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ADVANCED OXIDATION/REDUCTION TECHNOLOGIES: AN PERSPECTIVE FROM IBEROAMERICAN COUNTRIES

Photoactivation and photoregeneration of TiO2/PAC mixture applied in suspension in water treatments: approach to a real application

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Abstract

The process TiO_2/PAC/UV-vis has been under study and compared with the isolated treatments of adsorption and photocatalysis determining possible synergies between adsorption and photocatalysis of target antibiotics: amoxicillin, enrofloxacin, sulfadiazine, and trimethoprim. The characterization of the TiO2/PAC mixture was carried out via FESEM and FTIR. Moreover, a kinetic study has been performed. The effect of UV-vis radiation and the type of matrix was analyzed in TiO_2/PAC/UV-vis process. The performance of this treatment has been monitored during three cycles, evaluating also the regeneration of TiO_2/PAC mixture by UV-vis light. TiO_2/PAC/UV-vis process allowed the removal of the antibiotics in the range 90–100% (an average removal of 93% of the initial concentration) after 60 min of treatment. However, only amoxicillin showed a significant synergy applying TiO_2/PAC/UV-vis process. Regarding matrix effect, no influence of the matrix type (ultrapure water or treated wastewater) was observed. Since PAC tends to be deactivated gradually, the TiO_2/PAC/UV-vis process performance decreases after each cycle in a 15% average. Finally, regeneration via UV-vis light started to be effective after a total of 4 h of regeneration.

Keywords TIO_2-UV/vis photocatalysis · Antibiotic · Powered activated carbon (PAC)

Introduction

Antibiotics have shown an incipient use to fight a variety of diseases, leading to a rise of its global consumption. Nowadays, antibiotics are mainly destined to human and veterinary uses, thus creating a waste problem, as more than a half of the antimicrobial agent given is excreted (Klein et al., 2018; Kuehn, 2007). It is widely believed that massive and improper use of these pharmaceuticals might cause a serious problem on environment (Mceneff et al., 2014). Since the consumption of antibiotics leads to the subsequent generation of antimicrobial-resistant bacteria (AMR), apart from the environment, public health is also involved in the negative effects caused by the current use of antibiotics.

Urban wastewater treatment plants (WWTP), which receive the antibiotics and metabolites excreted, as well as other pollutants, are not designed to remove antibiotics. Although they reduce some of them (Mceneff et al., 2014), many studies have monitored the occurrence of the most commonly administered pharmaceuticals in urban wastewater, groundwater, and surface water worldwide. The literature informs that concentrations of antibiotics from ng/l to μg/l are detected in waters (García-Galán et al., 2010; Jurado et al., 2019; Boy-Roura et al., 2018; García-Gil et al., 2018). Among the different families of antibiotics, sulfonamides (Senta et al., 2013; Babić et al., 2006), trimethoprim (Golovko et al., 2014; Aukidy et al., 2012), β-lactams (Tuc Dinh et al., 2011;

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Highlights
- The application of TiO2/PAC/UV-vis in suspension is a promising process, because it is environmentally friendly reducing energy and chemicals. This process allows effectively the removal of target antibiotics.
- There is no influence of the matrix type (ultrapure water or treated wastewater) in TIO_2/PAC/UV-vis process applied in suspension.
- The TiO_2/PAC mixture tends to be deactivated among various cycles. According to the results, an average of 15% removal is reduced for the target antibiotics per cycle. Nevertheless, the regeneration of PAC is possible by applying, at least, 4 h of exposure to 3 W/l of UV-vis light, allowing its reuse.

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Rossmann et al., 2014), and fluoroquinolones (Tamtam et al., 2008; Wagil et al., 2014) represent a potential risk for the environment. Consequently, a representative antibiotic from each one of these groups was analyzed in this research work, more precisely: sulfadiazine (veterinary use, sulfonamide), trimethoprim (human and veterinary use, trimethoprim), amoxicillin (human and veterinary use, β-lactam), and enrofloxacin (veterinary use, fluoroquinolone).

Conventional treatments, such as coagulation-flocculation-decantation or biologic processes, are not able to completely remove these pollutants. However, other type of treatments has been studied in the last decade to remove emerging pollutants. Photocatalysis and adsorption have been demonstrated to be effective for pharmaceuticals removal (USEPA, 2007; Mirzaei et al., 2017; Biancullo et al., 2019; Cai & Hu, 2017). An alternative approach to remove antibiotics from water could be the combination of the adsorbent activated carbon (AC) and the catalyst TiO_2. The immobilized system based on porous adsorbents, such as carbon fibers or zeolites, is quite common for carbonaceous-TiO2 composites. Activated carbon (AC), carbon nanotubes or carbon fibers, and graphene are mainly applied to synthetize carbonaceous-TiO_2 composites, for instance, by means of thermal treatments which induces to high-energy consumption. Many methods have been developed for preparing carbonaceous-TiO2 composites. These systems have been widely investigated and are promising materials for future high-activity photocatalysts for pharmaceuticals such as amoxicillin (Moura et al., 2018; Awfa et al., 2018). The presence of the carbonaceous material may facilitate enhanced photocatalytic activity through one or all of the three primary mechanisms: (i) band-gap tuning or extension of excitation wavelength through photosensitization, (ii) retardation of electron–hole recombination, and (iii) provision of high-surface area for adsorption of reactants and provision of active sites. The carbonaceous-TiO_2 photocatalysts have the potential to address all three aspects. Moreover, they are widely reported to enhance photocatalytic activity over that of TiO_2 alone. However, many of them require many chemicals and are expensive, complicated, and time-consuming. Therefore, the development of relatively cheap, easy, scalable, and environmentally friendly method is a one of the very high priorities according to literature (Awfa et al., 2018).

However, though immobilized systems such as the aforementioned carbonaceous-TiO_2 composites are the most common way to combine carbon and TiO_2, more options are reported in literature to achieve this combination (Awfa et al., 2018; Moles et al., 2020; Andriantsiferana et al., 2014; Matos et al., 1998). The general trend nowadays consists on the immobilization of the catalyst in the surface or the adsorbent (Andriantsiferana et al., 2014). Nevertheless, in this research, work is considered the application of powered activated carbon (PAC) and TiO2 in suspension resulting in an amalgam of them. The application of TiO2/PAC mixture in suspension allows a better contact surface between the pollutants and the mixture and previous results in our research group show that separation processes based on coagulation-flocculation-decantation work very well (Moles et al., 2020). This alternative has been applied for the removal of emerging pollutants from waters, such as azo-dye (Andriantsiferana et al., 2014), phenol (Matos et al., 1998), or 4-clorophenol (Herrmann et al., 1999), reporting a synergistic effect. This effect was observed not only in the photocatalysis but also in the adsorption (Herrmann et al., 1999; Bahrudin & Nawi, 2018). Some authors have pointed that this synergy does not really takes place, and it comes from a misinterpretation of the Langmuir-Hinshelwood equation (Asenjo et al., 2013). Some previous studies can be found coupling two metal oxides (Qiu et al., 2012), or combining metal oxides and MOFs, reporting a synergetic effect in the removal of sulfamethazine (Yu et al., 2019), methylene blue (Mills, 2012), and bacterial inactivation (Milosevic et al., 2017). However, there is not literature about the removal of antibiotics applying TiO_2/PAC mixture in suspension combined with UV-vis light (TiO_2/PAC/UV-vis). Consequently, there is a need to determine the possible synergy of these materials in water treatments.

This work evaluates the capacity of PAC/TiO_2/UV-vis process applied in suspension in the removal of antibiotics. The TiO2/PAC mixture was characterized via FTIR and FESEM. Moreover, the kinetic mechanism was proposed for the removal of antibiotics. The performance of this treatment has been monitored during three cycles. Finally, this research work has evaluated the effect of the TiO_2/PAC mixture regeneration applying UV-vis light. Furthermore, a comparison with the isolated processes (PAC adsorption and TiO_2 photocatalysis) is featured to determine possible synergies of PAC/TiO2/UV-vis in the removal of target antibiotics. The effect of the matrix and UV-vis radiation per unity of volume has been investigated as well.

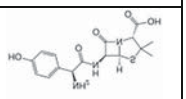
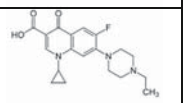
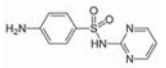
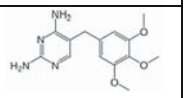
Materials and methods

Antibiotic characterization

The four target antibiotics were supplied by Sigma-Aldrich. Their characteristics are shown in Table 1 including the molecular structure and physicochemical properties of the molecules.

Antibiotic concentration was quantified by UV-vis absorption molecular spectrometry, using a *Helios ThermoSpectronic* and a quartz cell with a 1.0 cm path and repeating the absorbance measure of the solution by triplicate. The samples were filtrated with *GVS* 0.45 μm nylon filters previously to the analysis. The characteristic wavelength for sulfadiazine was 254

Table 1 Characteristics of the antibiotics selected: name, group, CAS number, molecular weight, acid dissociation constant, and molecular structure

Antibiotics	Group	CAS	pKa	MW (g/mol)	Structure
Amoxicillin	β-lactam	26787-78-0	3.2 (carboxyl) 11.7 (amine)	365.4	
Enrofloxacin	Fluoroquinolone	93106-60-6	6.2	359.4	
Sulfadiazine	Sulfonamide	68-35-9	6.4	250.3	
Trimethoprim	Trimethoprim	738-70-5	7.1	290.3	

nm, 202 nm for trimethoprim, 225 nm for amoxicillin, and 271 nm for enrofloxacin. Calibration curves were made using solutions of each antibiotic in deionized water in a range of 1–20 mg/l. The calibration curves for all the antibiotics showed a high linearity ($r > 0.99$). Therefore, concentrations as low as 1 mg/l could be reliably measured under these conditions.

Adsorbent characterization

VPlus vegetal powdered activated carbon (PAC) supplied by *Chemivall* was used as the adsorbent. According to the specifications given by the manufacturer, the particle size of 90% of the constituent particles was under 0.044 μm. Further specifications given are 10.3% humidity when packaging, 1.8% ashes on dry basis, as well as an iodine index of 950 mg/g.

Partial elemental analysis was also carried out, obtaining the carbon (95.8%), hydrogen (0.1%), and nitrogen (0.2%) contents. A scanning electron microscope (SEM) study complemented this information with other relevant elements such as oxygen (2.9%), aluminum (0.4%), silicon (0.7%), and iron (0.2%). In addition, a BET isotherm was performed, using a Chemisorb 2700 (micrometrics Instruments), measuring the flux of N_2 at a temperature of 77 K, yielding a superficial area of 745.4 m^2/g.

Catalyst characterization

In this study, TiO_2 FN2 was used (aqueous suspension) commercialized by Levenger. Crystalline phases were analyzed by X-Ray Diffraction (XRD) with a diffractometer Rigaku D/Max-2500, provided with a graphite monochromator to select the Cu Kα radiation. Measure interval (2θ) went from 10 to 80° at a speed of 1.8°/min. Determination and quantification of phases and size particle calculus were carried out with the software MDI-Jade7 and the data base JCPDS-International Centre for Diffraction Data-2000. For the semi-quantitative analysis of X-Ray fluorescence (XRF), a sequential XRF spectrophotometer Thermo Electron ARL ADVANT'XP was used. This XRF equipment was provided with an X-Ray tube with frontal window of beryllium (Be) and a rhodium (Rh) anode and it permitted the semi-quantitative detection of the elements between sodium (Na) and uranium (U). Particle morphology was studied by field emission scanning electron microscopy (FESEM) with a FESEM microscope Carl Zeiss MERLIN™ containing a secondary and retro-dispersed electrons detector.

Figure S1 presents the XRD patterns of TiO_2 Levenger. The peaks observed in the diffractogram showed crystalline structures of gypsum $CaSO_4{\cdot}H2O$ (8%) and smithsonite $ZnCO_3$ (4%), along with the phases of TiO_2, anatase (79%), and rutile (9%).

The results obtained by XRD were confirmed by the semi-quantitative elemental analysis of X-ray fluorescence. Average particle size was calculated from the XRD data, resulting in 23 nm for TiO_2 Levenger. Figure S2 shows a FESEM image of the catalyst. TiO_2 Levenger features the presence of bigger size (> 300 nm) particles with straight edges was also detected. Probably, these particles correspond to the CaSO4·H2O identified by XRD and XRF. TSS in TiO_2 Levenger was 106 g/l, which means a concentration of around 93 g/l TiO_2.

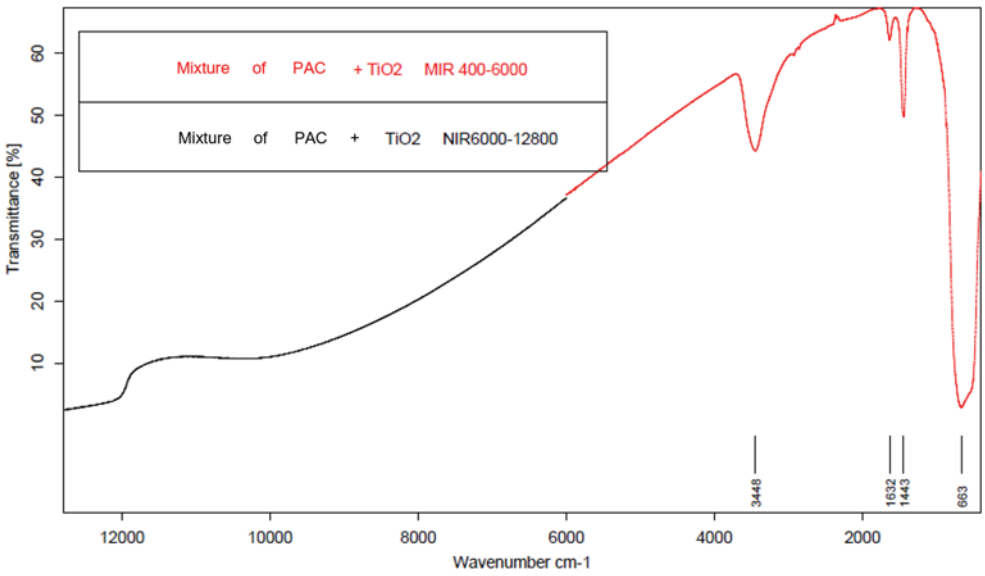


Fig. 1 FTIR-NIR of the mixture TiO2/PAC entre 400–12800 cm^{-1}

TiO2/PAC mixture characterization

The TiO2/PAC mixture was characterized via FTIR spectroscopy before and after the adsorption of amoxicillin in a Bruker Vertex 70 spectrometer. The measurement of the samples was carried out in a KBr disk. The acquisition range of the characterization was 400–12800 cm^{-1}, the resolution was 4 cm^{-1}, and the number of cumulative spectra was 32.

The characterization of the solid TiO2/PAC is shown in Fig. 1. According to the graph, the main functional groups of the TiO2/PAC mixture present vibrations at 633, 1443, 1632, and 3448 cm^{-1}, which usually appear in TiO2 according to literature (León et al., 2017; Maletić et al., 2019; Al-Amin et al., 2016). The 3448 cm^{-1} corresponds to the stretching of O–H bonds formed between the hydrogen atoms present in PAC or the water molecules entrapped and the oxygen atoms of TiO2, and the 1632 cm^{-1} corresponds to the bending of an O–H bond associated to a Ti atom. The peak in 1443 cm^{-1} could be related to the Ti-O bond, as well as the peak present in 663 cm^{-1}. In the NIR, a composed peak is observed around 12000 cm^{-1} that could be associated with the "band gap" of the mixture. The findings would confirm the formation of TiO2 nanoparticles.

To complement the characterization of the TiO2/PAC mixture, particle morphology was studied by field emission scanning electron microscopy (FESEM) with a FESEM microscope Carl Zeiss MERLIN™ containing a secondary and retro-dispersed electrons detector.

FESEM results are shown in Fig 2. According to the graphs, it can be observed that activated carbon has a porous and smooth surface of the order of 5–10 μm, while TiO2 is agglomerated in round particles (300–1500 nm). Electron backscatter diffraction allows the determination of the particles and the lightest ones. In this case, titanium oxide particles are the heaviest ones (white) while PAC is observed in black. Figures 2c and 2d (zoom of the graph) suggest that TiO2 is adsorbed covering the small pores and surface of the PAC. Since PAC has an affinity for antibiotics, the application of the catalyst and the adsorbent simultaneously could have a capacity to generate synergy and increase the performance of the process, as occurs in other treatments in which the carbonaceous material is impregnated with titanium dioxide

Experimental procedure

The experiments were performed in ultrapure water (pH 6.5) and in a real-treated urban wastewater (WWTP of 80,000 inhabitants located in the Ebro Basin) fortified with 15 mg/l of the selected antibiotics individually.

PAC adsorption experiments were conducted in presence of PAC Vplus (supply by ChiemiVall) concentration of 0.1 g/l in the dark in 200 ml of sample with a stirring of 150 rpm.

Atlas Suntest CPS+ solar chamber provided with a xenon lamp was used for the photo-treatments. For the TiO_2/UV-vis experiments, the samples were exposed to a light intensity of 540 W/m^2 and temperature of 35 °C in presence of 1 g/l of TiO_2 FN2. The essays were carried out with 200 ml of sample in sterile 250 ml quartz beakers with continuous stirring of 150 rpm. TiO_2/PAC/UV-vis experiments were carried out in the aforementioned solar chamber applying a dose of 0.1 g/l of PAC and 1 g/l of TiO_2. The samples were exposed to different light intensities per volume unit (Iv) ranging from 1 to 3 W/l. The rest of the parameters remain constant for each tested antibiotic.

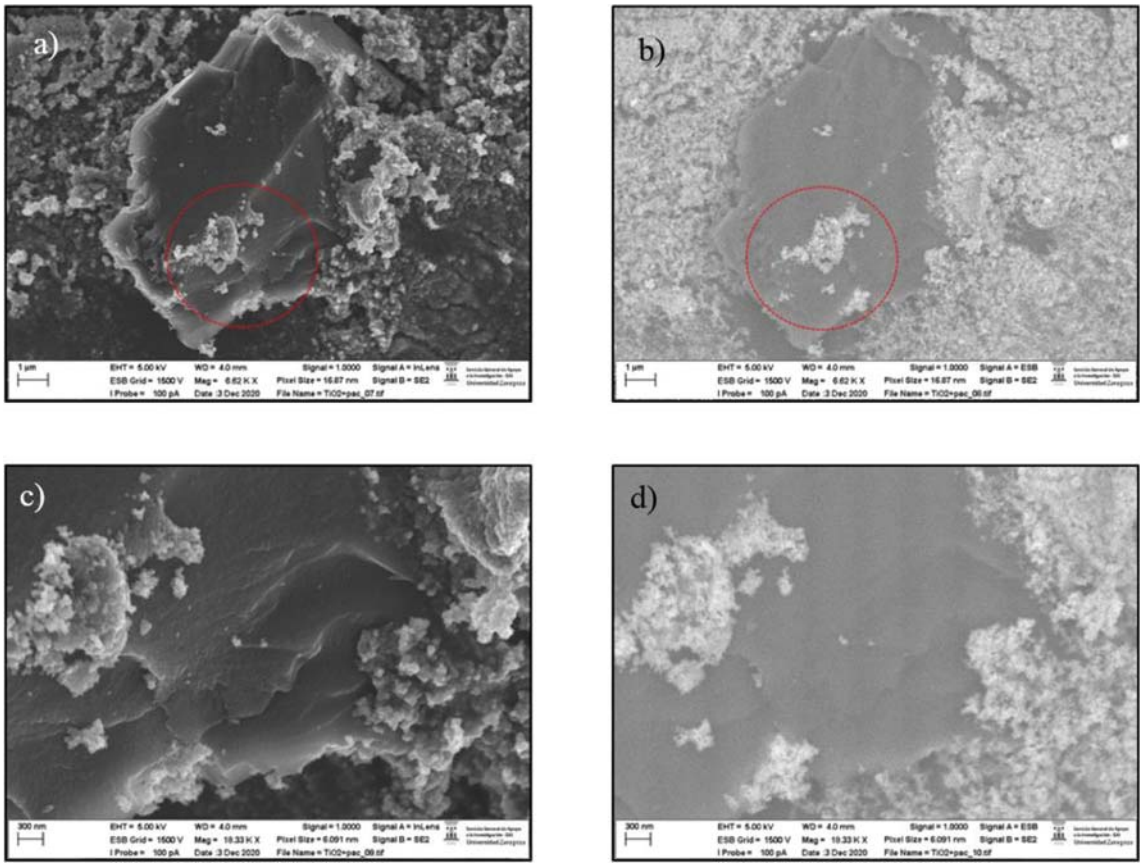


Fig. 2 FESEM of the mixture TiO2/PAC. Electron dispersive spectroscopy (**a**, **c**). Electron backscatter diffraction (**b**, **d**)

The three tested processes were conducted for treatment times of 10, 30, and 60 min. The antibiotic removal rate from the solution was calculated following Eq. 1:

$$\%\text{Removal} = \frac{C_0 - C_f}{C_0} 100 \quad (1)$$

Reuse experiments in PAC/TiO_2/UV-vis process

Reuse experiments were performed in ultrapure water fortified individually with 15 mg/l of the four target antibiotics, applying a suspension of 0.1 g/l of PAC and 1 g/l of TiO_2, as well as a radiation per volume unit of 1 W/l. These experiments consist of three consecutive cycles of 60 min. The mixture was filtered with a nylon filter, manufactured by GVS (0.45 μm pore size). Between each cycle, the TiO_2/PAC mixture was dried in a stove at 105 °C for 30 min and was weighed before and after the drying in order to quantify mass losses between cycles.

Regeneration experiments in PAC/TiO_2/UV-vis process

Regeneration essays were performed applying a radiation per volume (Iv = 1 W/l) in ultrapure water fortified with 15 mg/l of sulfadiazine. The experiment was composed of three cycles with a maximum treatment time of 60 min. The control parameter (molecular absorbance) was measured at 30 and 60 min in presence of 1 g/l of TiO_2 and 0.1 g/l of PAC. The TiO_2/PAC mixture was recovery from the solution by mean of 0.45 μm nylon filters. The regeneration procedure consists of two steps; first, dried in a stove at 105 °C for 15 min to determine mass losses. Immediately after, the dried catalyst was rinsed with 200 ml of water and was placed in a flask and mixed in the solar chamber for 2 h at Iv = 3 W/l.

Results and discussion

Performance comparison of the three treatments

In Fig. 3, the TiO_2/PAC/UV-vis results are reflected, the individual treatments (PAC adsorption and TiO_2/UV-vis), and the results of the application of both treatments as sequential steps (TiO_2/UV-vis process followed by PAC adsorption). The results suggest that higher removal of amoxicillin, enrofloxacin, and sulfadiazine was found in the TiO_2/PAC/UV-vis treatment compared to the individual PAC adsorption and TIO_2/UV-vis oxidation. By contrast, trimethoprim removal degree was similar in the isolated treatments and in the TiO_2/PAC/

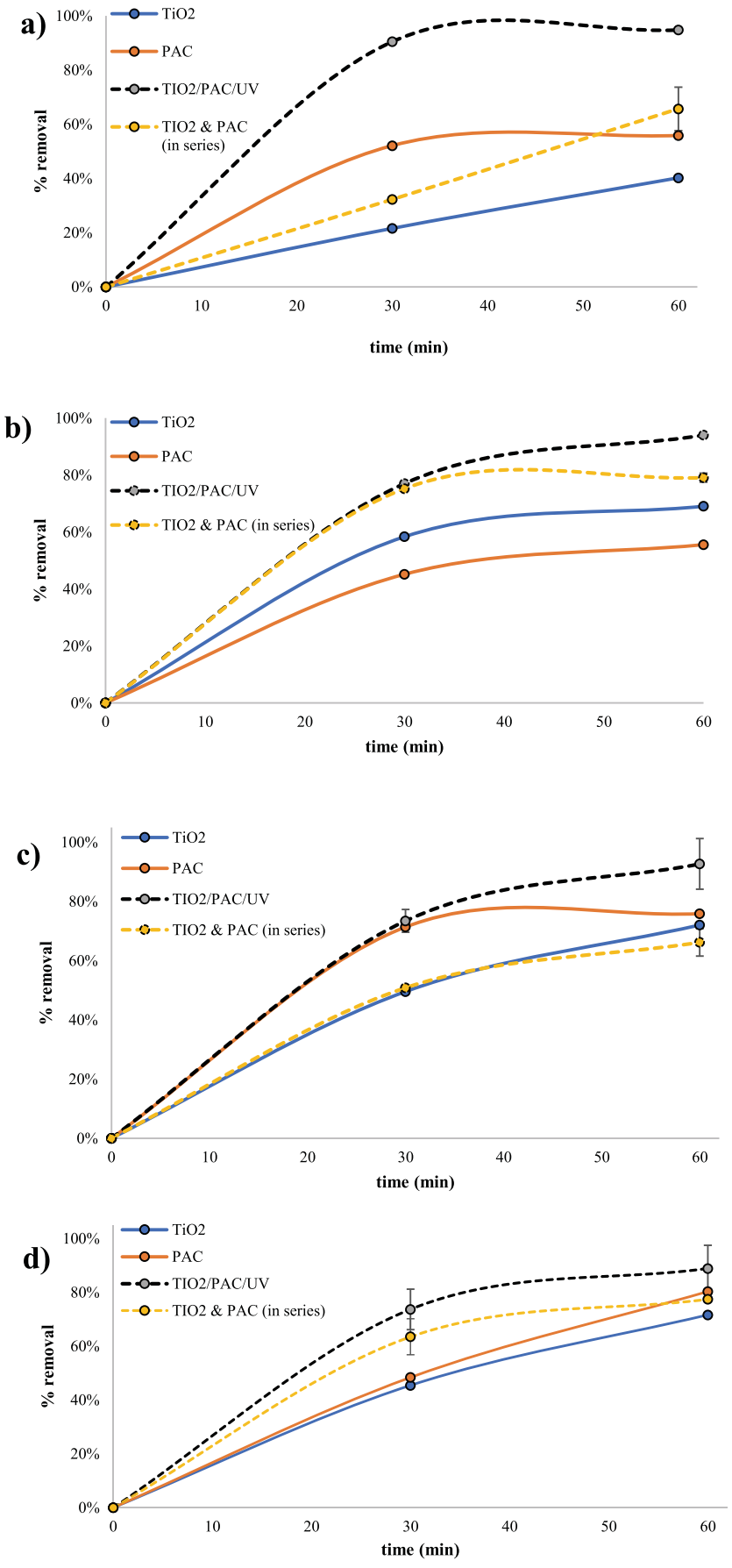


Fig. 3 Evolution of antibiotic removal degree applying different treatment **a** amoxicillin, **b** enrofloxacin, **c** sulfadiazine, **d** trimethoprim. $C_0 = 15$ mg/l, Iv = 1 W/l, 1 g/l TiO_2, 0.1 g/l PAC

Table 2 Kinetic fitting parameters for amoxicillin, enrofloxacin, sulfadiazine, and trimethoprim

Pseudo-second order	Amoxicillin	Enrofloxacin	Sulfadiazine	Trimethoprim
q_e (mg/g)	133.7	158.5	152.05	134.8
k_2 (g/mg min)	3.31×10^{-3}	7.76×10^{-4}	1.08×10^{-3}	1.61×10^{-3}
R	0.999	0.9992	0.9991	0.9984
Intraparticular diffusion	Amoxicillin	Enrofloxacin	Sulfadiazine	Trimethoprim
k (mg/g $min^{1/2}$)	2.83	7.13	7.14	4.91
I (mg/g)	103.6	77.0	75.8	81.9
R	0.9073	0.9622	0.8445	0.9023
Pseudo-first order	Amoxicillin	Enrofloxacin	Sulfadiazine	Trimethoprim
q_e (mg/g)	21.2	88.1	60.3	22.1
K_1 (l/min)	0.034	0.041	0.052	0.023
R	0.9301	0.9894	0.9726	0.55

UV-vis treatment. The enhancement of photocatalytic degradation of pharmaceuticals by using TiO2/PAC mixture is in accordance with the finding of other researchers who examined the immobilization of TiO_2 on activated carbon for removal of different organic compounds (Asenjo et al., 2013). This fact suggests that the process improvement depends on the antibiotic family and chemical properties. Amoxicillin was the only of the four antibiotics that showed a significant synergy applying the TiO_2/PAC/UV-vis treatment, reaching a 30% higher removal than the removal percentage obtained by applying TiO_2 photocatalysis and PAC adsorption in sequential treatments. This fact could be explained by a combined adsorption and decomposition process under light and OH radicals, leading to a higher availability of unoccupied adsorption sites. Moreover, since carbonaceous material is well known as an effective adsorbent due to hydrophobic interactions, hydrogen-bounding interactions, and electrostatic and dispersion interactions (Awfa et al., 2018), the adsorption is enhanced by the structure of the amoxicillin degradation products (Trovó et al., 2011), capable of establishing π-π interactions, as well as hydrogen bonds and electrostatic interactions (Moura et al., 2018; Peng et al., 2016). The antibiotic removal degree achieved by TiO_2/PAC/UV-vis process in suspension in 30 min of treatment is significantly higher if it is compared to research works where other pharmaceuticals were treated by composite of AC impregnated with TiO_2/UV-vis (Gu et al., 2019; El Mouchtari et al., 2020). The results of amoxicillin removal are consistent with the trend reported in

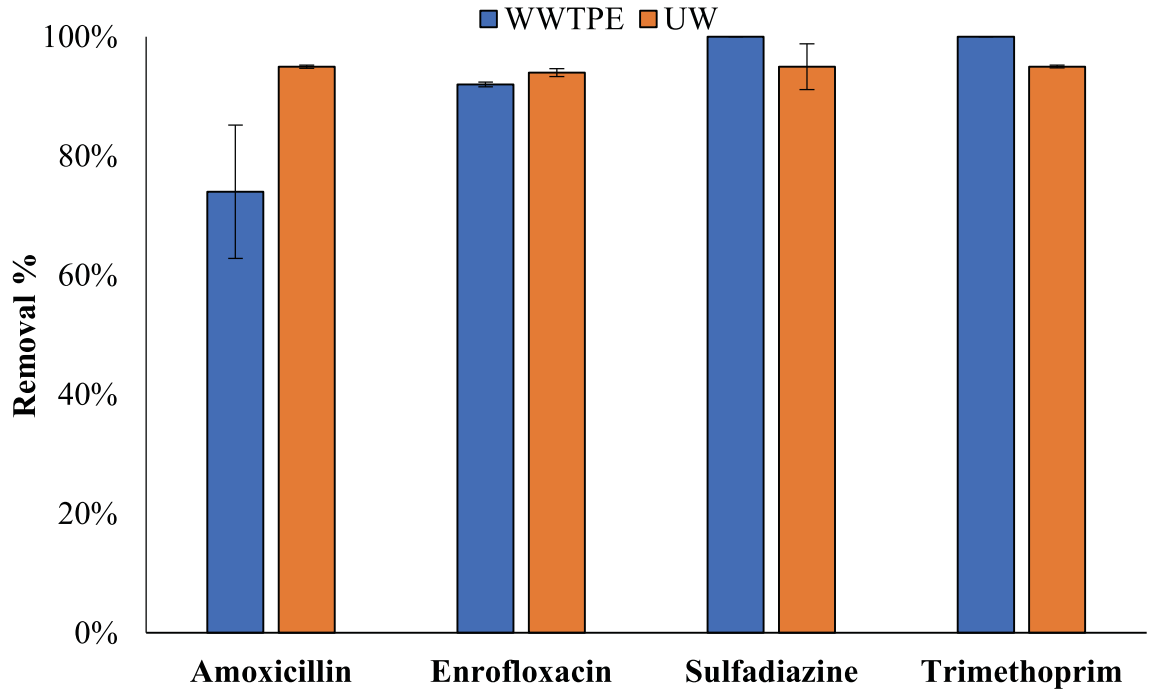


Fig. 4 Percentage of removal in WWTPE and Ultrapure water after 60 min of treatment of PAC/TiO_2/UV-Vis

Table 3 Influence of UV-vis radiation in the % removal of amoxicillin and enrofloxacin after among 60 min of TiO_2/PAC/UV-vis. C_0 = 15 mg/l Iv = 1 W/l, 1 g/l TiO_2, 0.1 g/l PAC

Amoxicillin		% Removal			Enrofloxacin		% Removal		
Radiation/volume		1 W/l	2 W/l	3 W/l	Radiation/volume		1 W/l	2 W/l	3 W/l
Time	10 min	81%	81%	78%	Time	10 min	62%	68%	73%
	30 min	90%	93%	90%		30 min	77%	84%	92%
	60 min	95%	94%	95%		60 min	94%	97%	98%

other studies focused on the removal of sulfamethazine (Yu et al., 2019) and methylene blue (Mills, 2012) with MOFs and metal oxides, while the rest of the selected antibiotics do not show the same behavior.

Regarding the antibiotics removal achieved by other advanced oxidation processes, the photo-Fenton treatment is reported to be more effective in Fenton-like processes. Furthermore, some authors suggested that the estimated costs of TiO_2/PAC photocatalysis and photo-Fenton are similar (Gar Alalm et al., 2016). Comparing the operational conditions of both advanced oxidation processes, photo-Fenton process is reported known to be favored at acidic conditions (Zepp et al., 1992), which might induce to operational problems such as corrosion. Moreover, since traces of iron remained in the treated effluent, it might cause environmental problems; meanwhile, TiO_2 is not harmful to the environment (Byrne et al., 2018).

Kinetic study

Regarding the kinetics, the experimental data fulfills follows pseudo-first order (Eq. 2), pseudo-second order (Eq. 3), and Weber-Morris intraparticular diffusion (Eq. 4) and as reported in the bibliography (Ensano et al., 2019; Yue et al., 2014; Ahmed & Theydan, 2014). In Eq. 2, k_1 is the rate constant of the pseudo-first-order model (L/min). In Eq. 3, K_2 is the rate constant of the pseudo-second-order model (g/(mg·min)). In Eq. 4, l is a parameter relating to the thickness of the boundary layer and k is the intraparticle diffusion rate constant.

$$\ln(q_e - q_t) = lnq_e - k_1 t \tag{2}$$

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

$$q = kt^{1/2} + l \tag{4}$$

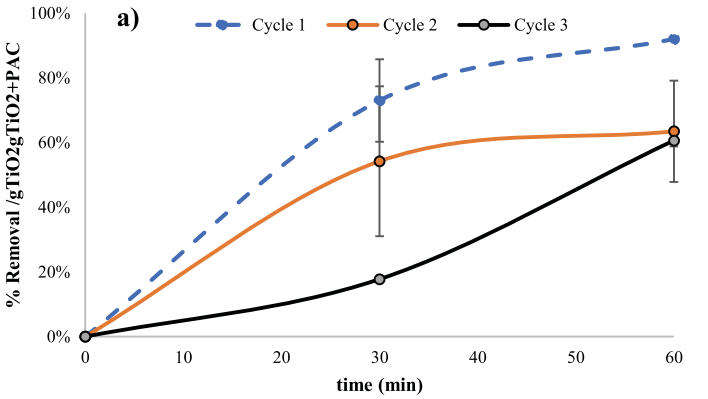
The q (mg/g) of every experiment was fitted to the pseudo-second order, Morrison-Weber intra-particle diffusion, and pseudo-first order models. Regardless of the tested antibiotic or the initial concentration, the kinetics of the adsorption process presented an overall better fitting to the pseudo-second order equation, ruling out intraparticle diffusion as a limiting step. Table 2 gathers the adsorption kinetics parameters for the fitting the equations to the data of the antibiotics. The suggested kinetics are consistent with the reported bibliography for enrofloxacin (Berges et al., 2020; Chowdhury et al., 2019), trimethoprim (Ngo et al., 2010), amoxicillin (Moussavi et al., 2013; Limousy et al., 2017), and sulfadiazine (Liu et al., 2017).

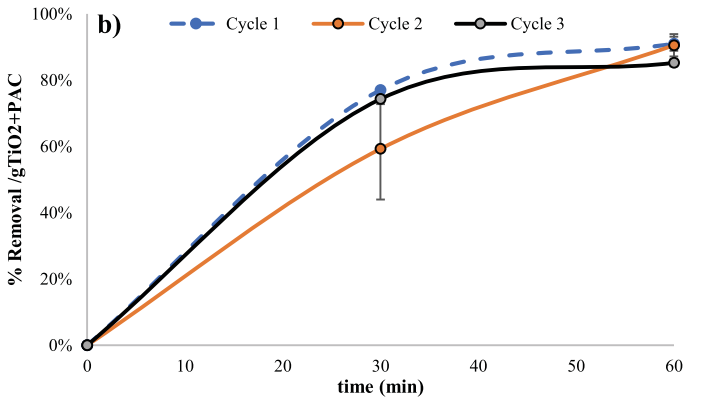
Matrix influence

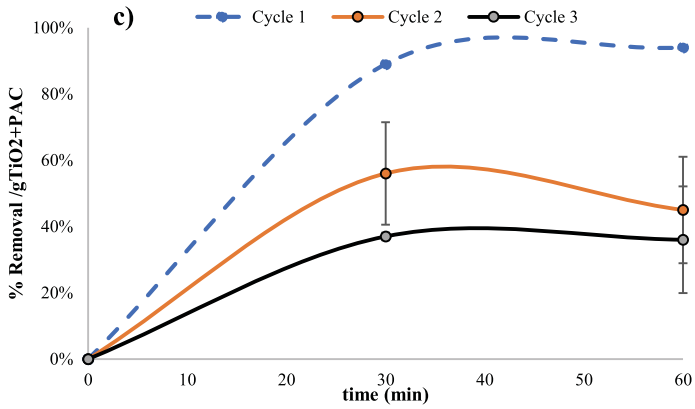
The influence of matrix has been studied in the TiO_2/PAC/UV-vis treatment, comparing the performance of the treatment in ultrapure water (UW) and real-treated urban wastewater (WWTPE). Literature suggests that the removal percentage tends to decrease when the treatment is applied in real wastewaters rather than ultrapure water. This behavior has been reported by other authors, using treatments based onTiO_2/UV-vis oxidation (Cabrera-Reina et al., 2019) or PAC adsorption (Guillossou et al., 2020). The presence of suspended

Table 4 Influence of UV-vis radiation in the % removal of sulfadiazine and trimethoprim after among 60 min of TiO_2/PAC/UV-vis. C_0 = 15 mg/l Iv = 1 W/l, 1 g/l TiO_2, 0.1 g/l PAC

Sulfadiazine		% Removal			Trimethoprim		% Removal		
Radiation/volume		1 W/l	2 W/l	3 W/l	Radiation/volume		1 W/l	2 W/l	3 W/l
Time	10 min	37%	51%	68%	Time	10 min	63%	58%	69%
	30 min	73%	84%	91%		30 min	74%	80%	86%
	60 min	93%	95%	97%		60 min	89%	89%	90%







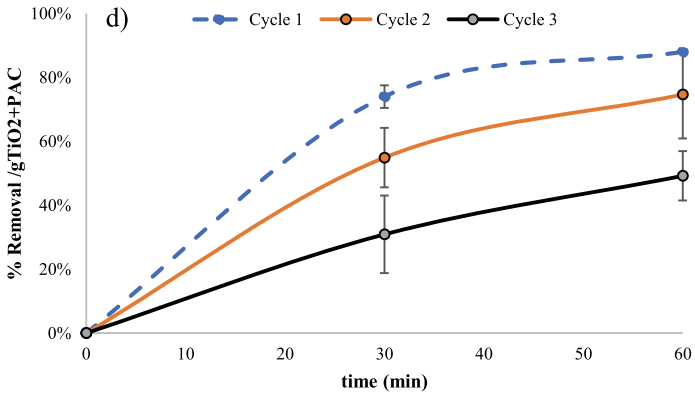


Fig. 5 Evolution of % removal per gram of TiO_2 + PAC during 3 cycles of 60 min for each antibiotic. **a** Enrofloxacin, **b** sulfadiazine, **c** amoxicillin, **d** trimethoprim. C_0 = 15 mg/l Iv = 1 W/l, 1 g/l TiO_2, 0.1 g/l PAC

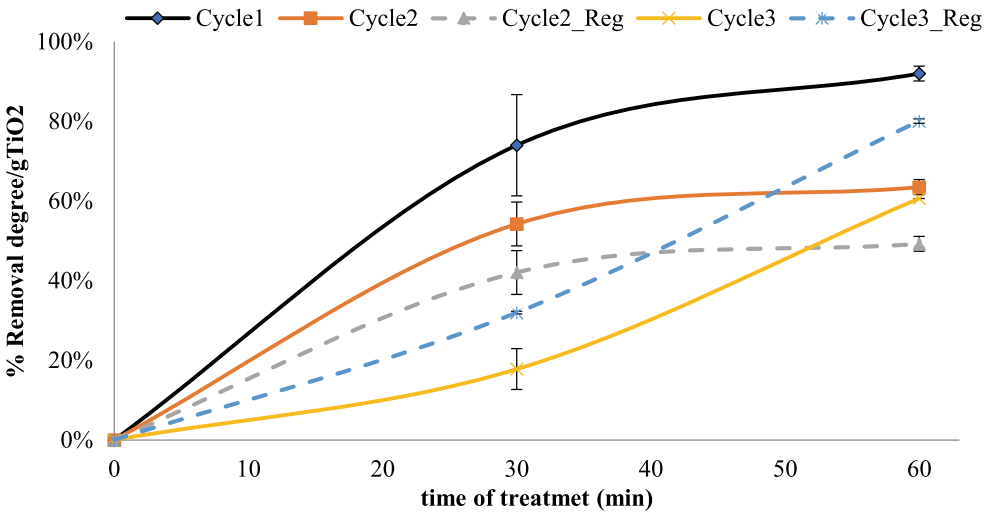


Fig. 6 Reuse performance without regeneration (cycle 1, cycle 2, and cycle 3) and applying UV-light regeneration (Cycle2_Reg and Cycle3_Reg). Evolution of sulfadiazine removal per gram of TiO_2/PAC. C_0 = 15 mg/l, Iv = 1 W/l, 1 g/l TiO_2, 0.1 g/l PAC

solids, organic matter, and other substances known as scavengers is known to lead to a reduction in the concentration of OH·radicals in water, having also an effect on light propagation through the reactor, resulting in the aforementioned decrease of photocatalytic efficiency of the process TiO2/PAC/UV-vis. Moreover, the presence of organic matter and suspension solids and other substances susceptible to be adsorbed causes a reduction of available adsorption sites in the TiO2/PAC mixture (Wang et al., 2019). However, the results of antibiotics removal after 60 min of TiO_2/PAC/UV-vis treatment in treated wastewater and ultrapure water (Fig. 4) show that the effect of water matrix is practically negligible. The TiO2/PAC/UV-vis process reaches the complete removal of trimethoprim and sulfadiazine, in these operational conditions in both matrixes. By contrast, amoxicillin and enrofloxacin do not reach the total removal; more than 90% removal was achieved for both antibiotics in the studied matrixes. This trend might be attributed to the presence of inorganic species such as H_2O_2, SO_3^{2-}, and BrO_3^- present in wastewater. Literature suggest that these species can improve the photocatalytic remediation of pharmaceuticals by acting as electron scavengers, and consequently increasing the production of hydroxyl radicals and thus generating oxidizing species (Lee et al., 2017).

Some authors suggest that dissolved organic matter competes with some micro pollutants for the available active sites (Maletić et al., 2019; Al-Amin et al., 2016). By contrast, the results might suggest that antibiotics adsorption is enhanced by their structure, and the structure of degradation products capable of establishing electrostatic interactions (Moura et al., 2018; Peng et al., 2016). Finally, since OH· radicals are non-selective, the results suggest the concentration of OH radicals enough to remove simultaneously dissolved organic matter and target antibiotics.

Study of radiation per unity of volume influence

Antibiotic removal evolution during 60 min of TiO_2/PAC-UV treatment is shown in Tables 3 and 4. The results suggest an influence of the radiation intensity in the effectivity of the process. In a treatment time of 10 min, an increase of the removal rate is observed when the applied radiation by volume unit increases as well. However, as treatment progresses, the influence of the radiation decreases. As a result, taking into account that at least an hour of treatment is needed in order to reach removal rates superior to 90%, it would be convenient to work at the minor radiation (1 W/l), as it would constitute energy savings. Other authors have obtained similar results studying the influence of radiation in photocatalytic processes, such as the degradation of phenol (Chiou et al., 2008).

Independently from the studied antibiotic and the scheduled radiation, the antibiotic rate removal remains constant with treatment times superior to 30 min. For these treatment times, a removal rate near to 100% is observed: up to 98% of initial enrofloxacin, 97% of sulfadiazine, 95% of amoxicillin, and a 90% of trimethoprim (Tables 2 and 3).

Study of TiO2/PAC mixture reuse and regeneration

Figure 5 shows the efficiency of the mixture of TiO_2/PAC in the antibiotic removal process for each one of the three-reuse cycles. The highest antibiotic removal rate corresponds to the first cycle and the removal decreases with subsequent cycles as other authors have suggested (Moles et al., 2020; Wang et al., 2019), presenting the second cycle lesser removal rates than the first one and higher rates than the third cycle. This reduction could be explained by the clogging of the surface of PAC active sites by the antibiotics and its degradation products, causing a reduction on the pore size. This phenomenon allowed the adsorption of less antibiotic molecules in each cycle, with the subsequent reduction on the removal

percentage (Wang et al., 2019). This reduction on the efficiency of removal is greater for the antibiotics which can be easier removed when they are treated exclusively with PAC rather than a treatment using only TiO_2 (amoxicillin, sulfadiazine, and trimethoprim) supporting this theory.

Finally, catalyst regeneration is considered a key step to achieve a cheap, scalable, and environmentally friendly method to apply photocatalysis by means of TiO_2/PAC mixture. The results of the regeneration experiment carried out with sulfadiazine and a radiation intensity of 1 W/l are shown in Fig. 4. It can be observed that, while the second cycle (C2) presents less efficiency when the TiO2/PAC mixture is regenerated (C2_Reg), the third cycle of the regeneration (C3_Reg) experiments is able to remove more antibiotics than its homologue for the reuse experiments (C3). The change in efficiency relative to the reuse experiments between cycles might be explained by the time of the regeneration stage. Each regeneration cycle consists of 2 h of treatment, insufficient for a complete regenerate the TiO2/PAC mixture, and reach the initial performance, leading to smaller efficiencies (Andriantsiferana et al., 2014; Sharma & Lee, 2017). However, in the (C3_Reg), TiO_2/PAC mixture has been exposed to a total of 4 h of regeneration, and thereby, it gets higher capacities than its homologue without regeneration via UV-vis (C3) Fig 6.

Conclusions

The application of TiO2/PAC/UV-vis in suspension is a promising process, because it reduces energy and chemical consumption. Consequently, this research work has studied the performance of the process, as well as operational conditions such as radiation per unity of volume and performance evolution after three cycles. Regarding the results of this study, the following conclusions can be drawn:

(1) The application of TiO2/PAC mixture in suspension allows the removal of the target antibiotics in the range 90-97% in 60 min of treatment
(2) Amoxicillin was the only of the four antibiotics that showed a significant synergy applying the TiO_2/PAC/UV-vis treatment, and this fact might be attributed to their structure capable of stablishing electrostatic interactions with the TiO_2/PAC mixture.
(3) There is no influence of the water matrix (ultrapure water or treated wastewater) in TIO_2/PAC/UV-Vis process. Though dissolved organic matter of treated wastewater might decrease the performance of the process, the effluent of the WWTP also contains inorganic matter, which increases the concentration of oxidizing species resulting in a similar performance of the process in both matrixes.
(4) The regeneration of the TiO2/PAC mixture is possible applying, at least, 4 h of exposure to 3 W/l of UV-vis light. By contrast, the reuse essays without regeneration showed that the aforementioned mixture tends to be deactivated gradually among various cycles, according to the results a 15% inferior removal of all antibiotics per cycle in average.
(5) FTIR and FESEM characterization of the material prove the formation of TiO2 nanoparticles in both the pores and the surface of PAC, thus confirming the possibility of establishing a synergy on the degradation of certain antibiotics.

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Compliance with ethical standards

Competing interests The authors declare that they have no competing interest.

Ethical approval Not applicable.

Consent to participate Not applicable.

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