocatalysts for hydrogenation reaction. Scientia Iranica, 25(2018) 1364-1370. https://doi.org/10.24200/sci.2018.5023.1048

[31] B.S. Mirhoseini, A. Salabat, A novel surfactant-free microemulsion system for the synthesis of poly(methyl methacrylate)/Ag nanocomposite, J. Mol. Liq. 342 (2021) 117555. https://doi.org/10.1016/j.molliq.2021.117555

[32] A. Salabat, F. Mirhoseini, Z. Masoumi, M. Mahdie, Preparation and characterization of polystyrene-silver nanocomposite using microemulsion method and its antibacterial activity, JNS 4 (2014) 377-382.

[33] F. Alimohamadi, A. Salabat, Effect of surfactant type on the particle dispersion in Ag/polystyrene nanocomposite prepared by microemulsion method, Colloid Nanosci. J. 1 (2023) 112-118. https://doi.org/10.52547/CNJ.1.2.112

[34] F. Mirhoseini, A. Salabat, Polymer nanocomposite based composition and method for controlling water hardness, United States patent 11136247

[35] A. Salabat, F. Mirhoseini, A novel and simple microemulsion method for synthesis of biocompatible functionalized gold nanoparticles, J. Mol. Liq. 268 (2018) 849–853. https://doi.org/10.1016/j.molliq.2018.07.112

[36] J. G. Yu, Q. J. Xiang, and M. H. Zhou, Preparation, characterization and visible-light-driven photocatalytic activity of Fe-doped titania nanorods and first-principles study for electronic structures, Appl. Catal. B, 90 (2009) 595–602. https://doi.org/10.1016/j.apcatb.2009.04.021

[37] S. Rafaqat, N. Ali, C. Torres, B. Rittmann, Recent progress in treatment of dyes wastewater using microbial-electro-Fenton technology. RSC Advances, 12(27) (2022) 17104–17137. https://doi.org/10.1039/d2ra01831d