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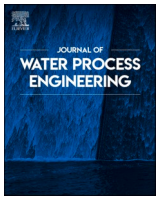

Photocatalytic metallic nanomaterials immobilised onto porous structures: Future perspectives for at-source pharmaceutical removal from hospital wastewater and potential benefits over existing technologies

Manuel-Thomas Valdivia [a,b,*], Mark A. Taggart [b], Sabolc Pap [b], Alistair Kean [a], Sharon Pfleger [c], Ian L. Megson [a]

[a] Division of Biomedical Sciences, Institute of Health Research and Innovation, University of the Highlands and Islands, Old Perth Road, Inverness IV2 3JH, United Kingdom
[b] Environmental Research Institute, University of the Highlands and Islands, Castle Street, Thurso KW14 7JD, United Kingdom
[c] NHS Highland, Public Health Dept, Larch House, Stoneyfield Business Park, Inverness IV2 7PA, United Kingdom

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ABSTRACT

Active pharmaceutical ingredients (APIs) are continuously released via hospital effluents and have been shown to be toxic to aquatic organisms, even at very low concentrations. Future risks to human health might also emerge due to accumulation of these compounds in food chains, through contamination of water supplies and propagation of antimicrobial resistance (AMR). The ongoing global rise in drug prescribing rates is increasing API concentrations in aquatic environments. Current wastewater treatment plants (WWTPs) are ineffective at removing many of these compounds. Pilot-scale advanced oxidation processes (AOPs) at WWTPs, such as UV-irradiation or ozone, are not considered sustainable at the industrial scale, due to their high operating cost and the potential for formation of toxic by-products. By contrast, photocatalytic AOPs only require light-induced activation of a reusable photocatalyst to eliminate the most persistent APIs. Despite their sustainable characteristics, photocatalytic AOPs have rarely been assessed for suitability in flow environments, such as hospital wastewater. This review highlights the advantages of photocatalytic AOP based wastewater treatment compared to existing AOPs. It also explores the immobilisation of effective photocatalytic metallic nanomaterials onto carbon-based porous support structures as a future-proof treatment concept for the elimination of APIs from hospital wastewater.

1. Introduction

Organic micropollutants of anthropogenic origin, such as pesticides and pharmaceuticals, have been detected in surface water (rivers, lakes), groundwater and drinking water worldwide [1–3]. APIs have attracted attention as priority substances of emerging concern, given their potential to cause detrimental toxic effects on biota, even at trace (μg L^{-1}) or ultra-trace (ng L^{-1}) concentrations in the aquatic environment [4–6]. Over the last 40 years, drug residues and their metabolites in wastewater effluents have been shown to cause acute and chronic adverse effects in aquatic organisms, such as behavioural changes in fish (exposed to antidepressants) or feminisation of species (exposed to the synthetic birth control hormone ethinylestradiol (EE2)) [6–8]. In addition, antibiotics in wastewater are contributing to the ongoing and dramatic spread of antimicrobial resistance (AMR) in microbial populations [9–12]. The harmful effects of APIs in the aquatic environment raise concerns regarding human health given their presence in receiving water and their inadequate removal by conventional wastewater treatment [6]. In turn, this may result in low-level API occurrence in water supplies and/or potential accumulation in food chains [13]. Although the ecotoxicity of some APIs has been investigated in detail, most of the ~4000 APIs licenced for disease treatment worldwide are still poorly classified in terms of their ecotoxicity, or not monitored by national water quality regulatory bodies [14–17].

* Corresponding author at: Division of Biomedical Sciences, Institute of Health Research and Innovation, University of the Highlands and Islands, Old Perth Road, Inverness IV2 3JH, United Kingdom.
E-mail addresses: manuelthomas.valdivia@uhi.ac.uk (M.-T. Valdivia), mark.taggart@uhi.ac.uk (M.A. Taggart), szabolcs.pap@uhi.ac.uk (S. Pap), alistair.kean@uhi.ac.uk (A. Kean), sharon.pfleger@nhs.scot (S. Pfleger), ian.megson@uhi.ac.uk (I.L. Megson).

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Wastewater originating specifically from hospitals contains a wide variety of APIs and metabolites, associated with patient urine and faeces [18,19] (Table 1 [3,20–25]). Hospitals have been identified as key point-sources for environmental API pollution due to their substantial water consumption (200–1200 L/bed/day), continuous API release in hospital effluent and subsequent pollution of receiving waters [6,7]. These hospital-derived API mixtures, with potentially enhanced ecotoxicity due to synergistic toxicity, are commonly mixed with and diluted by domestic and industrial wastewater in communal sewers prior to wastewater treatment [6,26,27]. Most industrialised countries still use conventional activated sludge (CAS) systems to treat their wastewater from hospitals, households and industry. However, CAS systems were never designed to remove the multitude of often persistent APIs now discharged into WWTPs. They are primarily designed to remove readily degradable organic matter from wastewater, to meet quality standards for surface water discharge (i.e., set by the EU Water Framework Directive), and to prevent the spread of infectious microorganisms [17,21,28].

The combined environmental impact of hospital-derived APIs, the global rise in drug prescribing rates, the increasing threat posed by AMR, and the continuous release of toxic (chlorination) by-products from conventional wastewater treatment signals that global action is urgently needed to develop novel and more sustainable wastewater treatment solutions [6,11,29,30]. This review explores the use of light-driven (photocatalytic) API removal via advanced oxidation processes (AOPs) and its potential within flow environments, such as hospital wastewater. Existing biological, physico-chemical and pilot-scale AOPs for wastewater treatment are discussed and compared to novel photocatalytic approaches, to evaluate API elimination efficiency from hospital wastewater and to provide an outlook on sustainability and affordability.

This review is the first to provide a comprehensive perspective on both conventional and novel photocatalytic nanomaterials and their immobilisation within a diverse range of organic support structures. There is a particular focus on novel graphene-based carbon nanostructures that offer unique characteristics in this regard [31]. Research considering flow-through concepts for continuous photocatalytic wastewater treatment is still scarce in existing literature. Evaluating these novel approaches is essential for future research aimed at developing large-scale photocatalytic solutions to enable at-source elimination of APIs from hospital effluents.

2. Biological wastewater treatment

CAS systems are the most common biological treatment techniques used in communal WWTPs worldwide. Large-scale CAS systems, utilising aerated sludge basins to oxidise and eliminate dissolved organic carbon (DOC) using suspended aerobic and anaerobic microbes, widely produce water quality that meets national discharge quality standards. However, quality standards are becoming stricter and starting to consider a wider range of potentially harmful compounds. CAS systems in isolation have limited elimination efficiency for many APIs, especially those that are recalcitrant to oxidative biodegradation, such as diclofenac or carbamazepine [32]. Subsequent tertiary chemical oxidation processes, such as hydrogen peroxide enhanced UV-irradiation or ozonation, are able to oxidise and eliminate APIs via reactive oxygen species (ROS), such as hydroxyl radicals, but these processes are costly, consume high amounts of energy and can produce toxic oxidation by-products [33].

Promising alternatives to CAS treatment include membrane biological reactors (MBRs), which have been piloted (as a potential replacement for CAS) in several countries [34]. MBRs have improved removal rates for DOC, nutrients and APIs with high biodegradability (e.g., paracetamol) due to extended sludge retention and microorganism residence times and generation of smaller sludge flocs, which may alter physical API removal through increased sorption onto sludge particles [35–37]. In addition, MBRs utilise ultra- or nano filtration membranes (pore size: 0.03–0.06 μm) following the activated sludge process, to retain micropollutants [38]. MBRs have been found to provide higher removal rates for antibiotics (compared to CAS) and membrane filters can effectively retain antibiotic resistant bacteria, preventing their dissemination into the environment. In turn, this diminishes the potential for horizontal transfer of antibiotic resistant genes across diverse microbial populations [38,39]. However, decentralised MBR treatment of hospital wastewater specifically - with extended microorganism retention times - may act to promote resistant gene evolution due to the more concentrated loads of antibiotics in hospital wastewater [29]. Enhanced removal rates for APIs using MBR treatment have been shown for a diverse range of drug compounds, particularly for those that are highly biodegradable. Nevertheless, many APIs are still detectable in MBR permeates after membrane filtration [6,33,40]. MBR treatment features notable improvements over CAS, including a reduction in the need to use disinfecting chemicals due to the physical removal of pathogens, substantial removal of multiple APIs, and the production of a clear effluent, which does not require additional clarification (such as sludge-liquid separation) [34]. However, the cost of MBR set-up/operation is much higher than CAS due to additional sludge pumping needs, membrane air scouring and the requirement to regularly replace clogged membranes [34,38,41]. Also, some persistent APIs remain recalcitrant to biodegradation using MBR, and are thus poorly removed [6].

Table 1
Characteristics of various common APIs detected in hospital effluents.

Drug class	Compound	HWW[a] concentration (ng L^{-1})	HQ[b]	PNEC[c] (ng L^{-1})	K_a	logK_{ow}
Estrogen	17β- estradiol	<3–230	28,750	0.008	10.46	4.01
Estrogen	17α-ethynyl- estradiol	<0.3–432	10,800	0.04	10.2	3.62
Antibiotic	Trimethoprim	<2–14,993	2586	5.8	7.12	0.91
Antibiotic	Amoxicillin	<32–900	1154	0.78	3.23	0.87
Antibiotic	Clarithromycin	20–62,241	350	40	8.99	3.16
Antibiotic	Ciprofloxacin	<3–76,167	310	500	6.09	0.28
Cytostatic	Tamoxifen	0.2–170	447	0.38	8.76	6.30
Cytostatic	Methotrexate	<2–4689	16	45,000	4.7	−1.85
Anaesthetic	Propofol	1100–10,100	240	42	11.1	3.79
β-blocker	Propranolol	<0.5–41,000	130	50	9.67	0.25
Statin	Simvastatin	2–190	10	0.2	14.9	4.68
Statin	Atorvastatin	3–316	2	190	4.46	6.36
Antiepileptic	Carbamazepine	<16.7–6080	3	2000	13.9	2.45

[a] HWW: Hospital wastewater.
[b] HQ: Hazard quotient.
[c] PNEC: Predicted no-effect concentration.

3. Tertiary wastewater treatment

Multiple studies have investigated the application of MBRs in combination with a diverse range of tertiary physico-chemical treatment approaches designed to improve the elimination of API concentrations from hospital wastewater [40,42,43]. Amongst these studies, several hospitals have been equipped with on-site wastewater treatment (mostly MBRs in combination with subsequent physico-chemical techniques), with the aim of targeting persistent APIs recalcitrant to conventional secondary treatment. Such pilots have successfully demonstrated that a combination of treatment approaches enhances the elimination of a diverse range of APIs when compared to a single solution approach [44]. However, each tertiary treatment process holds considerable disadvantages, particularly with respect to enhanced operating costs, and sustainability limitations due to regular requirements to replace or regenerate system components, such as activated carbon. Overall, a combination of MBR as a secondary treatment technique, followed by advanced oxidation (such as H_2O_2-enhanced UV-irradiation or H_2O_2-enhanced ozonation), and subsequent filtration by powdered activated carbon were identified as the most effective solutions for sustainable elimination of APIs from hospital wastewater [33,45,46].

Advanced oxidation processes have emerged as promising wastewater treatment techniques for degrading organic pollutants (such as APIs) via ROS synthesis. Hydroxyl radicals ($^{\bullet}OH$) are the most reactive oxidisers amongst radical species with a redox potential between 1.95 eV (pH 14) – 2.8 eV (pH 0) and a reaction rate constant between 10^8 and 10^{10} M^{-1} s^{-1} [47]. $^{\bullet}OH$ can rapidly and non-selectively inactivate harmful APIs by reacting with the aromatic ring structures of the drug molecule [48]. However, due to the extremely short half-life of $^{\bullet}OH$, most AOPs only work sustainably with continuous supplementation with oxidising agents such as H_2O_2 or O_3. Alternatively, irradiation with light in combination with a reusable conductive nanomaterial can generate ROS (such as in heterogenous photocatalysis) [47].

H_2O_2 -enhanced UV-irradiation is the most popular AOP in large-scale tertiary wastewater treatment, due to its advantages over stand-alone UV-light induced photolysis to enhance elimination of organic material. This is achieved through light-induced formation of $^{\bullet}OH$ from H_2O_2, which non-selectively oxidises organic compounds, such as APIs [44,49,50]. A pilot-study within the EU 'Pharmaceutical Input and Elimination from Local Sources' (PILLS) project, revealed that H_2O_2 treatment, in combination with UV-light exposure of MBR pre-treated wastewater, substantially increased API elimination rates. However, high electrical energy costs and H_2O_2 dosage requirements were incurred. The study further showed that under pure UV-irradiation without H_2O_2, ~86 % of investigated pharmaceuticals, including persistent compounds like diclofenac and carbamazepine, could be eliminated by photolysis. Again, the energy requirements for this process were substantial (10 kWh m^{-3}). Under H_2O_2 treatment, ~94 % of the most non-persistent compounds could be oxidised, requiring only half as much energy. Successful elimination of persistent compounds (i.e., 67 % removal of carbamazepine vs only 10 % removal after MBR treatment), could be achieved under moderate UV-light exposure (2 kWh m^{-3}), but required more UV-light exposure time and higher H_2O_2 consumption.

Overall, H_2O_2 enhanced UV-light applications inevitably require considerable amounts of electrical energy [49]. Also, key wastewater matrix characteristics (e.g., turbidity/suspended solids), may negatively influence light penetration and impact photolytic API degradation. In addition, alkaline wastewater may contain bicarbonate ions which can scavenge $^{\bullet}OH$ and further impact overall API oxidation efficiency [51,52].

H_2O_2 enhanced ozonation is a highly effective technique to eliminate a diverse range of organic compounds. Ozone generates $^{\bullet}OH$ during its decay, and in the presence of H_2O_2, the decomposition of ozone is catalysed, accelerating the generation of $^{\bullet}OH$. Consequently, H_2O_2-enhanced ozonation oxidises most organic micropollutants, even recalcitrant APIs, efficiently. Another effective but extremely energy-demanding process, is the combination of UV-irradiation and aqueous ozone (known as photoinduced ozonation), which generates H_2O_2, initiating ozone decay and the production of $^{\bullet}OH$ [51]. At a hospital wastewater pilot-scale treatment plant in Switzerland where MBR was used for secondary treatment, several post-treatment technologies were tested, with ozonation successfully delivering removal rates of >97 % for all tested APIs, including carbamazepine, diclofenac, ciprofloxacin, clarithromycin, sulfamethoxazole and ranitidine. Overall, API removal efficiency was ~90 % using ozonation, 86 % using powdered activated carbon, while UV-irradiation only eliminated 33 % of APIs in this setting [50].

Ozone is a potent oxidiser for a broad spectrum of APIs at very low aqueous concentrations. It generally requires lower energy consumption when compared to UV-irradiation, during continuous application. However, ozone production is also a very wasteful process, as most of the energy required is lost as unused heat: the production of 1 kg O_3 from O_2 requires 12 kWh of electrical energy [44]. Wastewater matrix effects, such as suspended solids, only have a limited impact on ozone-promoted API oxidation rates [53]. However, pH may significantly influence ozone decay and compound elimination [54]. This pilot study [55] showed that drastically decreased ozone decomposition rates were seen at lower pH: at pH 7.75, the time taken to fully decompose 10 mg L^{-1} of ozone was <1 min, while at pH 5, it was ~10 min. This suggests that ozonation in more acidic wastewater (below pH 7.75) may not eliminate all pollutants effectively.

The main drawback of ozone-dependent processes in wastewater treatment is high energy consumption (albeit lower than for UV-irradiation) and a dependence on specific water characteristics, such as pH. This parameter may vary significantly in wastewater and be affected by diurnal/seasonal differences in water consumption and effluent composition at hospitals. The removal of ozone to prevent atmospheric pollution also requires final effluent filtration with, for example, activated carbon. This adds additional costs to the treatment process. Ozonation will non-selectively oxidise organic matter and eliminate many toxic API molecules. However, little research has been undertaken to determine the toxicity of the resulting oxidised transformation products, and most are ostensibly unknown [56]. A multitude of toxic by-products can also be produced during ozone exposure, such as carcinogenic substances like bromates or *N*-nitrosodimethylamines (NDMAs) [50,57].

Fig. 1 summarises currently available conventional and advanced wastewater treatment techniques, states their suitability for the elimination of APIs and their potential to introduce toxic transformation by-products into the environment.

4. Photocatalytic wastewater treatment

Photocatalysis has recently emerged as a novel and sustainable alternative for future wastewater treatment. Photocatalysis involves light activation of a reusable, conductive (metallic) nanomaterial [58]. Compared to conventional AOPs, such as ozone or pure UV-light treatment, photocatalysis is thought to be free of toxic by-products. In addition, the use of sunlight as the UV source (solar disinfection; SODIS) has been found to be a viable, eco-friendly means of disinfecting drinking water. However, the present drawback of photocatalysis is the extensive treatment time needed to achieve acceptable target compound removal rates [59]. Therefore, both future photocatalytic materials and plant designs need to be optimised, in order to increase photocatalytic efficiencies [60]. Heterogenous photocatalytic treatment settings, which use high energy UV-light, combined with reusable metallic nanomaterials, have been shown to degrade even persistent APIs [61]. The use of co-catalysts such as noble metals or porous metal organic frameworks (MOFs) in combination with UV-light effective photocatalysts may substantially reduce treatment times. Furthermore, immobilisation of photocatalysts onto porous carbonaceous support

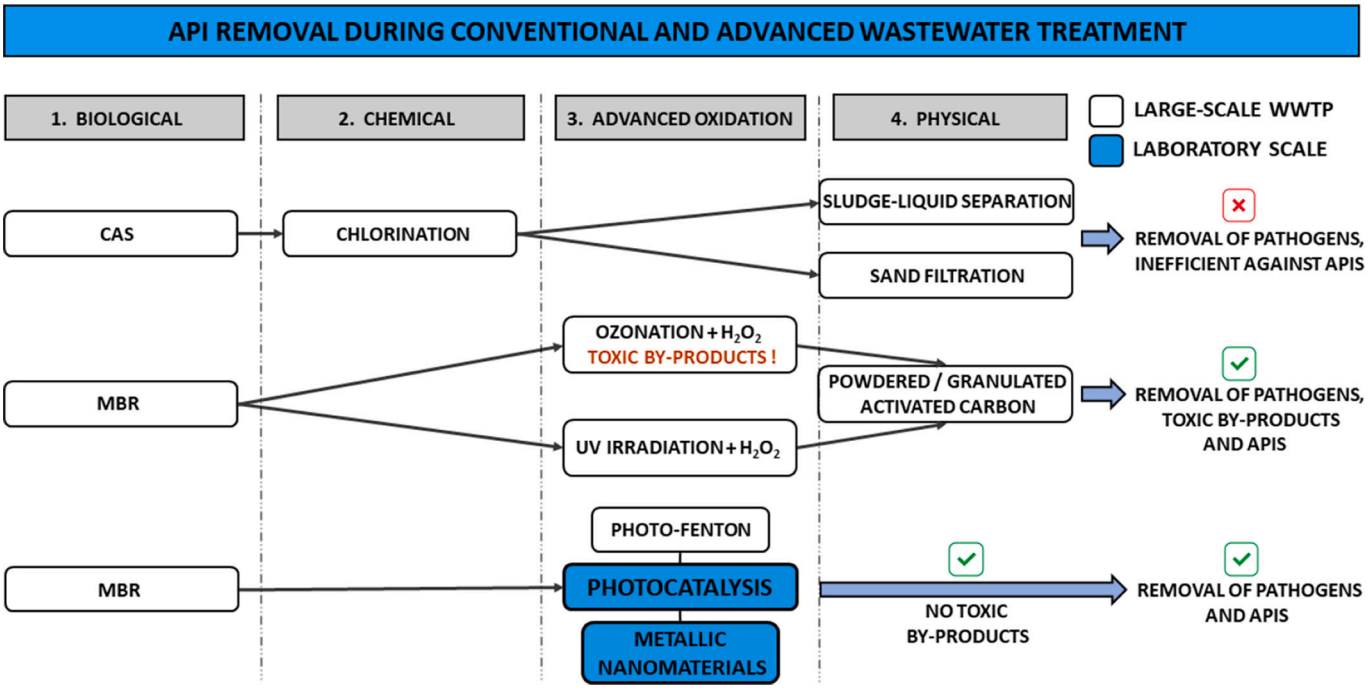

Fig. 1. Overview of conventional and advanced wastewater treatment techniques.

structures with superior mechanical stability could become a valuable approach in a flow-through treatment setting (i.e., for hospital wastewater).

4.1. Homogenous photocatalysis

Photo-Fenton is a light-driven water treatment process, which is effective at UV/Vis wavelengths up to 600 nm. Large-scale open systems - effectively sunlight based systems - can make use of ~28–35 % of total solar energy [62]. The photo-Fenton process is, however, dependent on supplementation with Fenton's reagent; a solution of H_2O_2 and ferrous iron (Fe^{2+}) salts (such as $FeSO_4$). The reaction of H_2O_2 and Fe^{2+} generates $^{\bullet}OH$ and ferric iron (Fe^{3+}) species. Conversely, aqueous Fe^{3+} can react photochemically to recycle Fe^{2+} under illumination. Overall, the photo-Fenton process generates ROS autocatalytically under UV/Vis irradiation and absorbs light over a relatively wide wavelength spectrum. It has significant potential for API removal, as the $^{\bullet}OH$ production rate is high until the H_2O_2 is fully depleted. Furthermore, limited toxic by-products are formed during photo-Fenton compared to other AOPs, ferric iron salts are environmentally benign if released in moderate amounts, and excess H_2O_2 is consumed during the Fenton reaction [51].

However, at large-scale, continuous supplementation with Fenton's reagent is expensive [38] and excess release of Fe^{3+} into the environment may be harmful [63]. Furthermore, an excess of H_2O_2 or Fe^{2+} can cause $^{\bullet}OH$ trapping. Therefore, optimal dosing of Fenton's reagent is essential to allow eco-friendly wastewater treatment that yields a high pollutant elimination rate. Other factors that limit full-scale application include the need for frequent pH adjustment. Photo-Fenton chemistry is most efficient under acidic conditions (pH <3), to prevent precipitation of stable ferric salts. In addition, since photocatalytic recycling of Fe^{2+} is slow, Fe^{3+} may form stable complexes with other organic compounds (such as carboxylic acids) which would block the photocatalytic cycle, i.e., the regeneration of ferrous iron [51].

4.2. Heterogenous photocatalysis

Novel AOPs for tertiary wastewater treatment, exclusively driven by light irradiation, show promise to disinfect wastewater and eliminate organic micropollutants, such as APIs, without adding harsh chemical oxidisers or producing toxic by-products. Such systems could be 'nature-based', and use renewable energy (e.g., sunlight) in a wastewater treatment setting [64,65]. Light-activated AOPs can generate $^{\bullet}OH$ under aqueous conditions in the presence of UV or visible light, oxygen and a reusable photocatalyst such as a metal oxide semiconductor (MOS). This process of light-activated $^{\bullet}OH$ production is known as heterogenous photocatalysis [66].

In solid materials, a specific band gap between the electronic valence and conduction bands of single atoms defines the material's capability to allow a flow of electrons from the valence to the conduction bands, ultimately specifying its conductivity. Under an external energy source (e.g., light irradiation), electrons of semiconductor materials, which have a relatively narrow band gap, can be excited from valence to conduction bands, leaving behind unfilled positively charged holes (h^+_{vb}) while filling conduction bands with an electronic negative charge (e^-_{cb}). MOS surfaces, often in the form of large-area nanomaterial coatings, immersed in an electrolyte (e.g., water), can generate charged holes (h^+_{vb}) and electrons (e^-_{cb}) at the electrolyte interface between the charged metallic surface and the aqueous phase. Both h^+_{vb} and e^-_{cb} can then promote redox reactions on the metallic surface under oxygenated aqueous conditions. These redox reactions ultimately generate mainly $^{\bullet}OH$ but also reaction intermediates such as superoxide ($^{\bullet}O_2^-$), hydrogen superoxide ($^{\bullet}HO_2$) and H_2O_2, all of which can oxidise and destroy pollutants such as APIs (which come into contact with the semiconductor surface) [51,60].

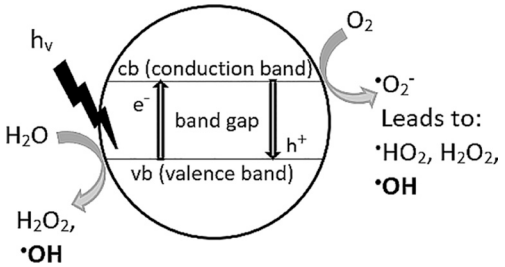

Fig. 2. The photocatalytic mechanism.

Fig. 2 describes the underlying redox reaction principle and photocatalytic mechanism on a semiconductor surface.

4.3. Redox reactions in photocatalytic water treatment

Hole and electron generating reaction on MOS surface

$$MOS + h_v(\text{energy of light} - \text{emitted photon}) \rightarrow MOS\ (h_{vb}^{+} + e_{cb}^{-})$$

ROS generating redox reactions

$$O_2 + e_{cb}^{-} \rightarrow {}^{\bullet}\mathbf{O_2}^{-} + H_2O \rightarrow {}^{\bullet}\mathbf{OH} + H^{+}$$

$$O_2 + H^{+} + e_{cb}^{-} \rightarrow {}^{\bullet}\mathbf{HO_2} + H^{+} + e_{cb}^{-} \rightarrow \mathbf{H_2O_2} + H^{+} + e_{cb}^{-} \rightarrow {}^{\bullet}\mathbf{OH} + H_2O$$

$$O_2 + 2H^{+} + 2e_{cb}^{-} \rightarrow \mathbf{H_2O_2} + H^{+} + e_{cb}^{-} \rightarrow {}^{\bullet}\mathbf{OH} + H_2O$$

$$H_2O + h_{vb}^{+} \rightarrow H^{+} + {}^{\bullet}\mathbf{OH}$$

$$2H_2O + 2h_{vb}^{+} \rightarrow \mathbf{H_2O_2} + 2H^{+} \rightarrow \mathbf{2}{}^{\bullet}\mathbf{OH} + 2H^{+}$$

Over the past two decades, a diverse range of MOS materials have been studied for potential application in photocatalytic water treatment, with much work devoted to enhancing their overall ˙OH yield and ultimately increasing organic contaminant elimination rates (including for APIs) [67]. However, upscaling photocatalytic approaches, using solar radiation (e.g., SODIS), remains challenging and has so far failed to efficiently eliminate organic pollutants. This has been demonstrated in multiple field studies using sunlight exposed batch containers, wherein the required incubation time to eliminate pathogen loads in 2 L PET water bottles is ~5 h with a photocatalyst vs ~6–48 h under bright sunlight [59,64,65].

5. New opportunities for novel photocatalytic materials

Most photocatalysts (such as TiO_2 or ZnO) absorb photons in the UV-A range ($\lambda = 315$–400 nm). However, UV light produces only 4–6 % of the whole solar spectrum, with UV-B and UV-C radiation ($\lambda \leq 315$ nm) largely absorbed by the stratosphere before reaching the earth's surface, whilst visible-light (≥ 400 nm) provides up to ~40 % of total solar radiation [64,65,67]. Consequently, many studies on photocatalysis focus on materials capable of absorbing light over a broad wavelength spectrum, particularly in the visible-light range, to increase solar-driven photocatalytic efficiency during water treatment [67–69].

However, TiO_2 and ZnO come with certain advantages when compared to other semiconductors. They are inexpensive and yield high photocatalytic efficiency under UV-light to generate ROS and destroy pollutants such as APIs. TiO_2 is also ostensibly largely non-toxic and is frequently applied in water treatment applications, due to its low-cost and its chemical, thermal and photolytic stability. However, unmodified TiO_2 and ZnO have relatively wide band gaps (3.21 eV and 3.37 eV), limiting their photocatalytic activity to the UV-A spectrum [70,71]. Photocatalysts with wider band gaps (≥ 3.1 eV), are unable to absorb light in the visible range. Hence, under solar radiation alone, many photocatalysts insufficiently excite electrons onto their conduction bands and most holes and electrons do not reach the electrolyte interface of the semiconductor surface to generate ROS. Consequently, excited electrons simply return to valence bands - a process defined as 'recombination' [60,72].

In recent years, substantial effort has been dedicated to investigating photocatalytic materials which exhibit narrower band gaps, such as alpha-phase bismuth oxide α-Bi_2O_3 (2.91 eV), bismuth vanadate $BiVO_4$ (2.40 eV) and graphitic carbon nitride g-C_3N_4 (2.70 eV), all of which allow rapid electron transfer to the MOS surface to facilitate ROS formation during visible-light exposure [67,73]. Furthermore, novel research is now focussing on 'surface-tuning' of photocatalytic materials. Noble metals, such as gold (Au), platinum (Pt) or silver (Ag), graphitic carbon structures, carbon metalloids (such as graphene) and various MOFs have all been successfully tested to extend the lifetime of photoexcited electrons and holes. Embedded into metal oxide nanostructures, these highly conductive elements lower the required band gap energy. Noble metals or carbonaceous dopants can further function as electron-traps and scavenge excited electrons from the conduction bands of the MOS surface, delaying recombination. Under visible light irradiation, these dopants can act as photosensitisers and release previously trapped electrons, which then migrate onto the conduction bands of the MOS, contributing to a controlled and constant charge separation of holes and electrons and improved photocatalytic performance [61,74–76]. Doping of MOS materials with metallic or carbon elements, allows light absorption of photocatalysts across a broad UV-VIS spectrum - ultimately altering ROS yields. This promising effect is yet to be fully tested using conventional wider band gap materials such as TiO_2 or ZnO.

Table 2 illustrates photocatalytic performances and material characteristics of various MOF containing nanocomposites.

Table 2
API removal efficiencies of photocatalyst containing MOFs.

Composite (g L^{-1})	Advantages	c_{API} (mg L^{-1})	API	Performance	Ref.
MIL-100 (Fe)/TiO2 (0.05)	High surface area, improved electron-hole separation and photocatalytic performance	100	TET	85.8 % in 1 h	[77]
MIL-125 (Ti)/In_2S_3 (0.3)	Highly porous mesoscale (2-50 nm) structure, excellent TET adsorption, superior visible light performance	46	TET	63.3 % in 1 h	[78]
NH_2-MOF (0.3) @Sm_2O_3-ZnO	Improved electron-hole mobility and electric permittivity of Sm_2O_3, enhanced O_2 evolution from water due to amine-functionalisation, superior reusability and visible light performance	300	AMX	100 % in 1.5 h	[79]
MIL-88A(Fe) (0.5) @$ZnIn_2S_4$	Wide light absorption range (200 -600 nm) of MIL-88A(Fe), excellent reusability, chemical stability and visible light performance	20	SMX	99.6 % in 1 h	[80]
CA@Ti-MIL-NH_2 (0.5)	Highly porous mesoscale cellulose acetate film with excellent applicability and reusability, improved light absorption due to amine functionalisation and performance in the visible light spectrum	30	ACE	96 % in 1 h	[81]

TET: tetracycline, AMX: amoxicillin, SMX: sulfamethoxazole, ACE: acetaminophen.

6. Immobilisation of photocatalysts

Photocatalyst leaching away from point of use may impact micropollutant degradation rates over time and/or introduce potentially toxic nanomaterials into the environment. Therefore, immobilisation of photocatalysts onto solid support materials, such as metals, plastics, edged glass surfaces, or embedding into porous carbon or membrane polymer structures, is preferable and may facilitate recovery and reuse

of photocatalytic materials. This is particularly desirable in flow-through applications, such as hospital wastewater treatment, where reusability of photocatalysts is considered essential for sustainable plant operation and leaching of nanomaterials into the environment is not desirable. The future effective elimination of APIs in immobilised photocatalytic systems will also largely depend on testing system parameters in a flow environment, to account for seasonal and diurnal changes in drug mixture concentrations released from hospitals, as well as wastewater temperature and pH, the dosage/coating density of the photocatalyst, the sorption equilibrium between the drug and the catalyst and the effect of contact time and its optimisation for prolonged photocatalytic reaction time between the photocatalyst and the drug compound [82,83].

Separation of photocatalysts from the liquid phase via affixation onto large-area surface supports, such as cartridge filters, is a relatively novel area of research and batch slurry reactors are still commonly preferred given their simple application. However, immobilised set-ups have been shown to enhance light delivery to the photocatalyst surface and are less impacted by inner filter effects, a common issue in slurry reactors caused by nanoscale catalyst suspensions inducing light scattering [60]. Edged glass beads are now a widely used support material in simple laboratory settings, particularly in SODIS applications, where low-temperature and cost-saving immobilisation, such as hydrothermal or sol-gel approaches, are favoured, and more complex electro- or vacuum deposition techniques are not feasible. However, in large-scale flow-through applications, free-floating support materials are simply impractical and may cause undesired hydrodynamic effects. Furthermore, in flow-through settings, such as hospital wastewater treatment, supports would be permanently exposed to fluid shearing stresses and common sol-gel dip-coating and subsequent low-temperature hydrothermal treatment at ~150–200 °C, may not sufficiently immobilise photocatalysts onto these solid supports.

A combination of drying and high-temperature calcination of photocatalyst films onto porous surfaces, has been shown to strongly incorporate photocatalytic nanomaterials onto surface structures. Calcination (above 400 °C) in a furnace enhances the mechanical and structural strength of photocatalytic films by sintering, densification and grain-growth. In an antipyrine degradation experiment, TiO_2 film synthesis from a precursor sol with subsequent calcination at 500 °C for 1 h in a furnace, produced crystalline TiO_2-anatase sites with superior photocatalytic characteristics [84]. In another study, consecutive multi-step heating (polycondensation) in a furnace produced a carbon-based support material (biochar) with excellent adsorption characteristics (e.g., porosity). Subsequent heating-steps in combination with g-C_3N_4 then synthesized a photocatalytic highly active nanocomposite [85].

Another effective approach for the deposition of photocatalytic nanomaterials on, for example, a membrane support, is vacuum deposition (i.e., physical vapour deposition (PVD) or chemical vapour deposition (CVD)). Vacuum deposition may become a preferable technique in future development of photocatalytic wastewater treatment designs, as this technique allows a controlled synthesis of metallic nanomaterial thin films with a defined homogenous thickness and even nanomaterial distribution over large surface areas [86–89]. PVD is already being deployed for mass production in areas such as electronics and the production of photovoltaics. Planar surfaces, 3-D objects and powders can all be coated.

7. Promising support materials for a flow-through water treatment approach

Carbonaceous materials (such as activated biochar, graphene, carbon nanotubes (CNTs), carbon quantum dots (CQDs)) feature unique surface characteristics which may be advantageous in a photocatalytic flow-through scenario. Due to their blackbody character, carbonaceous structures can absorb light across a broad UV-VIS spectrum [61]. Furthermore, they are mechanically sturdy, inert, temperature- and photo-stable. This makes them resistant to abrasion, chemical and photolytic degradation and facilitates high-temperature synthesis of photocatalyst thin films onto their surface. The large specific surface area and porosity of carbonaceous materials may also enhance long-

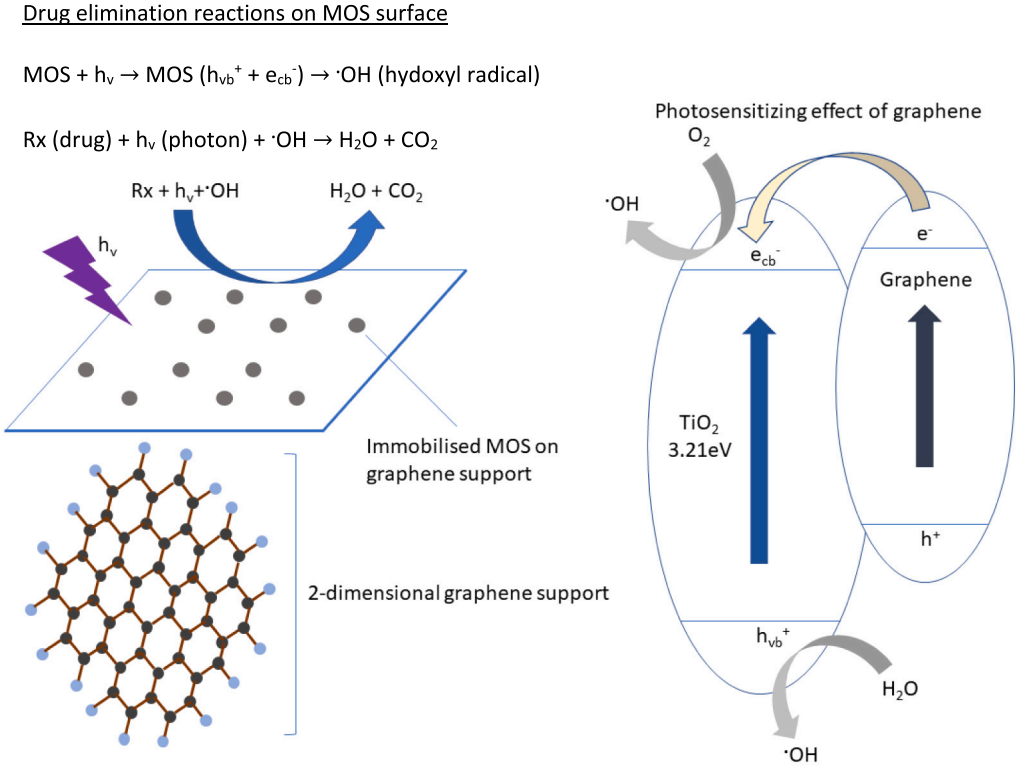

Fig. 3. Drug elimination mechanism of immobilised photocatalysts on graphene support.

Table 3
Photocatalytic API-removal efficiencies of various carbonaceous nanocomposites.

Composite (g L^{-1})	Advantages	c_{API} (mg L^{-1})	API/Matrix	Performance	Ref.
TiO_2/BC (1.25)	Low cost, reusability, excellent UV light performance, large surface area with oxygen containing functional groups	10	SMX in river water	91.27 % in 53 min	[95]
Zn-TiO_2/BC (1.25)	Low cost, reusability, excellent visible light performance, large surface area with oxygen containing functional groups	10	SMX in river water	81.21 % in 3 h	[96]
Ag/g-C_3N_4 (0.05)	Excellent visible light performance, improved efficiency via Surface Plasmon Resonance Effect of Ag-nano-particles	2.53	SMX in DI water	99.5 % in 1 h	[97]
ZnO/g-C_3N_4 (0.2)	Low cost, reusability, excellent UV and visible light performance superior electron-hole separation	20	TET in DI water	78.4 % in 50 min	[98]
		10	OTC in DI water	63.5 % in 50 min	
g-C_3N_4/TiO_2/ (1.0) Fe_3O_4@SiO_2	Improved catalyst recovery via magnetic Fe_3O_4@SiO_2, excellent UV and visible light performance due to g-C_3N_4/TiO_2 hetero-junction	2	IBU in DI water	97 % in 15 min	[99]
Graphene/TiO_2 (0.1) nanotubes, TiO_2 nanotubes	Low cost, excellent UV light performance, large surface area with oxygen containing functional groups, superior electron-hole separation	5	ACE in DI water	96 % in 3 h	[100]
		1	MTP in milli-Q	87.09 % in 2 h	[101]
		1	MTP in tap water	62.05 % in 2 h	

SMX: sulfamethoxazole, TET: tetracycline, OTC: oxytetracycline, IBU: ibuprofen, ACE: acetaminophen, MTP: metoprolol.

term adhesion of photocatalyst coatings and contribute to a sustainable application of these materials in a flow-through setting.

Many carbonaceous materials also contain a high number of active sites on their surface, comprising oxygen-containing functional groups (e.g., hydroxyl, carboxyl, and carbonyl groups). These surface groups interact strongly with water molecules and increase the hydrophilicity of carbonaceous structures. Combined with the porous characteristics of carbonaceous materials, hydrophilic surface groups enhance the superior water absorption capacities of these materials [90]. In a wastewater treatment setting for the removal of APIs, the high hydrophilicity of a porous support may increase the interaction between aqueous APIs and the photocatalyst surface, which is vital for the efficient removal of pollutants from the aqueous phase.

Graphitic carbon materials such as graphene have high electrical conductivity and electron-storage capacity, which allows them to scavenge electrons and regulate the separation of photoexcited holes and electrons (Fig. 3), preventing recombination and contributing to the excellent photocatalytic performance of metallic carbonaceous materials, e.g., carbon-metal oxide composites such as ZnO/g-C_3N_4, TiO_2/graphene or TiO_2/CNT [58,72,91]. One study on the photodegradation of organic compounds (4-chlorophenol and methyl orange) with a ZnO/g-C_3N_4 nanocomposite, demonstrated its excellent conductivity and improved electron-hole separation, compared to the metallic and carbonaceous precursor materials. Calcination for 1 h at 400 °C, formed a smooth interfacial layer between the two crystalline phases. This heterojunction interface synergistically linked the different band gap energies of both materials. The material combined the excellent UV-light performance of ZnO, with the capability of g-C_3N_4 to absorb photons in the visible-light spectrum, which enabled the superior photoactivity of the ZnO/g-C_3N_4 nanocomposite [92].

The use of biochar (BC) supported MOS materials may also be advantageous in future flow-through wastewater treatment scenarios, as they combine a highly functionalised carbonaceous surface with environmental sustainability. Biomass-derived photocatalytic supports are attractive for large-scale wastewater treatment due to their affordability and the circularity of the precursor materials, particularly when compared to surface enhancement with precious noble-metal dopants, as discussed previously. Multiple studies have shown that biochar produced from recycled waste (e.g., sawdust, coconut shell, potato stem and rice straw), which is then doped with metal oxide nanomaterials during biochar production (pyrolysis) provides superior API elimination vs non-functionalised biochar [93,94].

Table 3 highlights the photocatalytic performance and material characteristics of various carbon-based nanocomposites.

8. Conclusion and future perspectives

Heterogenous photocatalysis in an immobilised setting is an environmentally sustainable and effective approach for at-source treatment of pharmaceutical polluted hospital wastewater. Novel reactor designs, with immobilised photocatalysts, need to ensure strong adherence of the catalyst onto the solid support material to allow sustainable treatment performance. This is particularly true in a flow-through setting, where leaching of potentially harmful nanomaterials must be avoided at all costs. Incorporating affordable, non-toxic, reusable metallic nanomaterials into porous carbon-based support structures, with excellent light absorption and hydrophilic characteristics, alongside high physical, chemical and photolytic stability, could be a promising technique for future photocatalytic wastewater treatment. However, alongside ongoing efforts to improve photocatalytic efficiency of novel nanocomposites, treatment designs with excellent UV-A performance using conventional photocatalysts (such as ZnO or TiO_2) need to be optimised in order to become more economically viable. The energy efficiency of UV-driven approaches can also be improved by implementing low-energy LED light arrays, rather than using high energy xenon light bulbs. Energy saving plant designs with a reduced carbon footprint are ultimately essential to make future photocatalytic wastewater treatment more competitive vs established but energy demanding AOPs such as H_2O_2 enhanced UV-treatment or ozone applications. Furthermore, photocatalytic wastewater treatment shows potential as an environmentally friendly treatment alternative that does not release any toxic by-products compared to existing AOPs (e.g., ozone applications). Overall, immobilised photocatalysis has great potential to become an economical and reusable tertiary treatment technique for future application at large-scale to continuously eliminate various persistent and ecotoxic drugs from flow environments such as hospital wastewater without the risk of introducing additional pollutants, such as potentially toxic nanomaterials, into the environment.

CRediT authorship contribution statement

Manuel-Thomas Valdivia: Conceptualization, Visualization, Writing – original draft. **Mark A. Taggart:** Funding acquisition, Supervision, Writing – review & editing. **Sabolc Pap:** Funding acquisition, Supervision, Writing – review & editing. **Alistair Kean:** Funding acquisition, Supervision, Writing – review & editing. **Sharon Pfleger:**

Writing – review & editing. **Ian L. Megson:** Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

Prof. Alistair Kean has a direct interest in PolyCatUK Ltd., who have provided samples for the principal author's research. PolyCatUK has provided water filter prototypes free of charge for the research.

Data availability

No data was used for the research described in the article.

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References

[1] J.L. Wilkinson, A.B.A. Boxall, D.W. Kolpin, K.M.Y. Leung, R.W.S. Lai, D. Wong, R. Ntchantcho, J. Pizarro, J. Mart, S. Echeverr, J. Garric, A. Chaumot, P. Gibba, I. Kunchulia, S. Seidensticker, G. Lyberatos, J.M. Morales-salda, H. Kang, in: Pharmaceutical Pollution of the World's Rivers 119, 2022, pp. 1–10, https://doi.org/10.1073/pnas.2113947119/-/DCSupplemental.Published.

[2] Y. Luo, W. Guo, H.H. Ngo, L.D. Nghiem, F.I. Hai, J. Zhang, S. Liang, X.C. Wang, A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment, Sci. Total Environ. 473–474 (2014) 619–641, https://doi.org/10.1016/j.scitotenv.2013.12.065.

[3] T. aus der Beek, F.A. Weber, A. Bergmann, S. Hickmann, I. Ebert, A. Hein, A. Küster, Pharmaceuticals in the environment-global occurrences and perspectives, Environ. Toxicol. Chem. 35 (2016) 823–835, https://doi.org/10.1002/etc.3339.

[4] O.A.H. Jones, N. Voulvoulis, J.N. Lester, Human pharmaceuticals in the aquatic environment a review, Environ. Technol. 22 (2001) 1383–1394, https://doi.org/10.1080/09593330.2001.11090873.

[5] E. Carraro, S. Bonetta, C. Bertino, E. Lorenzi, S. Bonetta, G. Gilli, Hospital effluents management: chemical, physical, microbiological risks and legislation in different countries, J. Environ. Manag. 168 (2016) 185–199, https://doi.org/10.1016/j.jenvman.2015.11.021.

[6] P. Verlicchi, A. Galletti, M. Petrovic, D. BarcelÓ, Hospital effluents as a source of emerging pollutants: an overview of micropollutants and sustainable treatment options, J. Hydrol. 389 (2010) 416–428, https://doi.org/10.1016/j.jhydrol.2010.06.005.

[7] K. Kümmerer, Drugs in the environment: emission of drugs, diagnostic aids and disinfectants into wastewater by hospitals in relation to other sources - a review, Chemosphere 45 (2001) 957–969, https://doi.org/10.1016/S0045-6535(01)00144-8.

[8] K. Kümmerer, The presence of pharmaceuticals in the environment due to human use - present knowledge and future challenges, J. Environ. Manag. 90 (2009) 2354–2366, https://doi.org/10.1016/j.jenvman.2009.01.023.

[9] K. Kümmerer, Antibiotics in the aquatic environment - a review - part II, Chemosphere 75 (2009) 435–441, https://doi.org/10.1016/j.chemosphere.2008.12.006.

[10] E. Korzeniewska, A. Korzeniewska, M. Harnisz, Antibiotic resistant Escherichia coli in hospital and municipal sewage and their emission to the environment, Ecotoxicol. Environ. Saf. 91 (2013) 96–102, https://doi.org/10.1016/j.ecoenv.2013.01.014.

[11] J.O. Neill, Antimicrobial Resistance: Tackling a Crisis for the Health and Wealth of Nations The Review on Antimicrobial Resistance Chaired, 2014.

[12] L.T.Q. Lien, N.Q. Hoa, N.T.K. Chuc, N.T.M. Thoa, H.D. Phuc, V. Diwan, N.T. Dat, A.J. Tamhankar, C.S. Lundborg, Antibiotics in wastewater of a rural and an urban hospital before and after wastewater treatment, and the relationship with antibiotic use-a one year study from Vietnam, Int. J. Environ. Res. Public Health 13 (2016) 1–13, https://doi.org/10.3390/ijerph13060588.

[13] A.C. Johnson, M.D. Jürgens, R.J. Williams, K. Kümmerer, A. Kortenkamp, J. P. Sumpter, Do cytotoxic chemotherapy drugs discharged into rivers pose a risk to the environment and human health? An overview and UK case study, J. Hydrol. 348 (2008) 167–175, https://doi.org/10.1016/j.jhydrol.2007.09.054.

[14] E. Union, S. Approach, Update on Progress and Implementation European Union Strategic Approach to Pharmaceuticals in the Environment, (n.d.).

[15] N.J. Ayscough, J. Fawell, G. Franklin, W. Young, in: Review of Human Pharmaceuticals in the Environment. Environment Agency Technical Report, R&D Tech. Rep, 2000, pp. 1–105. https://www.gov.uk/government/publications/review-of-human-pharmaceuticals-in-the-environment.

[16] D.J. Caldwell, Sources of pharmaceutical residues in the environment and their control, issues environ, Sci. Technol. 2016-Janua (2016) 92–119, https://doi.org/10.1039/9781782622345-00092.

[17] European Commission, Decision (EU) 2020/1161, Off. J. Eur. Union L 257 (2020) 32–35. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2020.257.01.0032.01.ENG&toc=OJ:L:2020:257:TOC.

[18] J. Lienert, K. Güdel, B.I. Escher, Screening method for ecotoxicological hazard assessment of 42 pharmaceuticals considering human metabolism and excretory routes, Environ. Sci. Technol. 41 (2007) 4471–4478, https://doi.org/10.1021/es0627693.

[19] M. Al Aukidy, P. Verlicchi, N. Voulvoulis, A framework for the assessment of the environmental risk posed by pharmaceuticals originating from hospital effluents, Sci. Total Environ. 493 (2014) 54–64, https://doi.org/10.1016/j.scitotenv.2014.05.128.

[20] P. Verlicchi, M. Al Aukidy, A. Galletti, M. Petrovic, D. Barceló, Hospital effluent: investigation of the concentrations and distribution of pharmaceuticals and environmental risk assessment, Sci. Total Environ. 430 (2012) 109–118, https://doi.org/10.1016/j.scitotenv.2012.04.055.

[21] P. Verlicchi, M. Al Aukidy, E. Zambello, Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after a secondary treatment-a review, Sci. Total Environ. 429 (2012) 123–155, https://doi.org/10.1016/j.scitotenv.2012.04.028.

[22] F. Orias, Y. Perrodin, Characterisation of the ecotoxicity of hospital effluents: a review, Sci. Total Environ. 454–455 (2013) 250–276, https://doi.org/10.1016/j.scitotenv.2013.02.064.

[23] L.H.M.L.M. Santos, M. Gros, S. Rodriguez-Mozaz, C. Delerue-Matos, A. Pena, D. Barceló, M.C.B.S.M. Montenegro, Contribution of hospital effluents to the load of pharmaceuticals in urban wastewaters: identification of ecologically relevant pharmaceuticals, Sci. Total Environ. 461–462 (2013) 302–316, https://doi.org/10.1016/j.scitotenv.2013.04.077.

[24] O. Frédéric, P. Yves, Pharmaceuticals in hospital wastewater: their ecotoxicity and contribution to the environmental hazard of the effluent, Chemosphere 115 (2014) 31–39, https://doi.org/10.1016/j.chemosphere.2014.01.016.

[25] T.S. Oliveira, M. Al Aukidy, P. Verlicchi, Occurrence of common pollutants and pharmaceuticals in hospital effluents, in: Handb. Environ. Chem 60, 2018, pp. 17–32, https://doi.org/10.1007/698_2017_9.

[26] F. Pomati, C. Orlandi, M. Clerici, F. Luciani, E. Zuccato, in: Effects and Interactions in an Environmentally Relevant Mixture of Pharmaceuticals 102, 2008, pp. 129–137, https://doi.org/10.1093/toxsci/kfm291.

[27] T. Chonova, F. Keck, J. Labanowski, B. Montuelle, F. Rimet, A. Bouchez, Separate treatment of hospital and urban wastewaters: a real scale comparison of effluents and their effect on microbial communities, Sci. Total Environ. 542 (2016) 965–975, https://doi.org/10.1016/j.scitotenv.2015.10.161.

[28] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters, Water Res. 43 (2009) 363–380, https://doi.org/10.1016/j.watres.2008.10.047.

[29] C. Li, J. Lu, J. Liu, G. Zhang, Y. Tong, N. Ma, Exploring the correlations between antibiotics and antibiotic resistance genes in the wastewater treatment plants of hospitals in Xinjiang, China, Environ. Sci. Pollut. Res. 23 (2016) 15111–15121, https://doi.org/10.1007/s11356-016-6688-z.

[30] P.V.Mustafa Al Aukidy, Saeb Al Chalabi, in: Abstract, Hospital Wastewaters - Characteristics, Management, Treatment and Environmental Risks, Hosp. Wastewaters - Charact. Manag. Treat. Environ. Risks, 2018, pp. 171–188, https://doi.org/10.1007/698.

[31] I. Ali, A.A. Basheer, A. Kucherova, N. Memetov, T. Pasko, K. Ovchinnikov, V. Pershin, D. Kuznetsov, E. Galunin, V. Grachev, A. Tkachev, Advances in carbon nanomaterials as lubricants modifiers, J. Mol. Liq. 279 (2019) 251–266, https://doi.org/10.1016/j.molliq.2019.01.113.

[32] J. Radjenović, M. Petrović, D. Barceló, Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment, Water Res. 43 (2009) 831–841, https://doi.org/10.1016/j.watres.2008.11.043.

[33] S. Venditti, K. Klepiszewski, C. Köhler, Lessons learned from european experiences and presentation of case studies, in: Handb.Environ. Chem 60, 2018, pp. 153–169, https://doi.org/10.1007/698_2017_16.

[34] S. Rodriguez-mozaz, D. Lucas, Full-Scale Plants for Dedicated Treatment of Hospital Effluents, 2017, 10.1007/698.

[35] M. Clara, B. Strenn, O. Gans, E. Martinez, N. Kreuzinger, H. Kroiss, in: Removal of Selected Pharmaceuticals, Fragrances and Endocrine Disrupting Compounds in a Membrane Bioreactor and Conventional Wastewater Treatment Plants 39, 2005, pp. 4797–4807, https://doi.org/10.1016/j.watres.2005.09.015.

[36] S. Beier, C. Cramer, S. Ko, C. Mauer, L. Palmowski, H.F. Schro, in: Full Scale Membrane Bioreactor Treatment of Hospital Wastewater as Forerunner for Hotspot Wastewater Treatment Solutions in High Density Urban Areas, 2011, pp. 66–71, https://doi.org/10.2166/wst.2011.010.

[37] P. Verlicchi, M. Al Aukidy, E. Zambello, What have we learned from worldwide experiences on the management and treatment of hospital effluent? - an overview and a discussion on perspectives, Sci. Total Environ. 514 (2015) 467–491, https://doi.org/10.1016/j.scitotenv.2015.02.020.

[38] M. Badia-fabregat, I. Oller, S. Malato, in: Overview on Pilot-Scale Treatments and New and Innovative Technologies for Hospital Effluent, 2018, pp. 209–230, https://doi.org/10.1007/698.

[39] T. Stalder, M. Alrhmoun, J.N. Louvet, M. Casellas, C. Maftah, C. Carrion, M. N. Pons, O. Pahl, M.C. Ploy, C. Dagot, Dynamic assessment of the floc morphology, bacterial diversity, and integron content of an activated sludge

reactor processing hospital effluent, Environ. Sci. Technol. 47 (2013) 7909–7917, https://doi.org/10.1021/es4008646.
[40] L. Kovalova, H. Siegrist, H. Singer, A. Wittmer, C.S. McArdell, Hospital wastewater treatment by membrane bioreactor: performance and efficiency for organic micropollutant elimination, Environ. Sci. Technol. 46 (2012) 1536–1545, https://doi.org/10.1021/es203495d.
[41] C. Brepols, H. Schäfer, N. Engelhardt, Considerations on the design and financial feasibility of full-scale membrane bioreactors for municipal applications, Water Sci. Technol. 61 (2010) 2461–2468, https://doi.org/10.2166/wst.2010.179.
[42] S. Beier, C. Cramer, C. Mauer, S. Köster, H.F. Schröder, J. Pinnekamp, MBR technology: a promising approach for the (pre-)treatment of hospital wastewater, Water Sci. Technol. 65 (2012) 1648–1653, https://doi.org/10.2166/wst.2012.880.
[43] U. Nielsen, C. Hastrup, M.M. Klausen, B.M. Pedersen, G.H. Kristensen, J.L. C. Jansen, S.N. Bak, J. Tuerk, Removal of APIs and bacteria from hospital wastewater by MBR plus O3, O3 + H2O2, PAC or ClO2, Water Sci. Technol. 67 (2013) 854–862, https://doi.org/10.2166/wst.2012.645.
[44] X.T. Bui, T.P.T. Vo, H.H. Ngo, W.S. Guo, T.T. Nguyen, Multicriteria assessment of advanced treatment technologies for micropollutants removal at large-scale applications, Sci. Total Environ. 563–564 (2016) 1050–1067, https://doi.org/10.1016/j.scitotenv.2016.04.191.
[45] J. Reungoat, M. Macova, B.I. Escher, S. Carswell, J.F. Mueller, J. Keller, Removal of micropollutants and reduction of biological activity in a full scale reclamation plant using ozonation and activated carbon filtration, Water Res. 44 (2010) 625–637, https://doi.org/10.1016/j.watres.2009.09.048.
[46] K. Adamcza, S. Lyko, S. Nafo, H. Evenblij, A. Cornelissen, E. Igos, K. Klepiszewski, S. Venditti, L. Kovalova, C. McArdell, K. Helwig, O. Pahl, O. Barraud, M. Casellas, C. Dagot, C. Maftah, M.-C. Ploy, T. Stalder, Pharmaceutical residues in the aquatic system – a challenge for the future. Insights and activities of the of the European cooperation project PILLS. http://www.pills-project.eu/PILLS_summary_english.pdf, 2012.
[47] Y. Deng, R. Zhao, Advanced oxidation processes (AOPs) in wastewater treatment, Curr. Pollut. Rep. 1 (2015) 167–176, https://doi.org/10.1007/s40726-015-0015-z.
[48] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84, https://doi.org/10.1080/10643380500326564.
[49] C. Köhler, S. Venditti, E. Igos, K. Klepiszewski, E. Benetto, A. Cornelissen, Elimination of pharmaceutical residues in biologically pre-treated hospital wastewater using advanced UV irradiation technology: a comparative assessment, J. Hazard. Mater. 239–240 (2012) 70–77, https://doi.org/10.1016/j.jhazmat.2012.06.006.
[50] L. Kovalova, H. Siegrist, U. Von Gunten, J. Eugster, M. Hagenbuch, A. Wittmer, R. Moser, C.S. McArdell, Elimination of micropollutants during post-treatment of hospital wastewater with powdered activated carbon, ozone, and UV, Environ. Sci. Technol. 47 (2013) 7899–7908, https://doi.org/10.1021/es400708w.
[51] M.I. Litter, Introduction to photochemical advanced oxidation processes for water treatment, Environ. Photochem. Part II (2) (2005) 325–366, https://doi.org/10.1007/b138188.
[52] V.J. Pereira, H.S. Weinberg, K.G. Linden, P.C. Singer, UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm, Environ. Sci. Technol. 41 (2007) 1682–1688, https://doi.org/10.1021/es061491b.
[53] M.M. Huber, A. Go, A. Joss, N. Hermann, in: Oxidation of Pharmaceuticals During Ozonation of Municipal Wastewater Effluents: A Pilot Study 39, 2005, pp. 4290–4299.
[54] U.Von Gunten, Ozonation of drinking water: Part I. Oxidation kinetics and product formation, Water Res. 37 (2003) 1443–1467. http://www.sciencedirect.com/science/article/pii/S0043135402004578.
[55] K.M.S. Hansen, A. Spiliotopoulou, R.K. Chhetri, M. Escolà Casas, K. Bester, H. R. Andersen, Ozonation for source treatment of pharmaceuticals in hospital wastewater - ozone lifetime and required ozone dose, Chem. Eng. J. 290 (2016) 507–514, https://doi.org/10.1016/j.cej.2016.01.027.
[56] D. Stalter, A. Magdeburg, J. Oehlmann, Comparative toxicity assessment of ozone and activated carbon treated sewage effluents using an in vivo test battery, Water Res. 44 (2010) 2610–2620, https://doi.org/10.1016/j.watres.2010.01.023.
[57] J.B. Carbajo, A.L. Petre, R. Rosal, S. Herrera, P. Letón, E. García-Calvo, A. R. Fernández-Alba, J.A. Perdigón-Melón, Continuous ozonation treatment of ofloxacin: transformation products, water matrix effect and aquatic toxicity, J. Hazard. Mater. 292 (2015) 34–43, https://doi.org/10.1016/j.jhazmat.2015.02.075.
[58] M. Anjum, R. Miandad, M. Waqas, F. Gehany, M.A. Barakat, Remediation of wastewater using various nano-materials, Arab. J. Chem. 12 (2019) 4897–4919, https://doi.org/10.1016/j.arabjc.2016.10.004.
[59] B.E. Cowie, V. Porley, N. Robertson, Solar disinfection (SODIS) provides a much underexploited opportunity for researchers in photocatalytic water treatment (PWT), ACS Catal. 10 (2020) 11779–11782, https://doi.org/10.1021/acscatal.0c03325.
[60] G. Odling, N. Robertson, Bridging the gap between laboratory and application in photocatalytic water purification, Catal.Sci. Technol. 9 (2019) 533–545, https://doi.org/10.1039/c8cy02438c.
[61] A.S. Mestre, A.P. Carvalho, Photocatalytic Degradation of Pharmaceuticals, 2019.
[62] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, Catal. Today 147 (2009) 1–59, https://doi.org/10.1016/j.cattod.2009.06.018.
[63] P. Cadmus, S.F. Brinkman, M.K. May, Chronic toxicity of ferric iron for North American aquatic organisms: derivation of a chronic water quality criterion using single species and mesocosm data, Arch. Environ. Contam. Toxicol. 74 (2018) 605–615, https://doi.org/10.1007/s00244-018-0505-2.
[64] J.A. Byrne, P.A. Fernandez-Ibañez, P.S.M. Dunlop, D.M.A. Alrousan, J.W. J. Hamilton, Photocatalytic enhancement for solar disinfection of water: a review, Int. J. Photoenergy 2011 (2011), https://doi.org/10.1155/2011/798051.
[65] K.G. McGuigan, R.M. Conroy, H.J. Mosler, M. du Preez, E. Ubomba-Jaswa, P. Fernandez-Ibañez, Solar water disinfection (SODIS): a review from bench-top to roof-top, J. Hazard. Mater. 235–236 (2012) 29–46, https://doi.org/10.1016/j.jhazmat.2012.07.053.
[66] J.M. Herrmann, Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants, Catal. Today 53 (1999) 115–129, https://doi.org/10.1016/S0920-5861(99)00107-8.
[67] J. You, Y. Guo, R. Guo, X. Liu, A review of visible light-active photocatalysts for water disinfection: features and prospects, Chem. Eng. J. 373 (2019) 624–641, https://doi.org/10.1016/j.cej.2019.05.071.
[68] K. Mun, C. Wei, K. Sing, J. Ching, Recent developments of zinc oxide based photocatalyst in water treatment technology: a review, Water Res. 88 (2016) 428–448, https://doi.org/10.1016/j.watres.2015.09.045.
[69] T. Di, Q. Xu, W. Ho, H. Tang, Q. Xiang, J. Yu, in: Review on Metal Sulphide-based Z-scheme Photocatalysts, 2019, pp. 1394–1411, https://doi.org/10.1002/cctc.201802024.
[70] M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S. M. Dunlop, J.W.J. Hamilton, J.A. Byrne, K. O'Shea, M.H. Entezari, D. D. Dionysiou, A review on the visible light active titanium dioxide photocatalysts for environmental applications, Appl. Catal. B Environ. 125 (2012) 331–349, https://doi.org/10.1016/j.apcatb.2012.05.036.
[71] S. Teixeira, R. Gurke, H. Eckert, K. Kühn, J. Fauler, G. Cuniberti, Photocatalytic degradation of pharmaceuticals present in conventional treated wastewater by nanoparticle suspensions, J. Environ. Chem. Eng. 4 (2016) 287–292, https://doi.org/10.1016/j.jece.2015.10.045.
[72] W. Vallejo, A. Rueda, C. Díaz-Uribe, C. Grande, P. Quintana, Photocatalytic activity of graphene oxide-TiO 2 thin films sensitized by natural dyes extracted from Bactris guineensis, R. Soc. Open Sci. 6 (2019), https://doi.org/10.1098/rsos.181824.
[73] C.-H. Ho, C.-H. Chan, Y.-S. Huang, L.-C. Tien, L.-C. Chao, The study of optical band edge property of bismuth oxide nanowires α-Bi_2O_3, Opt. Express 21 (2013) 11965, https://doi.org/10.1364/oe.21.011965.
[74] K. Woan, G. Pyrgiotakis, W. Sigmund, Photocatalytic carbon-nanotube-Ti02 composites, Adv. Mater. 21 (2009) 2233–2239, https://doi.org/10.1002/adma.200802738.
[75] J. Prakash, S. Sun, H.C. Swart, R. Kumar, Noble metals-TiO 2 nanocomposites: from fundamental mechanisms to photocatalysis, surface enhanced Raman scattering and antibacterial applications, Appl. Mater. Today 11 (2018) 82–135, https://doi.org/10.1016/j.apmt.2018.02.002.
[76] Y. Pi, X. Li, Q. Xia, J. Wu, Y. Li, J. Xiao, Z. Li, Adsorptive and photocatalytic removal of persistent organic pollutants (POPs) in water by metal-organic frameworks (MOFs), Chem. Eng. J. 337 (2018) 351–371, https://doi.org/10.1016/j.cej.2017.12.092.
[77] X. He, H. Fang, D.J. Gosztola, Z. Jiang, P. Jena, W.N. Wang, Mechanistic insight into photocatalytic pathways of MIL-100(Fe)/TiO 2 composites, ACS Appl. Mater. Interfaces 11 (2019) 12516–12524, https://doi.org/10.1021/acsami.9b00223.
[78] H. Wang, X. Yuan, Y. Wu, G. Zeng, H. Dong, X. Chen, L. Leng, Z. Wu, L. Peng, In situ synthesis of In2S3 at MIL-125(Ti) core-shell microparticle for the removal of tetracycline from wastewater by integrated adsorption and visible-light-driven photocatalysis, Appl. Catal. B Environ. 186 (2016) 19–29, https://doi.org/10.1016/j.apcatb.2015.12.041.
[79] R. Abazari, A.R. Mahjoub, Amine-functionalized Al-MOF#@ yxSm2O3-ZnO: a visible light-driven nanocomposite with excellent photocatalytic activity for the photo-degradation of amoxicillin, Inorg. Chem. 57 (2018) 2529–2545, https://doi.org/10.1021/acs.inorgchem.7b02880.
[80] R. Yuan, J. Qiu, C. Yue, C. Shen, D. Li, C. Zhu, F. Liu, A. Li, Self-assembled hierarchical and bifunctional MIL-88A(Fe)@ZnIn2S4 heterostructure as a reusable sunlight-driven photocatalyst for highly efficient water purification, Chem. Eng. J. 401 (2020), https://doi.org/10.1016/j.cej.2020.126020.
[81] H.E. Emam, M. El-Shahat, R.M. Abdelhameed, Observable removal of pharmaceutical residues by highly porous photoactive cellulose acetate@MIL-MOF film, J. Hazard. Mater. 414 (2021), https://doi.org/10.1016/j.jhazmat.2021.125509.
[82] L. Niemi, M. Taggart, K. Boyd, Z. Zhang, P.P.J. Gaffney, S. Pfleger, S. Gibb, Assessing hospital impact on pharmaceutical levels in a rural 'source-to-sink' water system, Sci. Total Environ. 737 (2020), https://doi.org/10.1016/j.scitotenv.2020.139618.
[83] I. Ali, A.E. Burakov, A.V. Melezhik, A.V. Babkin, I.V. Burakova, E. A. Neskoromnaya, E.V. Galunin, A.G. Tkachev, D.V. Kuznetsov, Removal of Copper(II) and Zinc(II) ions in water on a newly synthesized polyhydroquinone/graphene nanocomposite material: kinetics,thermodynamics and mechanism, ChemistrySelect 4 (2019) 12708–12718, https://doi.org/10.1002/slct.201902657.
[84] B. Srikanth, R. Goutham, R.B. Narayan, A. Ramprasath, K.P. Gopinath, A. R. Sankaranarayanan, Recent advancements in supporting materials for immobilised photocatalytic applications in waste water treatment, J. Environ. Manag. 200 (2017) 60–78, https://doi.org/10.1016/j.jenvman.2017.05.063.

[85] L. Pi, R. Jiang, W. Zhou, H. Zhu, W. Xiao, D. Wang, X. Mao, Applied surface science g-C 3 N 4 modified biochar as an adsorptive and photocatalytic material for decontamination of aqueous organic pollutants, Appl. Surf. Sci. 358 (2015) 231–239, https://doi.org/10.1016/j.apsusc.2015.08.176.

[86] L. Escobar-Alarcón, D.A. Solís-Casados, J. Perez-Alvarez, S. Romero, J.G. Morales-Mendez, E. Haro-Poniatowski, Preparation of Bi:TiO2 thin films by an hybrid deposition configuration: pulsed laser deposition and thermal evaporation, Appl. Phys. A Mater. Sci. Process. 117 (2014) 31–35, https://doi.org/10.1007/s00339-014-8276-8.

[87] M. Zhou, S. Roualdès, J. Zhao, V. Autès, A. Ayral, Nanocrystalline TiO2 thin film prepared by low-temperature plasma-enhanced chemical vapor deposition for photocatalytic applications, Thin Solid Films 589 (2015) 770–777, https://doi.org/10.1016/j.tsf.2015.07.007.

[88] M. Taylor, R.C. Pullar, I.P. Parkin, C. Piccirillo, Nanostructured titanium dioxide coatings prepared by aerosol assisted chemical vapour deposition (AACVD), J. Photochem. Photobiol. A Chem. 400 (2020), 112727, https://doi.org/10.1016/j.jphotochem.2020.112727.

[89] A.M. Alotaibi, P. Promdet, G.B. Hwang, J. Li, S.P. Nair, S. Sathasivam, A. Kafizas, C.J. Carmalt, I.P. Parkin, Zn and N codoped TiO2Thin films: photocatalytic and bactericidal activity, ACS Appl. Mater. Interfaces 13 (2021) 10480–10489, https://doi.org/10.1021/acsami.1c00304.

[90] W.S. Koe, J.W. Lee, W.C. Chong, in: An Overview of Photocatalytic Degradation: Photocatalysts, Mechanisms, and Development of Photocatalytic Membrane, 2020, pp. 2522–2565.

[91] D. Awfa, M. Ateia, M. Fujii, M.S. Johnson, C. Yoshimura, Photodegradation of pharmaceuticals and personal care products in water treatment using carbonaceous-TiO2 composites: a critical review of recent literature, Water Res. 142 (2018) 26–45, https://doi.org/10.1016/j.watres.2018.05.036.

[92] M. Ismael, The photocatalytic performance of the ZnO/g-C3N4 composite photocatalyst toward degradation of organic pollutants and its inactivity toward hydrogen evolution: the influence of light irradiation and charge transfer, Chem. Phys. Lett. 739 (2020), 136992, https://doi.org/10.1016/j.cplett.2019.136992.

[93] S. Zhu, X. Huang, F. Ma, L. Wang, X. Duan, S. Wang, Catalytic removal of aqueous contaminants on N-doped graphitic biochars: inherent roles of adsorption and nonradical mechanisms, Environ. Sci. Technol. 52 (2018) 8649–8658, https://doi.org/10.1021/acs.est.8b01817.

[94] M. Ahmaruzzaman, Biochar based nanocomposites for photocatalytic degradation of emerging organic pollutants from water and wastewater, Mater. Res. Bull. 140 (2021), 111262, https://doi.org/10.1016/j.materresbull.2021.111262.

[95] H. Zhang, Z. Wang, R. Li, J. Guo, Y. Li, J. Zhu, X. Xie, TiO2 supported on reed straw biochar as an adsorptive and photocatalytic composite for the efficient degradation of sulfamethoxazole in aqueous matrices, Chemosphere 185 (2017) 351–360, https://doi.org/10.1016/j.chemosphere.2017.07.025.

[96] X. Xie, S. Li, H. Zhang, Z. Wang, H. Huang, Promoting charge separation of biochar-based Zn-TiO2/pBC in the presence of ZnO for efficient sulfamethoxazole photodegradation under visible light irradiation, Sci. Total Environ. 659 (2019) 529–539, https://doi.org/10.1016/j.scitotenv.2018.12.401.

[97] Y. Song, J. Qi, J. Tian, S. Gao, F. Cui, Construction of Ag/g-C3N4 photocatalysts with visible-light photocatalytic activity for sulfamethoxazole degradation, Chem. Eng. J. 341 (2018) 547–555, https://doi.org/10.1016/j.cej.2018.02.063.

[98] H. Jingyu, Y. Ran, L. Zhaohui, S. Yuanqiang, Q. Lingbo, A. Nti Kani, In-situ growth of ZnO globular on g-C3N4 to fabrication binary heterojunctions and their photocatalytic degradation activity on tetracyclines, Solid State Sci. 92 (2019) 60–67, https://doi.org/10.1016/j.solidstatesciences.2019.02.009.

[99] A. Kumar, M. Khan, X. Zeng, I.M.C. Lo, Development of g-C3N4/TiO2/Fe3O4@SiO2 heterojunction via sol-gel route: a magnetically recyclable direct contact Z-scheme nanophotocatalyst for enhanced photocatalytic removal of ibuprofen from real sewage effluent under visible light, Chem. Eng. J. 353 (2018) 645–656, https://doi.org/10.1016/j.cej.2018.07.153.

[100] T.A. Kurniawan, L. Yanyan, T. Ouyang, A.B. Albadarin, G. Walker, BaTiO3/TiO2 composite-assisted photocatalytic degradation for removal of acetaminophen from synthetic wastewater under UV–vis irradiation, Mater. Sci. Semicond. Process. 73 (2018) 42–50, https://doi.org/10.1016/j.mssp.2017.06.048.

[101] Y. Ye, Y. Feng, H. Bruning, D. Yntema, H.H.M. Rijnaarts, Photocatalytic degradation of metoprolol by TiO2 nanotube arrays and UV-LED: effects of catalyst properties, operational parameters, commonly present water constituents, and photo-induced reactive species, Appl. Catal. B Environ. 220 (2018) 171–181, https://doi.org/10.1016/j.apcatb.2017.08.040.