Enhanced photocatalytic degradation of doxycycline using a magnetic polymer-ZnO composite

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ABSTRACT

A novel magnetic polymer-ZnO composite was prepared by incorporating Fe3O4 and ZnO nanoparticles in the structure of an adsorbent polymer. Precipitation polymerization was used for synthesizing the adsorbent polymer and its efficiency for extracting doxycycline from aqueous solution was optimized according to several parameters including time, pH and amount of polymer. Results showed the highest extraction efficiency at neutral pH of the doxycycline solution in 20 min, and the capacity of the polymer was about 20 mg/g. The magnetic property of a material is important for fast and facile separation of composite particles after each use. Magnetic polymer-ZnO composite was synthesized by adding Fe3O4 and ZnO nano-particles to the polymerization mixture in order to take advantage of both sorption and photocatalytic degradation mechanisms. The obtained composite was characterized using X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy equipped with wavelength dispersive X-ray spectroscopy and used for enhanced photocatalytic degradation of doxycycline in aqueous solution. Results showed 76.5% degradation of doxycycline in 6 hours which was significantly higher than the degradation observed by an equivalent amount of ZnO nano-particles. Photocatalytic degradation of doxycycline fitted the pseudo first order kinetic model with a rate constant of $4 \times 10^{-3} \text{mg mL}^{-1} \text{min}^{-1}$.

Key words | aqueous solutions, composite, kinetics and equilibrium studies, photocatalytic degradation, wastewater treatment

INTRODUCTION

Tetracyclines are the second most commonly used antibiotic family in both human and veterinary medicine and have been frequently detected in surface water, ground water and even drinking water samples (Hao et al. 2012; Zhu et al. 2015). In recent years, widespread resistance to tetracycline has increased doxycycline administration and consequently its presence in the environment (Mompelat et al. 2009). The most dangerous consequence of the presence of antibiotics in the environment is the induction and development of antibiotic-resistant pathogens, which is a serious threat for human health (Auerbach et al. 2011). Since contaminated wastewater is the main source of antibiotics for the aquatic environment, the development of efficient wastewater treatment methods is necessary for removing these harmful compounds (Homer & Santos 2011).

Several methods have been studied for the removal or degradation of antibiotics present in aqueous matrices. These methodologies can be divided in two major categories: destructive methods that degrade the pollutant molecule to other chemical compounds, and non-destructive methods like adsorbent materials that transfer pollutants from a liquid to a solid phase, causing a secondary pollution site that needs further treatment (Daneshvar et al. 2004; Abdollahi et al. 2016). Photocatalytic degradation is a destructive wastewater treatment method that has gained considerable importance; especially when wastewater contains small amounts of refractory organic pollutants (Bhatkhande et al. 2002). This process is based on an oxidative reaction on the surface of a photocatalyst material (typically an inorganic semiconductor, such as zinc oxide), in the presence of a source of photon energy (Pourmoslemi et al. 2016a, 2016b).

Despite several advantages like probability of mineralization of toxic pollutants, low cost and simple facilities required, photocatalytic degradation has been rarely used in large scale treatment facilities (Calza et al. 2008; Duan
Poor adsorption capacity of photocatalyst materials for pollutant molecules has been the main limitation for the practical application of this methodology (Liu et al. 2011). Several studies have reported increasing the affinity of photocatalyst materials for pollutant molecules by incorporating them in composite structures with adsorbent materials such as carbon nano-tubes, graphene, cellulose or synthetic polymers (Nozawa et al. 2001; Kemell et al. 2005; Liu et al. 2011; Mokhtar Mohamed et al. 2015).

Molecularly imprinted polymers (MIP) are efficient adsorbents for organic compounds with advantages like stability at extremes of pH and temperature, ease of preparation, low cost and reusability. Introducing the substrate to be adsorbed (the template) during polymerization of these materials improves their adsorption capacity for that particular substrate. This ability is achieved by the incorporation of template molecules into the polymeric structure through non-covalent bonds. Washing the synthesized polymer using a suitable solvent removes the template molecules from the polymer structure, leaving cavities for more selective adsorption of template molecules (Luo et al. 2011). Composite materials composed of MIP adsorbents and semiconductor photocatalysts have advantages of both methodologies, including selective and efficient adsorption and subsequently photocatalytic degradation of pollutant molecules.

Another technique that has received increasing attention in the area of wastewater treatment is synthesizing magnetic polymers through encapsulating inorganic magnetic particles in the polymer structure. Magnetic polymers can easily be collected using an external magnetic field without centrifugation or filtration (Philippova et al. 2011; Shen et al. 2016). In recent years, a number of studies have investigated the combination of TiO$_2$ and imprinted polymers for the photocatalytic degradation of water pollutants. Tang and coworkers prepared core-shell magnetic imprinted nanoparticles via surface molecular imprinting. The synergistic effect of molecular imprinting and photocatalysis enhanced the photodecomposition of the highly toxic targets in this study. Magnetic MIPs could be rapidly separated and fixed by external magnetic fields (Tang et al. 2012). Arabzadeh and coworkers investigated applying a nano-composite of MIP-TiO$_2$ for the removal of tartrazine from water. The results of this study showed higher removal efficiency of MIP-TiO$_2$ nano-composite compared with the non-imprinted polymer-TiO$_2$ nano-composite or pure TiO$_2$ nano-particles (Arabzadeh et al. 2016). Escobar and co-workers synthesized molecularly imprinted composites containing low TiO$_2$ loading via an acid-catalyzed sol-gel route using different classes of pharmaceuticals as the template. Compared to the commercial sample of TiO$_2$, adsorption and degradation were enhanced in the MIP-TiO$_2$ composite (de Escobar et al. 2016). In another study Lai and coworkers prepared a molecularly imprinted TiO$_2$-graphene composite for the photocatalytic degradation of bisphenol A. Results of this study showed better adsorption capacity and selectivity towards the template molecule and enhanced photocatalytic efficiency compared with TiO$_2$-graphene or non-imprinted TiO$_2$-graphene composites (Lai et al. 2016).

In the present study, precipitation polymerization in the presence of doxycycline molecules and the subsequent washing step were used for preparing an adsorbent polymer material. The polymer was characterized according to scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy and applied to the extraction of doxycycline from aqueous solution. Effects of time, pH, doxycycline concentration and polymer amount on the extraction efficiency of the polymer were studied. In the next step, polymer-ZnO composite was synthesized by adding ZnO nano-particles to the polymerization mixture. After characterization using FTIR spectroscopy, SEM, X-ray diffraction (XRD) and wavelength dispersive X-ray spectroscopy (WDX), the polymer-ZnO composite was used for photocatalytic degradation of doxycycline in aqueous solution under UV-C irradiation. Finally, a magnetic composite was synthesized by adding Fe$_3$O$_4$ nano-particles to the structure of the polymer-ZnO composite in order to facilitate recovery of composite particles after each experiment.

**METHODS**

**Materials**

Doxycycline monohydrate (99.8% purity) was purchased from Changzhou Pharmaceutical Factory (Changzhou, China). Methacrylic acid (MAA), methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). MAA was distilled under elevated pressure to remove the inhibitor. Trimethylolpropanetriacrylate (TRIM) was purchased from Sigma-Aldrich and used as received. 2, 2'-azobis-isobutyronitrile (AIBN) was obtained from Aros Organics (Geel, Belgium) and recrystallized from methanol before use.

Fe$_3$O$_4$ nano-particles (99.5% purity, 15–20 nm) were supplied from Nano Rahpouyan Mahan (Tehran, Iran). ZnO nano-particles were synthesized using the microwave assisted gel combustion method described in our previous work (Assi et al. 2015; Pourmoslemi et al. 2016a, 2016b).
Chemical analysis

Doxycycline concentration in aqueous solution was determined through UV-Visible spectrophotometry (P80+ spectrophotometer, PG instruments, Japan). UV-Visible adsorption spectrums of all samples were obtained by full scan analysis in the range of 190–700 nm (2 nm increments). Absorbance of the solution at doxycycline λ\(_{\text{max}}\) = 344 nm was determined and spectrums were saved for further investigations.

For analytical investigation of samples using UV-Visible spectrophotometry, a calibration curve in the range of 0.1–50 \(\mu\)g/mL was depicted using data obtained from standard aqueous solutions of doxycycline made and analyzed on three different days (%RSD range, 1.04–4.11). The regression equation was \(Y = 0.029X - 0.004 \ (r^2 = 0.999)\) where \(Y\) and \(X\) are absorbance at 344 nm and concentration (\(\mu\)g/mL), respectively.

Preparation of stock and standard solutions

Doxycycline 500 \(\mu\)g/mL stock solution was prepared in deionized water obtained from a Milli-Q\(^\text{®}\) system (Millipore, Milford, MA, USA). Aliquots of stock solution were transferred into 10 mL A-grade volumetric flasks and diluted with deionized water to obtain standard solutions with final concentrations of 0.1, 0.5, 1, 2.5, 10, 20, 40 and 50 \(\mu\)g/mL to be used in the preparation of the calibration curve. Working solutions were prepared by dilution of stock solution by deionized water to the desired concentration and then adjusting pH using 1 N HCl or NaOH solutions.

Adsorbent polymer synthesis and characterization

Adsorbent polymer was synthesized according to the precipitation polymerization method developed by Jing and co-workers (Jing et al. 2011). To briefly explain the method, doxycycline (0.75 mmol) as template and MAA (6 mmol) as functional monomer were dissolved in 65 mL of a mixture of methanol and acetonitrile (30/35, v/v) and stirred for 18 hours. This pre-polymerization step allows efficient non-covalent bonds to form between template and functional monomer, which subsequently increases the number of sites for selective extraction of doxycycline in the polymer structure. In the next step TRIM (3 mL) as cross-linker and AIBN (30 mg) as free radical initiator were added and the mixture was deoxygenated by nitrogen purging for 15 min. Polymerization was performed in a 55 °C oil bath for 24 hours. The synthesized polymer was filtered and washed five times (each time for 6 hours) with 50 mL acetic acid/methanol (1/9, v/v) in order to remove doxycycline from its binding sites. Complete extraction of doxycycline creates selective binding sites in the polymer structure. This was achieved by continuing the washing step until analyzing the solvent using UV spectrophotometry at 344 nm did not show the presence of doxycycline. Finally, the polymer was washed twice (each time for 3 hours) with deionized water and dried in a 60 °C oven.

Characterization of synthesized polymer was performed using FTIR spectroscopy (Thermo Nicolet 8700, USA) using KBr pellets. The morphological characteristics of the polymer particles were studied by SEM (KYKY-EM3200, Beijing, China).

Adsorption studies

All experiments were performed in capped vials at room temperature. A suitable amount of polymer was added to 10 mL of doxycycline solution. The mixture was stirred continuously at room temperature for a certain time and then filtered through a 0.22 \(\mu\)m nitrocellulose membrane (Schleicher & Schuell, Germany) under a brief vacuum to separate the polymer particles. The filtered solution was analyzed using UV-Visible spectrophotometry in order to determine the concentration of doxycycline.

The percentage amount of doxycycline bound to the polymer (%Extraction) was calculated according to Equation (1):

\[
\text{%Extraction} = \frac{(C_0 - C)}{C_0} \times 100
\]

where \(C_0\) represents the initial concentration of doxycycline and \(C\) is the concentration of free doxycycline after the extraction experiment. The binding capacity of the polymer was defined by the maximum amount of doxycycline bound to 1 g of polymer (Equation (2)):

\[
\text{Binding capacity} = \frac{\text{%Extraction} \times C_0 \times v}{(100 \times m)}
\]

In Equation (2), \(v\) and \(m\) represent volume of doxycycline aqueous solution (ml) and amount of polymer (mg), respectively.

Effects of several factors including time, pH of doxycycline solution, amount of polymer and doxycycline initial concentration were investigated to obtain an optimized condition for the extraction of doxycycline from aqueous solution. Finally, the binding capacity of the synthesized
polymer for the extraction of doxycycline in the optimized conditions was determined.

**Polymer-ZnO composite synthesis and characterization**

The polymer-ZnO composite was obtained by the same procedure previously described for synthesizing the adsorbent polymer. The only difference was adding 0.4 g ZnO nanoparticles to the polymerization mixture together with TRIM and AIBN. Polymerization was performed while the mixture was magnetically stirred in order to prevent ZnO nano-particles from precipitating and to disperse them thoroughly in the polymer structure. The synthesized composite was filtered and washed five times (each time for 6 hours) with 50 mL methanol in order to remove doxycycline from its binding sites. The washing solvent did not contain acetic acid in this step, because intense acidic or basic solutions result in rapid corrosion of ZnO nano-particles (Valtiner et al. 2016). The washing step was continued until analyzing the solvent using UV-Visible spectrophotometer at 344 nm did not show the presence of doxycycline. Finally, the composite was washed twice (each time for 3 hours) with deionized water and dried in a 60°C oven.

Characterization of the synthesized polymer-ZnO composite was performed using a series of methods including FTIR spectroscopy and XRD (D8-advance diffractometer, cooperation product of Bruker AXS and Siemens). SEM imaging using a Philips XL-30 equipped with WDX was used to map the presence of Zn atoms in the composite structure. Portions of polymer and ZnO nano-particles in the composite structure were determined by placing a certain amount of composite in an electric furnace (Thermolyne 1,500, Sybron Corporation), at 600°C for 2 hours. This process removed the polymer, leaving the ZnO nano-particles.

**Photocatalytic degradation experiments using polymer-ZnO composite**

Photocatalytic degradation experiments were conducted inside a cabinet made from medium density fiberboard (120 cm length, 50 cm width and 30 cm height). Magnetic stirrers were placed in the cabinet and a light source was installed above them. Batch experiments were performed on 200 mL of doxycycline solution in a Pyrex container. The solution was stirred magnetically at 300 rpm. After adding the polymer-ZnO composite, the mixture was irradiated directly from a distance of 10 cm using a 30 W UV-C lamp (OSRAM®, Munich, Germany). Samples were collected immediately before starting the irradiation and then at 1 hour intervals during photocatalytic degradation. The doxycycline concentration was analyzed after removing composite particles by filtration through a 0.22 μm membrane, under a brief vacuum. The extent of photocatalytic degradation (%Degradation) was calculated using Equation (3):

\[
\%\text{Degradation} = \left(\frac{C_0 - C}{C_0}\right) \times 100
\]

**Magnetic polymer-ZnO composite synthesis and characterization**

The magnetic polymer-ZnO composite was synthesized by the same procedure previously described for synthesizing the polymer-ZnO composite. The only difference was adding 0.4 g Fe3O4 nano-particles together with ZnO nano-particles to the polymerization mixture. During the washing step performed as described for polymer-ZnO composite, solvent was easily removed from the surface after precipitating the magnetic composite on a magnet.

Characterization of the magnetic polymer-ZnO composite was performed using FTIR spectroscopy, SEM imaging equipped with WDX and XRD.

**Photocatalytic degradation experiments using magnetic polymer-ZnO composite**

Photocatalytic degradation experiments using magnetic polymer-ZnO composite were performed under the same conditions and using the same amounts previously used for studying the polymer-ZnO composite. The only difference was in the sampling step, which was performed using a pipette after precipitating the magnetic composite on a magnet.

**RESULTS AND DISCUSSION**

**Precipitation polymerization**

In precipitation polymerization, the polymer is formed in the presence of a large volume of solvent compared with conventional bulk polymerization. As a result, polymer chains grow individually by capturing newly formed oligomers and monomers and then separate from the solution in nano- or micro-scale spherical morphologies. A number of parameters can affect this process and significantly change the characteristics of the synthesized polymer. In the present study, polymerization parameters were chosen according to studies performed by Jing et al. (Jing et al.
They optimized the synthesis of adsorbent polymers for tetracycline antibiotics according to type and amount of cross-linking agent, proportional concentration of template and functional monomer and type and proportional amount of solvent used in the polymerization mixture. The interaction of template molecules with the functional monomer during the pre-polymerization step and then with the synthesized polymer during extraction experiments is mainly through hydrogen bonds. In the present research, MAA was employed as the functional monomer since its acid group can form strong hydrogen bonds with hydroxyl and amide groups of doxycycline (Cai & Gupta 2004; Suedee et al. 2004).

Characterization of adsorbent polymer

Characterization of the synthesized polymer was performed using FTIR spectroscopy before and after the washing step at 400–4,000 cm⁻¹ (Figure S1, available with the online version of this paper). The FTIR pattern provided valuable information about functional groups present and polymer chemical structure. Efficient washing of the polymer and complete extraction of template molecules can also be deduced from before and after washing spectra. As Figure S1 shows, characteristic peaks seen in both spectra are a strong peak at 2,973–2,975 cm⁻¹ (C-H stretching), a very strong peak at 1,735 cm⁻¹ (C=O stretching vibration of esters), absorption at around 1,631 cm⁻¹ (C=O stretching vibration of amides). Three characteristic bands at around 1,470 cm⁻¹ (bending vibration of CH₂), 1,265 cm⁻¹ (C-O stretching vibration), and 1,142 cm⁻¹ attributed to the asymmetric stretch of C-O-C in both spectra confirm the presence of cross-linked segments in the polymer structure (Nastasovic´ et al. 2007).

The presence of an absorption peak around 3,500 cm⁻¹, which can be attributed to N-H stretching vibration of the primary amine of doxycycline, in the non-washed polymer spectrum indicates formation of stable complexes between template and functional monomer in the polymerization mixture and then their preservation in the resulting polymer (Guerreiro et al. 2011). This peak has disappeared in the washed polymer spectrum because of the complete removal of the template from the polymer structure during the washing step.

An SEM image of the synthesized polymer is shown in Figure 1. As can be seen in this image, micrometer-sized spherical particles are formed. Particles are in good homogeneity in terms of size and shape and show porous surface morphology.

Evaluation of extraction ability

Effect of time

The rate of extraction or fast adsorption-desorption equilibrium is a critical parameter for sorbent materials, affecting their practical application (Zhu et al. 2002). Batch experiments were used to determine the extraction rate of the adsorbent polymer for doxycycline. Extraction experiments were performed on 10 mL of 25 μg/mL doxycycline aqueous solution using 5 g/L of adsorbent polymer. Results showed quite fast extraction of doxycycline in 20 min. Extending the extraction time to 60 min did not increase the extraction percentage significantly (Figure 2(a)). When all the adsorption sites in the polymer structure are occupied by doxycycline molecules, equilibrium forms between extracted and free doxycycline in aqueous solution. Based on these results, 20 min was chosen as the extraction time for further experiments.

Effect of pH

In extraction experiments, pH plays an important role by affecting the surface charge of both adsorbent and template molecules. Affinity of the adsorbent for template molecules present in aqueous solution and subsequent extraction efficiency vary based on the surface charge (Guerreiro et al. 2011). Doxycycline is an amphoteric molecule with pKₐ values of 3.5, 7.7 and 9.5 that cause the predominance of certain species as a function of pH. At pH < 4, doxycycline is mostly in its protonated form (DOX⁺), at pH values between 4 to 8, the neutral form (zwitterion) is predominant and at pH > 8 doxycycline is an anionic molecule (DOX⁻).
Extraction experiments were performed on 10 mL of 25 μg/mL doxycycline aqueous solutions adjusted to pH values 3, 7 and 10 using 1 N HCl or NaOH, by adding 5 g/L of adsorbent polymer. As shown in Figure 2(b), doxycycline extraction is favored at neutral pH value. This result indicates the importance of zwitterion formation for enhanced electrostatic interactions between polymer and doxycycline molecules. Since the pH of the doxycycline aqueous solution is around neutral, extraction experiments in this study were performed on doxycycline aqueous solution without further pH adjustment.

**Effect of amount of polymer**

Amount of adsorbent is a critical parameter in extraction experiments. Increasing the polymer amount improves extraction efficiency by providing more adsorption sites for template molecules (Abdollahi et al. 2017). In this study, extraction of doxycycline from its 25 μg/mL aqueous solution was investigated using four different polymer concentrations: 3, 5, 6 and 7 g/L. As shown in Figure 2(c), higher concentrations of polymer extract more doxycycline from its aqueous solution and complete extraction is achieved using 7 g/L polymer particles in the experimental condition of this study.

**Polymer capacity**

The capacity of an adsorbent is the maximum amount of a certain compound that can be retained by the adsorbent in a given condition (Shi et al. 2011). Normally the extraction condition should be previously optimized in order to use the optimum extraction time and pH. The capacity of the synthesized polymer was determined using extraction experiments on different concentrations of doxycycline aqueous solution in the range of 5–50 μg/mL. According to the results shown in Figure 3, the capacity of the synthesized polymer for adsorbing doxycycline is about 20 mg/g.

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![Figure 2](https://example.com/figure2.png)  
**Figure 2**  
Effect of (a) time, (b) pH and (c) polymer amount on doxycycline extraction; error bars indicate standard deviation (n = 3).

![Figure 3](https://example.com/figure3.png)  
**Figure 3**  
Capacity of the polymer for different initial concentrations of doxycycline aqueous solution. Experiments were performed on 10 mL of doxycycline aqueous solution without further pH adjustment, using 5 g/L of adsorbent polymer; error bars indicate standard deviation (n = 3).
Polymer-ZnO composite characterization

The FTIR spectrum of washed polymer-ZnO composite shown in Figure S2 contains all characteristic peaks previously observed for the adsorbent polymer. This similarity indicates the same polymer structure in the previously synthesized adsorbent polymer and polymer-ZnO composite. Absence of characteristic peak for doxycycline in this spectrum shows efficient extraction of template molecules using methanol as the washing solvent. XRD pattern of the synthesized polymer-ZnO composite contains typical peaks for standard zinc oxide and confirms presence of ZnO nano-particles in the composite structure (Figure S3). (Figures S2 and S3 are available online.)

Figure 4(a) shows SEM image of polymer-ZnO composite particles. The pattern and abundance of Zn atoms in the same area are also provided in the shape of light spots on a black background using WDX analysis in Figure 4(b). It can be deduced that ZnO nano-particles have been trapped in the structure of spherical polymer particles with good abundance and dispersity.

Photocatalytic degradation of doxycycline using polymer-ZnO composite

Photocatalytic degradation of doxycycline was investigated on 200 mL of 50 μg/mL doxycycline aqueous solution, using 2.5 g/L polymer-ZnO composite. The experiment was performed using a high doxycycline concentration and a small amount of polymer-ZnO composite in order to minimize the extraction of doxycycline by the polymeric portion of the composite. Therefore, any reduction in doxycycline concentration could be attributed to the photocatalytic degradation efficiency of the composite.

Weighing ZnO nano-particles after burning the polymeric fraction of the composite showed they constitute 10% of the composite mass. This finding enabled us to investigate the photocatalytic degradation and extraction efficiency of equivalent amounts of ZnO nano-particles and polymer particles in parallel experiments. Equivalent amounts of ZnO nano-particles (0.25 g/L) and adsorbent polymer (2.25 g/L) were separately added to 200 mL of 50 μg/mL doxycycline solutions and irradiated using UV-C light under the same condition used for the polymer-ZnO composite. Samples were collected at 1 hour intervals and the remaining doxycycline concentration was determined.

Results shown in Figure 5(a) indicate the limited efficiency of equivalent amounts of ZnO nano-particles for photocatalytic degradation of doxycycline in 50 μg/mL aqueous solution. This is mainly due to the large number of doxycycline molecules present in the solution that decrease production of hydroxyl radicals by inhibiting UV-C light from reaching the surface of ZnO nano-particles. Another explanation is coverage of the ZnO nano-particles’ surface by degradation products that inhibit adsorption of more doxycycline molecules on them (Pardeshi & Patil 2008). The low extraction efficiency of equivalent amounts of adsorbent polymer was predictable based on the limited capacity of adsorbent polymers. Doxycycline molecules rapidly get adsorbed onto the surface of polymer particles and when all sites are occupied, extraction can no longer continue. Regarding the small amount of polymer used, this phenomenon happened in 2 hours for about 20% of doxycycline molecules and polymer particles could not extract more doxycycline from the aqueous solution. Despite the limitations for equivalent amounts of ZnO nano-particles and adsorbent polymer, the polymer-ZnO composite showed high efficiency for removing doxycycline from its aqueous solution under

Figure 4 | (a) SEM image of polymer-ZnO composite and (b) WDX of the same area for Zn atoms.
UV-C irradiation. The polymer-ZnO composite removed 92.7% of doxycycline in 6 hours while equivalent amounts of ZnO nano-particles and polymer removed 35% and 20% of doxycycline in the same time, respectively. Escobar and coworkers, who investigated MIP-TiO2 composites for the removal of several compounds from different pharmaceutical classes, reported 1.05–5.27 times higher efficiency of the composites compared with commercial samples of TiO2 (de Escobar et al. 2016). In the same way Arabzadeh and coworkers reported 1.7 times higher tartrazine removal using MIP-TiO2 composite compared with pure TiO2 nanoparticles (Arabzadeh et al. 2016). These results are in good agreement with the enhanced photocatalytic efficiency of polymer-ZnO composite in the present study.

The combined actions of adsorbent polymer for extraction of doxycycline molecules and ZnO nano-particles for their photocatalytic degradation caused the powerful removal performance. This structure solves the limitation of ZnO nano-particles for efficient and selective adsorption of pollutant molecules. Degradation of adsorbed doxycycline molecules by ZnO nano-particles prevents the active sites of the polymer from becoming saturated and therefore, doxycycline molecules continuously get adsorbed and degraded. The efficient performance of this composite material can also be explained according to mechanisms underlying photocatalytic degradation reactions. Combining ZnO nano-particles and adsorbent polymer in a composite structure may lead to adsorption of the promoted electron from the valence band of ZnO nano-particles by the polymeric material. This will prevent the promoted electron and generated hole from recombinating, which is the main cause of insufficient photocatalytic degradation by semiconductor photocatalysts. Adsorbing the promoted electron allows the hole to produce sufficient amounts of hydroxyl radicals to attack the pollutant molecules and degrade them (Wang et al. 2008). Another explanation ascribes this synergy effect to the polymeric material as a photo-sensitizer. Polymer particles may absorb UV-C irradiation and inject a photo-induced electron to the conduction band of ZnO nano-particles. This electron acts as a promoted electron and can trigger the formation of reactive superoxide radical ions and hydroxyl radicals (Puma et al. 2008).

Magnetic polymer-ZnO composite characterization

The FTIR spectrum of magnetic polymer-ZnO composite is shown in Figure S4. All characteristic peaks previously observed for the polymer and polymer-ZnO composite are present in this spectrum. The XRD pattern of the magnetic polymer-ZnO composite (Figure S5) contains typical peaks of standard patterns for both zinc oxide and Fe3O4 that together with data obtained from WDX analysis (Figure 6(b) and 6(c)) confirms the presence of ZnO and Fe3O4 nanoparticles in the structure of the synthesized magnetic polymer-ZnO composite. The SEM image of the magnetic polymer-ZnO composite and WDX analysis of the same area for Zn and Fe atoms (Figure 6) shows the formation of micrometer-sized spherical polymer particles with ZnO and Fe3O4 nano-particles entrapped between the polymeric chains. (Figures S4 and S5 are available online.)

Photocatalytic degradation of doxycycline using magnetic polymer-ZnO composite

The photocatalytic degradation of doxycycline was investigated under the same condition previously used for polymer-ZnO composite, using 2.5 g/L magnetic polymer-ZnO composite. Sampling was performed after precipitation of composite particles in the magnetic field of an external magnet from the supernatant solution.
Results shown in Figure 5(a) indicate that the polymer-ZnO composite degraded doxycycline efficiently and with the same degradation profile, previously seen for polymer-ZnO composite. Magnetic particles make the separation process simple and fast, because they can be easily collected by an external magnetic field without the need for additional centrifugation or filtration (Sutka et al. 2017). This feature facilitates recovery of composite particles after each use that subsequently increases the chance for their reusability.

Comparing the results in Figure 6 shows about 15% decrease in removal efficiency of the magnetic polymer-ZnO composite. Based on the literature, Fe3O4 nano-particles do not seem to have an adverse effect on the photocatalytic efficiency of the magnetic composite. They even enhance the photocatalytic activity by trapping the promoted electron and inhibiting electron hole recombination (Susanti et al. 2011). Bolobajev and coworkers investigated photocatalytic degradation of doxycycline in the presence of Fe(III) ions. They found that at pH = 3, Fe(OH)2^2+ is the dominant species of the Fe(III)-hydroxy complex (Equation (4)), that undergoes photochemical reduction according to Equation (5). Therefore, the combination of Fe(III) ions and UV irradiation increased doxycycline degradation and mineralization through the formation of oxidative hydroxyl radicals (Bolobajev et al. 2016). Although trapping the promoted electron is possible, the second mechanism does not apply in our case. A doxycycline solution with pH = 3 is a prerequisite for reactions shown in Equations (4) and (5), while we performed degradation studies on neutral solutions of doxycycline. Furthermore, based on a previous study, Fe3O4 nano-particles are stable in a neutral environment for several weeks and do not get solved to produce Fe2^2+ and Fe3^3+ ions in the solution (Kalska-Szostko et al. 2014).

\[
\begin{align*}
\text{Fe(III)} + \text{H}_2\text{O} & \leftrightarrow \text{Fe(OH)}^2+ + \text{H}^+ \quad (4) \\
\text{Fe(OH)}^2+ + \text{hv} & \rightarrow \text{Fe}^2+ + \text{OH}^* \quad (5)
\end{align*}
\]

The decreased photocatalytic activity of magnetic composite is raised from performing both experiments using 2.5 g/L of composite materials. The presence of Fe3O4 in the magnetic composite structure decreases the portion of polymer and ZnO in a certain mass. Since the degradation process is the result of the adsorption of doxycycline molecules by the polymer and their photocatalytic degradation by ZnO nano-particles, the photocatalytic efficiency of magnetic composite was decreased to some extent.

**Kinetic of doxycycline photocatalytic degradation**

Kinetic models are used to gain a better insight into what happens during chemical reactions. Photocatalytic degradation of doxycycline using polymer-ZnO and magnetic polymer-ZnO composites occurs in three distinct steps: adsorption of doxycycline molecules, surface reaction and desorption of reaction products. However, removal of doxycycline is the only observed outcome of the reaction that can be described...
using a suitable kinetic model and apparent degradation rate constant. Photocatalytic degradation of doxycycline follows pseudo first order kinetics (Equation (6)).

\[
r = -\frac{dC}{dt} = k_{\text{obs}}
\]  (6)

This equation can be transformed to Equation (7), after integration.

\[
-\ln \left( \frac{C}{C_0} \right) = k_{\text{obs}} t
\]  (7)

In these equations, \( k_{\text{obs}} \) (\( \mu \text{g mL}^{-1} \text{ min}^{-1} \)) represents the apparent pseudo first order kinetic constant, \( C \) (\( \mu \text{g/mL} \)) is concentration at any time (t) and \( C_0 \) (\( \mu \text{g/mL} \)) is the initial concentration of doxycycline.

As Figure 5(b) shows, plots of \(-\ln \left( \frac{C}{C_0} \right)\) versus time for polymer-ZnO and magnetic polymer-ZnO composites are straight lines that confirm the pseudo first order kinetic of doxycycline photocatalytic degradation and provide the \( k_{\text{obs}} \) values equal to \( 7 \times 10^{-3} \) and \( 4 \times 10^{-3} \) \( \mu \text{g mL}^{-1} \text{ min}^{-1} \) for polymer-ZnO and magnetic polymer-ZnO composites, respectively. The lower rate of photocatalytic degradation for the magnetic polymer-ZnO composite is because of the lower amounts of polymer and ZnO nano-particles in a certain mass.

**CONCLUSIONS**

Highly efficient magnetic polymer-ZnO composite was synthesized, characterized and used for photocatalytic degradation of doxycycline in aqueous solution. The combined performance of adsorbent polymer for selective adsorption and ZnO nano-particles for photocatalytic degradation of doxycycline molecules provided an efficient method for removing doxycycline from aqueous solution. The magnetic property of the composite was obtained by incorporating Fe\(_3\)O\(_4\) nano-particles in its structure. Magnetic composite particles were easily collected using an external magnetic field, a property that facilitates their practical application. Photocatalytic degradation of doxycycline by the synthesized composite material was fitted to the pseudo first order kinetic model.

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