Tetracycline hydrochloride degradation by heterogeneous photocatalysis using TiO$_2$(P25) immobilized in biopolymer (chitosan) under UV irradiation

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ABSTRACT

TiO$_2$(P25) has been widely used to treat wastewater; however, the elimination of TiO$_2$(P25) suspended in the treated water causes running costs and induces secondary pollution, which greatly restricts its practical applications. Consequently, several methods have been implemented to immobilize TiO$_2$(P25) on various substrates. This work deals with the immobilization of TiO$_2$(P25) in chitosan film by using the cross-linking method. The prepared catalyst was characterized using X-ray diffraction (XRD), Fourier transform infrared spectrometry (FTIR), UV-Vis diffuse reflectance spectra (DRS) and scanning electron microscopy (SEM), and its catalytic activity in tetracycline hydrochloride (TC) degradation under UV light was explored. XRD, FTIR, DRS and SEM characterization indicated that TiO$_2$(P25) was successfully immobilized on chitosan film, the chemical structure of TiO$_2$(P25) did not change after the immobilization and the TiO$_2$(P25) was uniformly dispersed in the composite. Chitosan/TiO$_2$(P25) was used for the removal of TC by photocatalysis under UV irradiation. The effects of operational parameters such as amount of TiO$_2$(P25), agitation speed and the initial TC concentration were investigated. An 87% removal efficiency of TC was obtained with 0.12 g of TiO$_2$(P25) and TC removal was significantly enhanced by the agitation of the solution. The TC removal efficiency decreased from 72 to 44% when TC concentration increased from 30 to 40 mg/L after 60 min reaction time, the photocatalytic reactions followed the pseudo-second-order kinetic.

Key words | advanced oxidation process, composites chitosan/TiO$_2$(P25), tetracycline, UV light, wastewater treatment

HIGHLIGHTS

- Immobilizing TiO$_2$(P25) in chitosan film by cross-linking.
- The XRD, FTIR and DRS spectra indicated that the chemical structure of TiO$_2$(P25) did not change after the immobilization.
- The SEM revealed that the TiO$_2$(P25) were uniformly dispersed in the film.
- The photocatalytic activity performance of the composite was investigated under UV-irradiation to remove tetracycline.

doi: 10.2166/wst.2020.432
In the last years, the number of publications regarding the detection and removal of pharmaceuticals and personal care products from the aquatic environment has enormously increased (Sophia & Lima 2018; Rizzi et al. 2019), stressing the emergency related to their removal from water and wastewater, due to the insufficiency of the common wastewater treatment plants in removing these contaminants. These substances have been called emerging contaminants and are present in treated and untreated wastewater (Rizzi et al. 2019). In this regard, among the different sources of water contamination, antibiotics in general, and tetracycline in particular, are worth mentioning. The low cost and good oral absorption of tetracycline hydrochloride (TC) make it the most used antimicrobial in veterinary medicine and agriculture (Albero et al. 2016). Currently, in Germany, more than 17,156 kg of tetracycline (TC) is consumed in livestock as antimicrobial substances applied to pigs (Ledjeri et al. 2016; Yahiaoui et al. 2018); in 2011, approximately 5.6 million kilograms of TC was used for livestock production and disease control in the United States, equivalent to 42% of the total antibiotics administered to food-producing animals (Yahiaoui et al. 2018). The TC concentration in surface water locally and globally is about ng/L to μg/L (Yahiaoui et al. 2018; Wei et al. 2019) and the high concentration of TC in pharmaceutical wastewater is several 100 mg/L (Wei et al. 2019). These high levels of TC have a negative impact on various animals and plants since it is responsible for inhibition of microbial activity and growth, phytoplankton toxicity and inhibition of protein synthesis; it also endangers human health and causes damage to the blood, kidneys, liver and nervous system of the human body (Yahiaoui et al. 2015, 2018; Wei et al. 2019).

TC removal from water then becomes an urgent issue. Various physical, chemical, and biological technologies have been studied for treating refractory organic compounds. Conventional wastewater purification methods such as reverse osmosis, ultrafiltration, adsorption, membrane and magnetic separation, and traditional chemical oxidation can hardly achieve complete detoxification, and have non-flexible applications, high operating costs, with limited environmental compatibility. Therefore, advanced oxidation processes (AOPs) have been introduced for the treatment of dye effluents, pharmaceutical compounds and antibiotic residues, and have shown high efficiency. AOP technologies yield inspiring removal efficiency rates in pharmaceutical compounds and antibiotic residues and other refractory organic compounds. AOPs, based on the generation of highly oxidative hydroxyl radicals (·OH), can be considered for the removal of recalcitrant pollutants from wastewater. Among them, photocatalytic technology is attracting much attention, since it allows avoidance of the use of chemical compounds and can be easily implemented even in low-resource areas. For this purpose, TiO₂ P25 photocatalyst in suspension is the most widely used (Yahiai et al. 2011; Yahia Cherif et al. 2014; Gao et al. 2015) and it is activated under UV irradiation (λ < 390 nm). However, when used in suspension, the difficulty of its recycling, due to its low particle size, constitutes an important drawback for the industrial application of this technology. To overcome this drawback, different techniques for the immobilization and support of TiO₂ have been developed, including sol-gel processes (Tseng et al. 2010; Chen & Kumar 2012; Hana et al. 2014; Gao et al. 2015) and the
support of the TiO$_2$ on porous solids (Vicent et al. 2012; Belver et al. 2017; Li et al. 2017). These techniques require a strong adherence between the TiO$_2$ P25 and the substrate, and the crystal structure of TiO$_2$(P25) must be maintained during the preparation and immobilization process in order to avoid the loss of activity during reaction.

This work deals with the immobilization of TiO$_2$(P25) in chitosan film by using cross-linking. The prepared catalysts were characterized using X-ray diffraction (XRD), Fourier transform infrared spectrometry (FTIR), UV-Vis diffuse reflectance spectra (DRS) and scanning electron microscopy (SEM), for the first time. Furthermore, the photocatalytic activity of the prepared catalyst (TiO$_2$(P25)/chitosan film) was tested by the degradation of TC under UV light; for this purpose, the effects of operational parameters such as agitation speed, amount of TiO$_2$(P25) and the initial TC concentration on the degradation of TC were studied.

**MATERIALS AND METHODS**

**Chemicals**

The photocatalyst used in this study was TiO$_2$(P25), acetic acid (99.9%, purity) and NaOH (98% purity), purchased from Biochem Chemopharma (Montreal, Quebec, Canada). Tetracycline hydrochloride (C$_{22}$H$_{25}$N$_2$O$_8$Cl (96% purity) and citrate (99.9%, purity) were obtained from Sigma Aldrich.

**Composites chitosan/TiO$_2$(P25) film preparation**

The preparation of chitosan/TiO$_2$(P25) thin film was carried out by dispersing a known amount of chitosan in 15 mL of acetic acid (1 M). After obtaining a homogenous solution, a known amount of TiO$_2$(P25) was added and the obtained solution was maintained under stirring for 24 h to ensure that all the TiO$_2$(P25) powder was uniformly dispersed. The suspension was sonicated in an ultrasonic bath (J.P. Selectta, Barcelona, Spain) at a frequency of 30 kHz for 30 min, in order to improve the dispersion of TiO$_2$(P25) in the chitosan. The resulting solution was then filled onto a glass plate and dried at 100 °C for 4 hours. After the drying process, the films were subjected to cross-linking by using NaOH (2 M), before being carefully lifted from the glass plate. Chitosan/TiO$_2$(P25) ratio was set to 2.

**PHOTOCATALYST CHARACTERIZATION**

The XRD patterns of TiO$_2$(P25) and the composite chitosan/TiO$_2$(P25) film were obtained using a Bruker D8 diffractometer equipped with a SiO-X energy detector, using Cu Kα radiation. The 2θ scanning angle range was 2–70°. In addition, the band gap was estimated by means of UV-Vis diffuse reflectance spectra and by UV-Vis spectroscopy (Shimadzu, UV-2600). The FTIR spectroscopy (BRUKER ELPHA) was used to determine the bonding chitosan film and composite film chitosan/TiO$_2$(P25), All spectra were measured between 400 and 4,000 cm$^{-1}$. The surface morphology of chitosan film and composite chitosan/TiO$_2$(P25) film was studied using field emission scanning electron microscope (FEI QUANTA 250). The point of zero charge pH (pH$_{PZC}$) of the composite film was determined using the method reported by Boudrahem et al. (2019) and Saidi et al. (2019). Aliquots of 50 mL of 0.01 M NaCl solution were prepared in different flasks. Their pH values (pH$_{initial}$) were adjusted to 3 and 12 by adding 0.01 M solution of HCl or NaOH. A piece of the composite film (90 mm × 25 mm × 1 mm) was sorbent was added to each flask and the whole was maintained under agitation for 48 hours. When the pH value remained constant, the final pH (pH$_{final}$) was measured using a Denver Instrument UB5 pH meter. The pH$_{PZC}$ value is the point where the curve of pH$_{final}$ versus pH$_{initial}$ crosses the line, that is, pH$_{initial}$ = pH$_{final}$ (Boudrahem et al. 2019; Saidi et al. 2019).

**EXPERIMENTAL PROCEDURES**

**Photocatalytic activity experiments**

Photocatalytic activity of composite film chitosan/TiO$_2$(P25), was tested for the degradation of synthetic TC solution under UV irradiation, the effects of operational parameters such as agitation speed, amount of TiO$_2$(P25) and the initial TC concentration were investigated. Distilled water (conductivity < 2 μS/cm) was used to prepare an aqueous solution containing TC at 30 and 40 mg/L. In general, the acute toxicity (EC$_{50}$) of pharmaceutical compounds on aquatic and terrestrial organisms and wildlife is observed when the concentration of these molecules is in the range of 1–100 mg/L, for this the initial TC concentrations were chosen in this interval; that is, 30 and 40 mg/L. Aeration was provided by bubbling air into a synthetic TC solution by an air pump to ensure a constant supply of oxygen before starting each experiment. All the experiments were conducted at pH = 4. A piece of the composite film (90 mm × 25 mm × 1 mm) was placed in a vial containing 100 mL of TC solution. The vial was immediately irradiated using a UV
lamp (30 W, UVA, $\lambda_{\text{max}} = 360$ nm emission peak, manufactured by Philips, The Netherlands). Representative aqueous-phase samples were withdrawn at periodic intervals and immediately filtered through a 0.20 $\mu$m membrane syringe filter (Water Corporation 25 mm GHP, USA) for the determination of TC residual concentrations.

**Tetracycline analysis**

The TC concentration was spectrophotometrically determined at the maximum absorption wavelength (360 nm) using an ultraviolet-visible light system (Thermo-Scientific Evolution 2001 spectrophotometer connected to a PC) with a calibration method involving the Beer–Lambert's law.

**Adsorption, photolysis and photocatalysis experiments**

Adsorption in the dark, photolysis and photocatalysis experiments were performed at pH = 4, $T = 25$ °C, ratio (chitosan/TiO$_2$(P25)) = 2 and $[\text{TC}]_0 = 50$ mg/L and for 240 min of reaction time. Small volume solution samples were taken at different time intervals, filtered using 0.20 $\mu$m syringe filters and analyzed by UV-visible spectrophotometer at the maximum absorption wavelength of 360 nm.

**Kinetic study**

Generally, in photocatalytic degradation processes, the first-order and Langmuir–Hinshelwood (L-H) are the most widely used models to explain the kinetics of a heterogeneous catalytic system (Khenniche et al. 2015; Aissani et al. 2018). In this study, the first-order, second-order and L-H kinetics models were tested and the three models are given by Equations (1)–(3), respectively:

$$r = -\frac{dC}{dt} = k_1C$$  \hspace{1cm} (1) \\
$$r = -\frac{dC}{dt} = k_2C^2$$  \hspace{1cm} (2) \\
$$r = -\frac{dC}{dt} = \frac{kKC}{1 + KC}$$  \hspace{1cm} (3)

where: $r$ is the rate of TC degradation (mg/L min); $C$ is the concentration at any time (mg/L); $k_1$ (min$^{-1}$) and $k_2$ (L/mg min) are the first-order and second order rate constants respectively; $k$ and $K$ are the limiting rate constants of the reaction at maximum coverage under the given experimental conditions and the equilibrium constant for adsorption of TC onto composite film chitosan/TiO$_2$(P25) (Khenniche et al. 2015; Aissani et al. 2018).

In order to examine whether the photocatalytic degradation rate could be congruent with the three kinetic models, the non-linear method was used. The non-linear method is a mathematical method that uses the original form of the equation. The constants of the models were determined by minimizing the error function using the solver add-in with Microsoft’s spreadsheet, Microsoft Excel. The error function employed (Equation (4)) was as follows (Khenniche et al. 2015; Aissani et al. 2018):

$$D(\%) = \sum_{i=1}^{P} \left( \frac{C_{i}^{0} - C_{i}^{\text{Exp}}}{C_{i}^{\text{Cal}}} \right)^2$$  \hspace{1cm} (4)

where $C_{i}^{0}$ and $C_{i}^{\text{Exp}}$ are the experimental and calculated data, $P$ is the number of experimental data.

**Reusability of Chitosan/TiO$_2$(P25) film**

The stability experiments were conducted for four successive cycles under the following optimal conditions except for the agitation speed: $[\text{TC}]_0 = 30$ mg/L, ratio chitosan/TiO$_2$(P25) = 2, $T = 25$ °C, TiO$_2$(P25) dose = 0.12 g pH = 4 and without agitation for a reaction period of 480 min. After every run, the composite film was washed with distilled water. The chitosan/TiO$_2$(P25) film used four times was washed for the first time with distilled water and with a 0.1 M NaOH solution in order to study the effect of the washing solution on reusability of chitosan/TiO$_2$(P25) film.

**RESULTS AND DISCUSSION**

**Characterization study**

TiO$_2$(P25), which was immobilized on the composite film, was characterized by XRD. According to Figure 1, the following conclusion can be drawn: the XRD patterns of TiO$_2$(P25) nanoparticles shows that no diffraction peaks of other impurities were detected. The TiO$_2$(P25) nanoparticles’ diffraction peak appeared in the XRD pattern of TiO$_2$(P25) immobilized on chitosan film, indicating that the process of immobilization did not have an influence on the crystal form of the commercial TiO$_2$(P25) nanoparticles, corresponding to anatase and rutile phases, characteristic of the commercial TiO$_2$(P25) nanoparticles.
The chitosan and chitosan/TiO₂(P25) films were also characterized by FTIR spectroscopy (Figure 2) and the recorded spectra have characteristic bands of both components, the TiO₂(P25) catalyst and pure chitosan. The wide band appearing at 3,291.66 cm⁻¹ is attributed to the O-H stretching vibration of the adsorbed water. The bands between 1,646.81 and 1,027.72 cm⁻¹ are related to the composition of chitosan: the peak at 1,646.81 cm⁻¹ is attributed to the N-H band, the peak at 1,376.35 cm⁻¹ is assigned to the C-N band and the peak at 1,027.72 cm⁻¹ is assigned to the C-O-C band. The presence of TiO₂(P25) in the chitosan/TiO₂(P25) film is highlighted by the peak that appears at 451.97 cm⁻¹, due to the Ti-O stretching vibration.

Figure 3 shows the band gap of the TiO₂(P25) nanoparticles and the composite film (b). According to Figure 3, there is no change in the band gap potential of the semiconductor after immobilization.

Figure 4 shows the surface morphology of chitosan and chitosan/TiO₂(P25) films. The external morphology of the chitosan films revealed a smooth and flat surface as shown in Figure 4(a). The SEM images (Figure 4(b)) of chitosan/TiO₂(P25) film clearly show that the TiO₂(P25) nanoparticles were dispersed in the chitosan matrix with some agglomeration.

**Adsorption, photolysis and photocatalysis experiments**

An absence of adsorption of TC on the composite chitosan film was shown (Figure 5); it could be attributed to the absence of electronic attraction between TC and the catalysts (chitosan/TiO₂(P25)). Indeed, TC has a neutral form at pH = 4 and according to Figure 5(b), the point of zero charge (pHₚᵥₑ) of chitosan/TiO₂(P25) is 8.3. The results given in Figure 5(a) show the absence of TC degradation by direct photolysis. It was also found that TC photocatalysis...
using chitosan/TiO$_2$(P25) film under UV irradiation led to 64% TC removal within 240 min of reaction time.

**Photocatalytic activity of the composite film chitosan/TiO$_2$(P25)**

**Effect of the catalyst dose**

The effect of the amount of catalysts on the photodegradation efficiency is given in Figure 6. The results showed that the photodegradation efficiency increases with an increase in TiO$_2$(P25) up to 0.12 g of catalyst, and the removal efficiency was 87%; thereafter, it started decreasing when the amount of catalysts was increased from 0.12 g to 0.24 g. The photocatalytic destruction of other organic pollutants also exhibits the same dependency on the catalyst dose (Augliaro et al. 1991; Giménez et al. 1999; Kansal et al. 2008). This effect can be explained on the basis that the total active surface area increases with the amount of catalyst, leading to more active sites on the catalyst surface (Giménez et al. 1999; Kansal et al. 2008; Yahiat et al. 2011; Khenniche et al. 2015). At the same time, beyond a certain amount, higher dose of catalyst may not be useful due to both catalyst aggregation as well as reduced irradiation owing to decreasing light scattering surface (Giménez et al. 1999; Kansal et al. 2008; Yahiat et al. 2011; Khenniche et al. 2015).
Effect of the agitation speed

From Figure 7, agitation had a strong effect on the degradation of TC. Indeed, the removal efficiency increased from 25% without agitation to 72% with agitation within 60 min of reaction time. This result was confirmed by the values of the apparent constants rate ($k_{app}$); $k_{app}$ was increased from 0.0055 to 0.0301 min$^{-1}$ after 30 min of reaction time when the agitation speed was increased from 0 to 360 rpm. This effect can be explained on the one hand by the decrease in the thickness of the boundary layer surrounding the chitosan/TiO$_2$(P25) film, thus enhancing the photodegradation process; and, on the other hand, by the release of the degradation products at the solution-chitosan/TiO$_2$(P25) interface that can compete for the consumption of OH radicals.

Effect of the initial TC concentration

In order to determine the effect of the initial TC concentration, experiments were carried out for 30 and 40 mg/L (Figure 8). The result shows that the removal efficiency of TC was inversely proportional to the initial concentration, since the removal efficiency of TC after 60 min reaction time decreased from 72 to 44% for an increase of the initial amount from 30 to 40 mg/L (Figure 8). This result was expected, because matter that is more organic is oxidized by the same amount of generated hydroxyl radicals, causing then competitive consumption of hydroxyl radicals between intermediate products and the target molecule. The same result was reported by Aissani et al. (2016), Khenniche et al. (2015) and Yahia cherif et al. (2014).

The results given in Figure 9 and Table 1 show that the degradation kinetics of TC are perfectly described by the pseudo second-order model.

Reusability of chitosan/TiO$_2$(P25) film

The stability and reusability of the composite chitosan/TiO$_2$(P25) film is an important factor to be evaluated. The stability experiments were conducted for four successive
cycles. The removal efficiency of TC decreased significantly after the second run, from 87 to 57%, and then decreased only slightly on the third and fourth runs, to 54 and 52%, respectively. The decrease in the photocatalytic activity of the composite film can be probably attributed to saturation of the film surface by the degradation products adsorbed on the surface of the film and not removed during the hot water wash step. In order to confirm these results, we proceeded to wash the chitosan/TiO$_2$(P25) film used four times under UV irradiation with a 0.1 M NaOH solution. The washing of the film with the 1 M NaOH solution leads to the improved performance of the film, since TC removal increased from 52 to 58%.

CONCLUSION

In this study, chitosan/TiO$_2$(P25) composite films were prepared by immobilizing titanium dioxide (TiO$_2$ P25) nanoparticles in a chitosan matrix by cross-linking a mixture of chitosan/TiO$_2$(P25) in a NaOH solution (2 M). The XRD, FTIR spectra and DRS spectra indicated that the chemical structure of TiO$_2$ P25 did not change after the immobilization on the chitosan film. The SEM of the external morphology of the chitosan film revealed a smooth and flat surface in comparison with the microscopic surface of the chitosan films containing 0.12 g of TiO$_2$(P25); in addition, the TiO$_2$(P25) nanoparticles were uniformly dispersed in the chitosan/TiO$_2$(P25) composite. Regarding the impact on TC removal in the presence of the film under UV irradiation, the obtained results showed that increasing the initial TC concentration had a negative effect on the removal efficiency. In addition, agitation speed (360 rpm) had a positive effect on TC removal, which increased from 25 to 75% within 60 min reaction time. The removal efficiency of TC was also affected by the amount of TiO$_2$(P25), with an optimal value of 0.12 g. A pseudo-second-order kinetic model can describe the kinetics of TC degradation. The utilization of TiO$_2$(P25) immobilized in biopolymer (chitosan) and UV light radiation can be an interesting alternative since the use of biodegradable support is very attractive from an environmental perspective.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


First received 2 July 2020; accepted in revised form 27 August 2020. Available online 8 September 2020