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Pilot plant approach combining photocatalysis and adsorption for antibiotics removal from slaughterhouse and urban wastewater treatment plant effluents

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ABSTRACT

The main objective of this research is to perform a real case-study of antibiotic decontamination from real slaughterhouse and wastewater effluents by applying a sequential treatment of TiO_2/UV–vis photocatalysis and adsorption. More precisely, the removal of five classes of antibiotics: enrofloxacin, sulfadiazine, trimethoprim, azithromycin, amoxicillin and amoxicillin degradation products was studied in an 80 L/h photocatalytic and adsorption pilot-scale plant over multiple cycles, operating in semi-continuous mode. The results exhibited significant removal rates, ranging from 77% to 100% for the slaughterhouse effluent, and 61–89% for the wastewater treatment plant effluent, thus demonstrating that the treatment is more effective when it is applied directly in the emission source, previous to antibiotic dilution in the municipal collector. Using the two processes sequentially results in greater efficiency than when they are used in isolation. After photocatalysis, antibiotic degradation products are easily adsorbed, since they have more affinity for the adsorbent, and the presence of competing compounds decreases considerably. After applying several cycles of treatment, the adsorption performance remains almost constant. By contrast, the photocatalysis performance decreased, which was attributed to catalyst agglomeration determined by Asymmetric Flow Field-Flow Fractionation (AF4) coupled with Dynamic Light Scattering (DLS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

1. Introduction

Antibiotics have played a crucial role in human and veterinary medicine for treating bacterial infections. However, their increasing use and misuse has led to the generation of antibiotic-resistant bacteria and environmental pollution (Chen et al., 2021; Cacace et al., 2019). Antibiotics and their degradation products have been frequently detected in aquatic environments, including rivers, lakes, and wastewater treatment plants, posing significant threats to aquatic ecosystems and public health (Barbosa et al., 2016; Moles et al.,

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2022). In the last five years, several veterinary pharmaceuticals, such as amoxicillin, sulfamethoxazole and trimethoprim, have been included in the EU watch lists of substances for union-wide monitoring in the field of water policy, established in 2015 and updated in 2018, 2020 and 2022 (European Commission, European Commission, 2015; European Commission, 2018, 2020, 2022).

According to the most recent report on the sales of antimicrobial agents sales in Europe (ESVAC, 2021) (European Medicines Agency, 2022) Spain leads sales (in tonnes) for food-producing animals, representing about 25% of the total. Slaughterhouses generate a significant amount of wastewater due to the extensive water usage in their operations, including their cleaning and manufacturing practices. High concentrations of antibiotics have recently been identified during long-term monitoring studies of slaughterhouses in Spain and Europe (Moles et al., 2022). As a result, new regulations are being implemented in the EU to control the presence of veterinary medicinal products, such as Regulation (EU) 2019/6 (European Parliament and the Council of the European Union). Once wastewater containing antibiotics is discharged, it undergoes treatment in wastewater treatment plants (WWTPs). The effectiveness of these plants in removing antibiotics varies significantly, influenced by the specific properties of the antibiotic, such as its hydrophobicity, chemical structure, and electrostatic interactions (Berges et al., 2021; Moles et al., 2021). Conventional treatment methods, such as coagulation, sedimentation, and biological processes, are often insufficient to remove persistent and hazardous organic contaminants, including antibiotics, from wastewater (Jewell et al., 2016; Homem and Santos, 2011a; Moles et al., 2020a; Pan et al., 2015). They can reduce the concentrations of several pharmaceutical compounds considerably, such as sulfadiazine or amoxicillin (Gozlan et al., 2013; Moles et al., 2020b). However, they have a low removal efficiency for certain antibiotics, such as trimethoprim (Moles et al., 2020b). As a result, there is a need to develop new technologies that can address antibiotic pollution directly at their emission sources, thus avoiding pollution in the water cycle.

Advanced oxidation processes (AOPs) have emerged as a promising solution, offering a powerful and versatile approach for the removal of emerging pollutants, such as antibiotics, pesticides or microplastics (Guerra-Rodríguez et al., 2018; Deng and Zhao, 2015). Some of the most widely studied AOPs include Fenton's reagent, photocatalysis, ozonation, and ultrasound-assisted processes (Barbosa et al., 2016; Miklos et al., 2018; Matafonova and Batoev, 2018; Guillossou et al., 2019). These processes can be further enhanced by combining them with other treatment methods, such as adsorption (Moles et al., 2021; Nidheesh et al., 2021), to create integrated treatment systems that offer improved pollutant removal efficiencies. A recently studied example is sequential ozonation and adsorption treatment (Guillossou et al., 2020). Moreover, AOPs have been successfully applied to the treatment of various types of wastewater, including industrial effluents, municipal sewage, and agricultural runoff (Rodríguez-Chueca et al., 2013; Peng et al., 2016). Furthermore, AOPs have demonstrated their potential for the removal of emerging contaminants, such as microplastics and antibiotic resistance microorganisms (Lim et al., 2022; Núñez-Núñez et al., 2020), which are of growing concern due to their potential impacts on human health and the environment.

Among AOPs, photocatalysis is a powerful process for removing antibiotics in aquatic environments (Loeb et al., 2019; Byrne et al., 2018; Maletić et al., 2019; Yu et al., 2019; Pereira et al., 2011). Photocatalytic treatment can be further enhanced by combining it with adsorption techniques, such as using metal-organic frameworks (MOFs) or graphene-based materials, which can adsorb antibiotics onto their surfaces (Berges et al., 2021; Byrne et al., 2018; Limousy et al., 2017). This synergistic approach offers efficient removal of antibiotics from water while minimizing the formation of degradation products, which could still present significant risk to the environment (Moles et al., 2021; Bahrudin and Nawi, 2018). It is important to remark that degradation substances have been found in high concentrations in water sources, but few studies in the literature have addressed their effects. Among several photocatalysts, such as ZnO, $SrTiO_3$, TiO_2 or WO_3, TiO_2 was chosen for this study due to its high activity under UV light, chemical stability, biocompatibility, cost-effectiveness, versatility, stability, and efficacy in degrading diverse pharmaceuticals. Moreover, TiO_2/UV–vis have been demonstrated effectively for removing antibiotics from different families (*i.e.* enrofloxacin, sulfadiazine, trimethoprim, azithromycin, and amoxicillin) (Moles et al., 2020b).

Adsorption is another commonly used method for antibiotic removal from wastewater. Carbonaceous materials, such as commercial powdered activated carbon (PAC), have a large surface area and porosity, allowing effective adsorption of various pollutants through electrostatic and hydrophobic interactions (Peñafiel et al., 2019, 2021; Ahmed and Theydan, 2014; Balarak et al., 2021). However, PAC requires periodic replacement or regeneration, since its removal capacity diminishes after multiple adsorption cycles (Moles et al., 2021; Andriantsiferana et al., 2014). Key factors such as the matrix composition, energy consumption, adsorbent reuse, and scale-up can significantly impact treatment efficiency (Issues and Trends, 2021), especially considering that most studies are conducted at laboratory scale. Therefore, further research is needed to gain a better understanding of these factors in real wastewater scenarios.

The sequential combination of photocatalysis and adsorption could have numerous advantages, specifically for the removal of antibiotics and other persistent compounds in water environments (Barbosa et al., 2016). For instance, when employed separately, they may face limitations that can affect their efficiency (Mailler et al., 2015). Photocatalysis, although capable of degrading various pollutants, often leads to the formation of potentially toxic by-products (Gozzo et al., 2023). Adsorption, on the other hand, is an effective method for removing pollutants, but the capacity of the adsorbent can diminish over time, requiring regular replacement or regeneration (Moles et al., 2021). If adsorption is applied after a photocatalytic process, the generated by-products would be adsorbed in the PAC. Moreover, the PAC adsorption capacity over time would be improved, since the concentration of antibiotics, organic matter, bacteria and other substances would be lower. This also implies higher antibiotic adsorption performance, since these aforementioned substances compete with antibiotics for PAC active sites.

This study focused on five widely-used antibiotic families: enrofloxacin, sulfadiazine, trimethoprim, azithromycin, and amoxicillin. Additionally, the study also examined the main degradation products of amoxicillin: amoxicillin diketopiperazine, penilloic acid, and penicilloic acid. These antibiotics are commonly used in human and veterinary medicine (European Medicines Agency, 2019), as well as frequently detected in wastewater treatment plants and aquatic environments, particularly in previous studies conducted in the

POCTEFA territory (Moles et al., 2022; López-Serna et al., 2011). In this specific region, which has significant intensive farming (Moles et al., 2022), the highest frequency of detection in wastewater has been observed for azithromycin (detected in 92% of the samples), sulfamethoxazole (92%), trimethoprim (75%), ciprofloxacin (75%), and enrofloxacin (61%) (Moles et al., 2022).

The main goal of this research is to study antibiotic decontamination in real wastewater directly from antibiotic emission sources, such as slaughterhouses. In this context, the specific objectives are: (i) Evaluate the efficacy of TiO_2 photocatalysis and powdered activated carbon (PAC) adsorption in tandem for the decontamination of antibiotics from real wastewater emissions. (ii) Conduct comprehensive treatment of real effluents in an 80 L/h photocatalysis and adsorption pilot scale plant, marking a significant step towards the practical application of these processes in real-world scenarios. (iii) Investigate the efficiency over multiple cycles in semi-continuous operation mode, assessing the recyclability of PAC and TiO_2 to determine their impact on process performance. (iv) Assess antibiotic removal directly at the slaughterhouse, before it becomes mixed with urban and industrial wastewater at the municipal wastewater treatment plant. Additionally, employ Asymmetric Flow Field-Flow Fractionation (AF4) coupled with Dynamic Light Scattering (DLS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to meticulously evaluate and control potential Ti emissions, ensuring their proper separation from the solution. (v) Explore different classes of antibiotics and various removal techniques to offer valuable insights and strategies for improving the management of antibiotic-contaminated wastewaters directly at their emission sources, aiming to protect both aquatic ecosystems and public health.

2. Materials and methods

2.1. Antibiotics quantification

Antibiotic standards were purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France), except for amoxicillin diketopiperazine and penicilloic acid (LGC, Molsheim, France). The purity of the antibiotic standards was >99% wt. in all cases. Their physicochemical properties are shown in Table 1. The solvents (HPLC grade methanol and acetonitrile), formic acid (≥ 95%), ammonium formate (≥ 99%), ammonium acetate and ammonium bicarbonate (≥ 99%) were purchased from Sigma-Aldrich.

Antibiotic and degradation concentrations were quantified by HPLC/MS/MS at the Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux (IMPREM, France) following a methodology described in previous research works (Moles et al., 2020b; Gozzo et al., 2023). The samples were centrifuged for 10 min at 13,000 rpm in Eppendorf tubes and then diluted 40 times with 0.1% formic acid/MeOH/ACN (80% /10%/10%) before LC-MS/MS analysis. The separation by chromatography was carried out in an ultra-high performance liquid chromatography system (UPLC) Ultimate 3000 RSLC (Thermo Fisher Scientific). An Accucore C18 100 2.1 mm, 2.6 m column (Thermo Fisher Scientific) was used. The mobile phases were (A) H_2O with 0.4% formic acid + 5 mM ammonium formate and (B) MeOH / ACN 1:1 (v/v). An aliquot of 20 µl of sample was injected. Detection was performed on a Q Exactive Spectrometer Mass Plus (Thermo Fisher Scientific) operated in selective ion monitoring (MSI) positive mode with a resolution of 70,000. External calibration was used for quantification prepared from standards of selected antibiotics and degradation products. Samples were analyzed in triplicate. The limits of detection and quantification of each antibiotic as well as the main MS detection parameters implemented in the quantitative analysis are shown in Table 2.

The effectiveness of removing the target compounds was calculated as the difference between the initial concentration (C_0) in the wastewater and the final antibiotic concentration (C_F) after the treatment, divided by the initial concentration and expressed as a percentage, as shown in Eq. 1.

$$\text{Removal efficiency}(\%) : \frac{(C_0 - C_F)}{C_0} \times 100 \quad (1)$$

2.2. Total Ti determination by ICP-MS and characterization of Ti forms by AF4-DLS-ICP-MS

The Ti concentration in the pilot-scale treated effluent was quantified by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (ELAN DRC-e, PerkinElmer, Toronto, Canada). A discrete volume sample (100 µL) was injected through a six-way valve, and the carrier was delivered directly to the nebulizer of the spectrometer. A glass concentric slurry nebulizer with a cyclonic spray chamber (Glass Expansion, Melbourne, Australia) was used. Default values were used for the rest of the instrumental parameters. The

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

Antibiotics	Group	CAS	pKa	MW (g/mol)
Azithromycin (AZI)	Macrolide	83905–01–5	8.74	749.0
Enrofloxacin (ENR)	Fluoroquinolone	93106–60–6	6.2	359.4
Sulfadiazine (SDZ)	Sulfonamide	68–35–9	6.4	250.3
Trimethoprim (TMT)	Diaminopyridine	738–70–5	7.1	290.3
Amoxicillin (AMX)	β-lactamase	26787–78–0	7.4 2.5	365.4
Amoxicillin Diketopiperazine (AMX DIK)		108736–10–3	-	370.44
Penicilloic acid (AMX PENI)		64527–07–7	-	262.29
Penilloic acid (AMX PENIL)		501–34–8	-	339.4

Table 2
MS detection parameters used in quantitative analysis of antibiotic species.

Antibiotic	RT (min)	Parent ion (m/z) [M+H]+	CE (eV)	Product ion 1	Product ion 2	LOD (ng/L)	LOQ (ng/L)
Azithromycin (AZI)	8.99	366.11	10	349.08	208.04	0.02	0.067
Enrofloxacin (ENR)	10.47	360.17	35	316.18	245.11	0.041	0.135
Sulfadiazine (SDZ)	6.71	251.06	30	156.01	108.04	0.015	0.050
Trimethoprim (TMT)	9,06	291,15	50	261,0979	230,1158	0026	0085
Amoxicillin (AMX)	8.99	366.11	10	349.08	208.04	0.152	0.500
Penicilloic acid (AMX PENIC)	5.50	384.12	10	367.09	323.11	0.015	0.050
Penilloic acid (AMX PENIL)	6.97	279.09	35	124.09	204.04	0.015	0.050
Diketopiperazine (AMX DIK)	9.36	366.11	10	207.08	160.04	0.100	0.300

quantification of TiO_2 was based on monitoring the ICP-MS signal of the isotope ^{49}Ti, using ^{74}Ge as an internal standard. From an on-line calibration with an ionic titanium standard diluted in nitric acid (1%), intensity signals from the ICP-MS for samples were transformed into mass values by integrating the area of the transient signals obtained (Ojeda et al., 2020). All samples were injected in triplicate. The limit of detection of the method was established at 0.81 μg/L and the limit of quantification at 2.70 μg/L.

The size characterization of Ti forms in the effluents was carried out in a AF2000 (Postnova Analytics, Landsberg, Germany) system, with a channel of reduced dimensions. A regenerated cellulose (RC) membrane with a 5 kDa cut-off was used. The carrier solution consisted of a mixed surfactant Novachem 0.05% (v/v) and the sample injection volume was 100 μl in all cases. The injection program conditions can be found elsewhere (Ojeda et al., 2020). The outlet flow rate was 1 mL / min and the crossflow remained constant at 0.1 mL/min for 5 min, followed by a linear decay to 0 mL/min in 2 min. The eluent at the end of the channel was analyzed by a UV-Vis diode-array detector (Shimadzu, Duisburg, Germany) recording signals between 200 and 650 nm. Simultaneously, AF4 was also coupled with a DLS detector (Zetasizer Nano ZS, ZEN3600, Malvern, Worcestershire, United Kingdom) equipped with a flow cell (ZEN 0023) for size characterization of the eluted fractions and with the ICP mass spectrometer for the elemental detection of titanium. The outflow from the system was delivered directly to the nebulizer of the spectrometer. DLS signal intensity and hydrodynamic diameter (Z-average) estimations were collected every 15 s and default values were used for the rest of instrumental parameters (at 25 ºC). Before the analysis, all the samples were centrifuged at 300 rpm for 2 min to remove large particles.

2.3. Raw wastewater

Antibiotic removal from effluent was studied directly at the points of emission to the environment: a rabbit slaughterhouse and a WWTP. Samples were filtered through a 0.45 μm nylon filter. Dissolved Organic Carbon (DOC) measurement was carried out following the standard method 5310 B using a SHIMADZU TOC-VCSH. Chemical Oxygen Demand (COD) was determined using a multiparameter photometer from Hanna Instruments, model HI 83099, using an adaptation of EPA Method 410.4. Turbidity was determined by means of the standard method UNE-EN ISO 7027:2001. A HANNA Instruments turbidimeter, model LP 2000 (error $\leq$ 0.2 NTU) was used. The method used to determine the solution pH was 4500-HB. The pH quantification was conducted in a CRISON pH meter, model GLP 21, was used for this purpose, and previously calibrated with buffer solutions of pH 7.00 and 4.01. Table 3 shows the wastewater physicochemical characteristics as well as the initial antibiotic concentrations. It can be seen that the antibiotic concentration in the slaughterhouse effluent was higher than in the WWTP effluent for all the antibiotics except AMX and AMX_DIK.

Antibiotic decontamination tests were carried out in semi-continuous mode without fortifying real wastewater. In the case of the TiO_2 and PAC reusability assays, the real effluent from the wastewater treatment plant (WWTP) was fortified with antibiotic standard. The initial concentration of the antibiotics (enrofloxacin, sulfadiazine, trimethoprim, and azithromycin) was 100 μg/L.

Table 3
Physicochemical characteristics and antibiotic quantification at the selected emission sources.

Parameter/Water matrix	Slaughterhouse effluent	WWTP effluent
pH	7.5	7.5
Chemical Oxygen Demand (COD) (mg/L)	140	100
Turbidity (NTU)	60	22
Dissolved Organic Carbon (DOC), (mg/L)	1400	190
SDZ (ng/L)	1380	324
AZI (ng/L)	4970	3399
ENR (ng/L)	2205	1281
TMT (ng/L)	3370	66
AMX (ng/L)	n/d	195
AMX PENIC (ng/L)	540	23
AMX PENIL (ng/L)	206	17
AMX DIK (ng/L)	n/d	42

2.4. Pilot-scale plant: description and operational conditions

The catalyst concentration of Levenger FN2 TiO_2 was 1 g/L in the photoreactors, while the PAC concentration was kept constant at 100 mg/L in the adsorption tank. Catalyst and PAC characterization can be found in the supplementary material. The intensity of the radiation applied during these experiments was set at 0.3 W/l. Operational conditions were kept within a temperature range of 15–20 ºC, and the photocatalytic treatment time was 120 min. The adsorption treatment was applied during 30 min, as this had been found to be optimal in previous research works (Moles et al., 2021, 2020a, 2020b). The antibiotic removal assays were conducted in a facility comprising several components, as illustrated in Fig. 1.

Initially, a 1000 L stainless steel storage tank (see Fig. 1) was filled with the wastewater which was then stirred. The wastewater was then pumped at a rate of 8–16 L/min to a 100 L stainless steel mixer containing TiO_2, where it was mixed with the catalyst. The mixture was then transferred to four identical TiO_2 slurry reactors (17 L) made of aluminium, to improve light reflection, where TiO_2/UV–vis oxidation was carried out for 120 min. Each annular reactor was equipped with a 40 W UVA lamp and an inlet of compressed air, which were used during the 120 min of TiO_2 UV–vis treatment. The wavelength range of the UVA light source was 330–390 nm, excluding the visible region (420–800 nm). The compressed air flow provided stirring in the reactor as well as keeping the concentration of dissolved oxygen constant to achieve the correct generation of hydroxyl radicals. After the photocatalytic treatment in the reactors, the treated water was pumped back to the decanter for catalyst separation. The separation process involved a first stirring step applying 200 rpm for 5 min, mechanical flocculation at 40 rpm for 25 min, and decantation for 90 min, without the addition of any chemical substance. Subsequently, the catalyst remained in the decanter for the next cycle, while the wastewater treated by TiO_2/UV–vis was pumped to the adsorption tank.

Afterwards, the wastewater was pumped to another identical 100 L stainless steel tank, containing the adsorbent PAC. Adsorption of the remaining antibiotics and intermediate degradation products took place for a contact time of 30 min. At the end of this process, PAC separation was then carried out in the same tank, which was stirred through coagulation-flocculation-decantation for 120 min, this time with the addition of 50 mg/L of iron (III) chloride as coagulant. Finally, the treated effluent was monitored to quantify the final antibiotic and degradation product concentrations.

Performance analysis of PAC and TiO_2 reusability was conducted across seven treatment cycles. These experiments were planned to establish the specific mechanisms involved in the photocatalysis and the adsorption processes during several operational cycles. The evaluations of the antibiotic concentration and removal efficacy were selectively performed only for the first to third cycles and the sixth to seventh cycles.

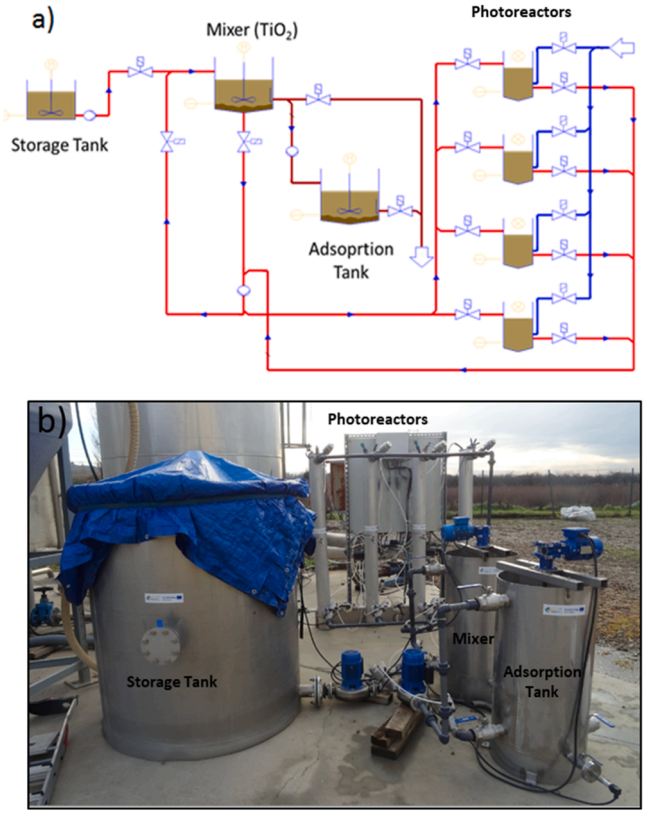

Fig. 1. 80 L/h TiO2/UV–vis and PAC adsorption pilot-scale plant: (a) process Flow diagram (b) pilot scale facility.

3. Results

3.1. Antibiotic removal in real wastewater

The research presents a real case-study for the treatment of slaughterhouse and WWTP effluents using a sequential treatment of TiO_2/UV–vis photocatalysis and PAC adsorption. The results are shown in Fig. 2. It should be noted that the removal in the slaughterhouse effluent of AMX and AMX-DIK were not shown since these products were not detected initially (see Table 3).

As can be observed, the removal efficiency for antibiotics in both effluents was similar: ranging from 77% to 100% for the slaughterhouse wastewater and 61–90% for the WWTP effluent. Comparisons across different antibiotics showed a varying degree of removal efficiency. For example, there were similar removal efficiencies for ENR, SDZ, AMX, and AZI in both effluents, while the highest degradation was achieved for AMX degradation products. This suggests that these substances are easier to remove than their parent compounds, even in low concentrations. It should be noticed that degradation products are usually easier than parent compounds (Zeghioud et al., 2019). In this particular case, it could be attributed not only to the affinity of AMX degradation products for PAC suggested previously in the literature (Berges et al., 2021; Moles et al., 2021), but also to the usually higher degradation rates of β-lactamases such as AMX by TiO_2/UV–vis photocatalysis (Issues and Trends, 2021; Cabrera-Reina et al., 2019). In recent studies conducted at pilot-scale, photocatalysis has been recognized as an efficient technique for the efficient degradation of carbapenem antibiotics in aqueous solutions, which belong to β-lactamase family (Cabrera-Reina et al., 2019). More precisely, in the aforementioned work a 60% removal of imipenem was obtained applying solar photocatalysis versus the 92% obtained in the present work. In our research work, we have decided to apply artificial UV-light instead of solar radiation to have the possibility to work in continuous mode.

In contrast, TMT showed the lowest degradation rates, aligning with previous research indicating the relative stability of this antibiotic under different AOPs and conventional processes, moreover the obtained removal rates for TMT are higher than the obtained in the literature (Moles et al., 2020b; Iakovides et al., 2019; Cai and Hu, 2017). However, it can be observed that the sequential treatment removes a high concentration of this stable antibiotic in the slaughterhouse effluent (82%). The removal efficiency of TMT in WWTP was lower (61%). Since TMT degradation follows a pseudo-first order kinetic, according to the literature (Jewell et al., 2016), this can be attributed to the higher initial concentration in the slaughterhouse effluent, which improves the intrinsic kinetic of the photocatalytic degradation process.

The significant removal of selected antibiotics in both real matrixes shows the potential of this process for the efficient removal of antibiotics in general. Previous studies highlighted the effectiveness of photocatalysis in degrading various antibiotics, including AMX and ENR (Li et al., 2012; Rodríguez-Chueca et al., 2023; Le et al., 2018) in simulated wastewater, as a result this work provides a validation applying these processes in real effluents, such as a raw effluent from a slaughterhouse

The results show that the sequential combination of photocatalysis and adsorption has been particularly effective. Comparing the removal of antibiotics by sequential TiO_2/UV–vis and PAC treatments with the removal achieved applying simultaneous TiO_2/PAC/UV treatment in a previous study (Moles et al., 2021), we find that the sequential treatment requires more time to achieve similar antibiotic removal. However, the real-world applicability of simultaneous TiO_2/PAC/UV–vis treatment faces some significant challenges, such as the formation of a complex of PAC and powdered TiO_2, leading to catalyst agglomeration (Moles et al., 2021).

Photocatalysis presents two primary mechanisms for organic compounds degradation: (i) direct photolysis under solar radiation, extensively detailed in the literature (Cabrera-Reina et al., 2019) and (ii) photocatalytic degradation, a process initiated by various intermediate reactive chemical species formed from TiO_2 in aqueous suspensions under UV–vis light. The intricate mechanism of photocatalytic degradation of organic pollutants in aqueous TiO_2 suspensions has been widely explored in the scientific literature (Schneider et al., 2014; Hoffmann et al., 1995). Photocatalysis has a high capability for degrading antibiotics (Sundar and Kanmani, 2020). Nevertheless, during antibiotic degradation, intermediary compounds, such as AMX degradation products, are inevitably formed (Homem and Santos, 2011b). Here is where adsorption plays a crucial role, removing residual compounds from the photocatalytic process. Hence, the combination of photocatalysis and adsorption brings together the best of both processes: the capacity to degrade complex organic pollutants with photocatalysis and residual by-products removal from wastewater by PAC adsorption (Moles

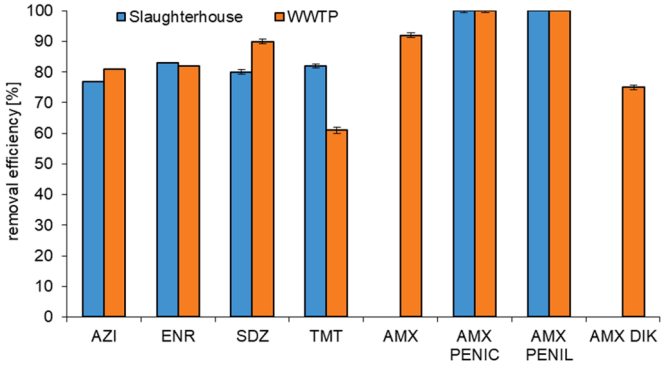

Fig. 2. Antibiotic removal in the rabbit slaughterhouse and WWTP effluents after the sequential treatment TiO_2/UV–vis and PAC adsorption.

et al., 2020b; Nidheesh et al., 2021). This sequential treatment approach significantly minimizes the ecological risks (Nieto-Juárez et al., 2021), since some antibiotic degradation products are hazardous for the environment (Szymańska et al., 2019; López-Serna et al., 2013; Goessens et al., 2020).

Taking into account the energy consumption, as well as the different chemicals involved, the operating cost of the water treatment plant is estimated to be 1.15 €/m^3 of treated water. Some authors have calculated a cost of 0.95 €/m^3, 0.75 €/m^3, 0.80 €/m^3 for other tertiary treatments such as photo-fenton, ozonation and membrane bioreactor (MBR), respectively (Andronic et al., 2016; Shaalan et al., 2015; Raquel Iglesias Esteban, La reutilización de efluentes depurados en españa: retrospectiva, desarrollo del marco normativo, estudio de las tecnologías de regeneración frente a los biorreactores de membrana y sus costes en función del uso, 2016). It should be noted that these costs are calculated at lab-scale, while the cost calculated in this research (1.15 €/m^3) is conducted at pilot-scale.

Finally, the Ti concentration has been evaluated in the treated effluent to determine the TiO_2 discharged into the environment after the sequential treatment (see experimental Section 2.2). The results showed that the Ti concentration in the treated rabbit slaughterhouse effluent was 12 ± 1 mg/L. Since the initial TiO_2 concentration in the catalytic treatment is 1 g/L, less than a 1.3% wt. of the initial TiO_2 is emitted in the treated effluent. In the case of WWTP effluents, the result showed a concentration ca. three times higher, 39 ± 3 mg/L, but this is still negligible in terms of the catalyst loss (3.5% wt.). This result confirms that the mechanical coagulation-flocculation-decantation method efficiently recovers the catalyst.

3.2. Reuse experiments

3.2.1. TiO_2 reusability

The findings presented in Fig. 3 illustrate a noticeable decrease in catalyst efficiency after several operational cycles, averaging around 30% after 7 cycles. The extent of this decline varied substantially across the studied antibiotics, ranging from a 20% drop for SDZ to a more significant 50% decrease for TMT. A marked drop in process efficacy from the third operational cycle was evident for TMT and ENR, an average of 20% for these antibiotics. In contrast, for SDZ and AZI, the elimination percentages remained relatively stable during the first three operational cycles, which could be attributed to the higher degradation kinetics of these substances, as the literature suggests (Moles et al., 2020b). However, prior investigations conducted by the authors at lab scale have focused on the reusability of TiO_2 for organic pollutant removal, such as caffeine and coliform bacteria disinfection, demonstrating minimal activity loss in TiO_2 after multiple operational cycles (Moles et al., 2020a; dong Xue et al., 2008). This behaviour underlines the importance of scaling up TiO_2 photocatalytic processes, as well as determining methods for catalyst regeneration (Moles et al., 2021), taking into account that these results indicate that TiO_2 requires periodic replacement or regeneration.

The performance drop could be attributable to multiple factors, including potential catalyst loss in the treated effluent. To ascertain the primary cause for the TiO_2/UV–vis process performance drop, a characterization of Ti in the treated effluent of each cycle was conducted. The titanium quantification results are illustrated in Fig. 4. They reveal that the titanium concentration in the treated effluent diminishes after each cycle, pointing to a favourable separation of Ti from the treated effluent, with increased catalyst usage.

The size characterization of Ti forms in the effluents performed by AF4-DLS-ICP-MS (Fig. 5) showed that the particles eluted at 6-min containing Ti (ICP-MS signal) have a hydrodynamic diameter larger than 5 μm, according to the DLS signal (green dots). Given that the initially added FN2 product contains titanium dioxide particles measuring between 150 and 300 nm, the presence of these larger particles suggests that the titanium dioxide particles are either agglomerating in the treated effluent or forming aggregates with some other sample component. This should be considered together with the fact that smaller particle aggregation occurs during the catalyst separation (see Section 2.4), thus justifying the larger-than-expected sizes. Therefore, the photocatalytic performance decrease could be explained by this agglomeration that occurs during the catalyst separation (see Section 2.4). Taking these facts into account, agglomeration could be favoured due to the presence of total suspended solid in the WWTP.

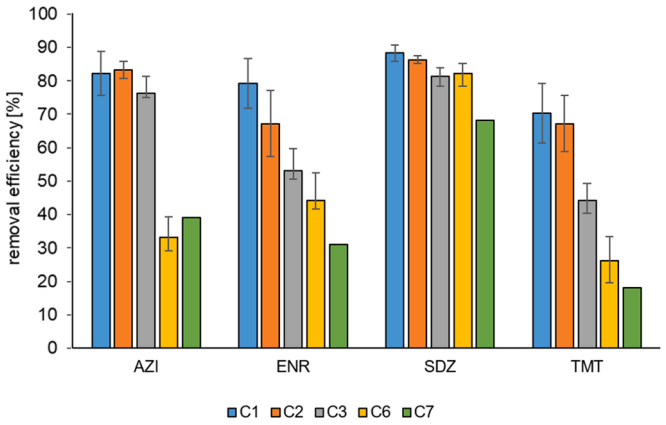

Fig. 3. Antibiotic removal applying TiO_2/UV–vis photocatalysis to antibiotic-fortified WWTP effluent during 7 cycles.

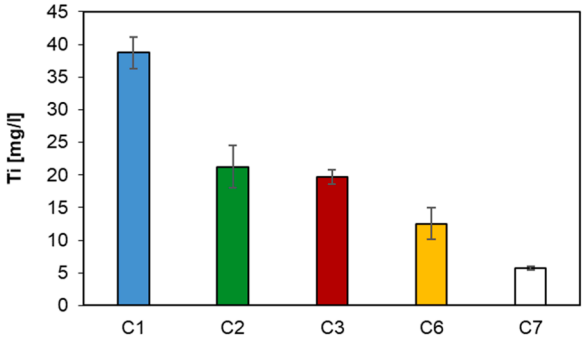

Fig. 4. Ti concentration (mg/L) after TiO_2/UV–vis photocatalysis.

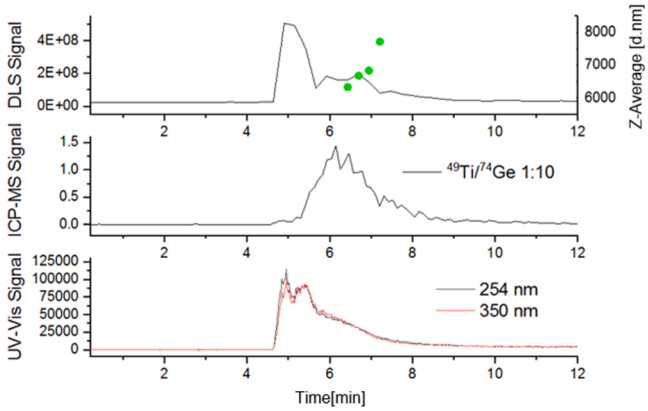

Fig. 5. Fractograms of cycle 7 (centrifuged at 3 μm) recorded by different detectors: DLS (size information), ICP-MS (composition) and UV-Vis. The green dots correspond to the hydrodynamic diameter determined by AF4-DLS.

3.2.2. PAC reusability

Fig. 6 shows that the adsorption efficiency of antibiotics in PAC remains almost constant after several operational cycles. The results indicate a negligible decrease in the PAC adsorption performance for SDZ, ENR, and TMT across the seven operational cycles. Regarding degradation by-products of AMX, we observe that AMX_PENIC acid registered a removal percentage of 40%. In contrast, AMX_DIK demonstrated superior adsorption in PAC, approximately 80% under the examined operational conditions. According to the results, the adsorption performance is similar to that obtained in ultrapure water in previous research (Berges et al., 2021; Choi et al., 2008; Liu et al., 2017). The degradation by-products are capable of establishing a larger number of electrostatic interactions, due to the presence of aromatic rings in their structure and their lower molecular weight, and consequently showing greater affinity for the adsorbent, as suggested by other authors (Gu et al., 2019; El Mouchtari et al., 2020). In this way, the negative effect of the presence of organic matter on the performance of the process is counteracted due to its lower affinity for the adsorbent.

The limitations inherent in pilot-scale studies introduce additional complexity. Consequently, the observed variability in the results (e.g. AZI and SDZ) should be associated to the fact that this study was conducted at a pilot scale in a 100 L adsorption tank. As a result, the mixing process executed via mechanical stirring, as described in Section 2.2, could present room for improvement. A more uniform and efficient mixing process might contribute to reducing variability, enhancing the overall performance, and therefore should be the focus of future optimization efforts.

4. Practical applications and future research prospects

This study not only advances our understanding of antibiotic decontamination in real wastewater but also holds significant implications for practical applications and future research. The outcomes of this research offer direct applications in wastewater treatment, particularly in the context of antibiotic removal at their emission sources, such as slaughterhouses. The successful implementation of TiO_2 photocatalysis and powdered activated carbon (PAC) adsorption in a pilot scale plant underscores their potential for real-scale plants.

The findings of this study can guide the development of efficient and environmentally friendly methods for managing antibiotic-contaminated wastewaters, safeguarding both aquatic ecosystems and public health. The knowledge gained from exploring different classes of antibiotics and various removal techniques is remarkable for designing targeted strategies for specific antibiotic. This

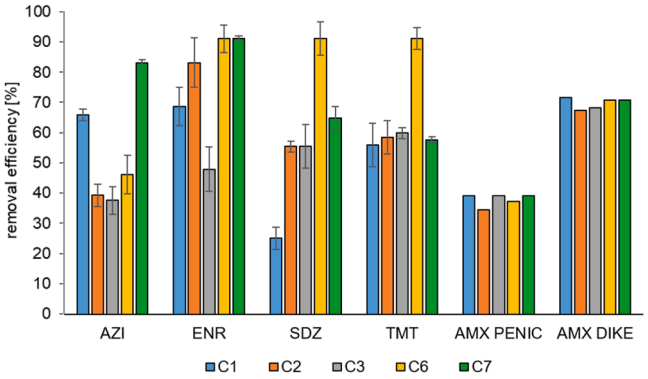

Fig. 6. Antibiotic removal applying PAC adsorption from fortified WWTP effluent during 7 cycles.

research paves the way for the optimization and scale-up of decontamination methods, thereby contributing to the ongoing global efforts to combat antibiotic resistance and mitigate environmental pollution.

However, future research prospects emerge after this work. Further investigations could delve into the long-term performance operation of the TiO_2 photocatalysis and PAC adsorption combination in diverse wastewater matrices, such as natural waters or hospital effluents. Additionally, understanding the fate of degradation products and assessing their potential ecological impact constitutes an interesting and unexplored investigation field. By addressing these aspects, future research can contribute to study sustainable solutions for antibiotic pollution.

5. Conclusions

Our study presents an evidence for the efficient removal of antibiotics and degradation products from real wastewater through a sequential photocatalytic and adsorption treatment at pilot-scale. This efficacy is demonstrated for the first time with slaughterhouse effluent, suggesting that employing pilot-scale facilities directly at emission sources could be a viable strategy for avoiding antibiotics in the water cycle. The achieved removal rates surpass those of conventional wastewater treatment processes and isolated photocatalysis or adsorption treatments, emphasizing the potential of this sequential approach. This synergistic combination combines the strengths of both processes, effectively degrading complex organic pollutants through photocatalysis and removal of the generated by-products via adsorption. Despite these promising results, challenges in scaling up, particularly the decline in photocatalytic treatment efficiency over cycles, need further investigation for the successful transition of these pilot-scale processes to full-scale applications.

CRediT authorship contribution statement

Eduardo Bolea: Writing – review & editing, Supervision, Software, Methodology, Data curation. **Jairo Gómez:** Validation, Supervision, Methodology, Funding acquisition. **Joanna Szpunar:** Methodology, Formal analysis, Data curation, Conceptualization. **Samuel Moles:** Writing – review & editing, Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **María P. Ormad:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition. **Rosa Mosteo:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Investigation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.eti.2024.103586.

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