

## Review

# Photodegradation of pharmaceuticals and personal care products in water treatment using carbonaceous-TiO<sub>2</sub> composites: A critical review of recent literature

Dion Awfa <sup>a,1</sup>, Mohamed Ateia <sup>a,b,d,\*</sup>, Manabu Fujii <sup>a</sup>, Matthew S. Johnson <sup>c</sup>,  
Chihiro Yoshimura <sup>a</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, School of Environment and Society, Tokyo Institute of Technology, 2-12-1, M1-4, Ookayama, Meguro-ku, Tokyo, 152-8552, Japan

<sup>b</sup> Department of Environmental Engineering and Earth Sciences, Clemson University, Clemson, SC 29634, United States

<sup>c</sup> Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

<sup>d</sup> PSIPW Chair, Prince Sultan Institute for Environmental, Water and Desert Research, King Saud University, Saudi Arabia

## ARTICLE INFO

## Article history:

Received 3 March 2018

Received in revised form

9 May 2018

Accepted 19 May 2018

Available online 23 May 2018

## Keywords:

TiO<sub>2</sub>

Carbonaceous-TiO<sub>2</sub> composites

Photocatalysis

Pharmaceuticals and personal care products

(PPCP)

Wastewater

## ABSTRACT

The high concentrations of pharmaceuticals and personal care products (PPCP) that found in water in many locations are of concern. Among the available water treatment methods, heterogeneous photocatalysis using TiO<sub>2</sub> is an emerging and viable technology to overcome the occurrence of PPCP in natural and waste water. The combination of carbonaceous materials (e.g., activated carbon, carbon nanotubes and graphene nanosheets) with TiO<sub>2</sub>, a recent development, gives significantly improved performance. In this article, we present a critical review of the development and fabrication of carbonaceous-TiO<sub>2</sub> and its application to PPCP removal including its influence on water chemistry, and the relevant operational parameters. Finally, we present an analysis of current priorities in the ongoing research and development of carbonaceous-TiO<sub>2</sub> for the photodegradation of PPCP.

© 2018 Elsevier Ltd. All rights reserved.

## Contents

1. Introduction	27
2. Pharmaceuticals and personal care products	28
3. Heterogeneous photocatalysis	28
4. Carbonaceous-TiO <sub>2</sub> photocatalysis	29
4.1. Activated carbon-TiO <sub>2</sub> composites	33
4.2. Carbon nanotube-TiO <sub>2</sub> composites	34
4.3. Graphene-TiO <sub>2</sub> composites	35
5. The role of water chemistry in photocatalytic performance	36
5.1. Effect of pH	36
5.2. Effect of water temperature	36
5.3. Effect of initial concentration of PPCP	36
5.4. Effect of dissolved oxygen	37
5.5. Effect of natural organic matter	37
5.6. Effect of inorganic species	37

\* Corresponding author. Department of Environmental Engineering and Earth Sciences, Clemson University, Clemson, SC 29634, United States.

E-mail address: [iateia@clemson.edu](mailto:iateia@clemson.edu) (M. Ateia).

<sup>1</sup> These authors contributed equally to this work.

Abbreviations			
<b>PPCP</b>	pharmaceuticals and personal care products	<b>SMP</b>	soluble microbial products
<b>NSAIDs</b>	nonsteroidal anti-inflammatory drugs	<b>SWCNT</b>	single walled carbon nanotubes
<b>AOPs</b>	advanced oxidation processes	<b>MWCNT</b>	multi walled carbon nanotube
<b>OH</b>	hydroxyl radical	<b>CVD</b>	chemical vapor deposition
<b>O<sub>2</sub><sup>-</sup></b>	superoxide anion radical	<b>EPD</b>	Electrophoretic vapor deposition
<b>HO<sub>2</sub></b>	hydroperoxyl radical	<b>PVD</b>	physical vapor deposition
<b><sup>1</sup>O<sub>2</sub></b>	Singlet molecular oxygen	<b>PZC</b>	point of zero charge
<b>H<sub>2</sub>O<sub>2</sub></b>	hydrogen peroxide	<b>pH<sub>PZC</sub></b>	pH of the PZC
<b>e<sup>-</sup><sub>aq</sub></b>	solvated electron	<b>AC</b>	activated carbon
<b><sup>3</sup>NOM<sup>*</sup></b>	triplet excited state of NOM	<b>CNT</b>	carbon nanotubes
<b>h<sup>+</sup><sub>TR</sub></b>	trapped conduction band hole	<b>GO</b>	graphene oxide
<b>e<sup>-</sup><sub>TR</sub></b>	surface trapped valence band electron	<b>rGO</b>	reduced graphene oxide
		<b>NOM</b>	natural organic matter
		<b>EfOM</b>	effluent organic matter

6.	Effect of system parameters on photocatalytic activity	38
6.1.	Effect of excitation wavelength	38
6.2.	Effect of the loading of carbonaceous-TiO <sub>2</sub>	38
6.3.	Effect of the ratio of carbonaceous material to TiO <sub>2</sub>	38
7.	Conclusions and recommendations	39
	Acknowledgements	39
	References	39

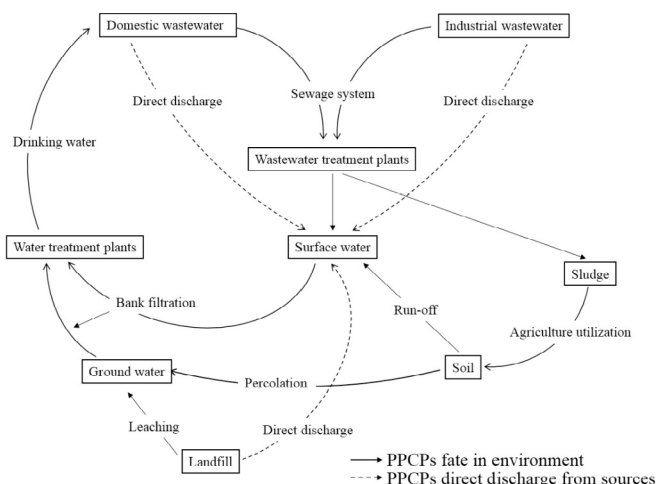
## 1. Introduction

Pharmaceuticals and personal care products (PPCP) are man-made persistent substances that are intended for human and/or animal healthcare and medical purposes (Jiang et al., 2013; Omar et al., 2016; Yang et al., 2017a). PPCP can be further classified as antibiotics, anticonvulsants, contrast agents, hormones, nonsteroidal anti-inflammatory drugs (NSAIDs),  $\beta$ -blockers, lipid regulators, painkillers, preservatives, disinfectants, insect repellants, fungicides, soaps and detergents, fragrances, and sunscreen UV filters (Yang et al., 2017a). PPCP are transported to the aqueous environment through domestic wastewater, industrial wastewater, runoff and landfill leachate (Cardoso et al., 2014; Chen et al., 2016; Kapelewska et al., 2016; Lu et al., 2015) (Fig. 1). Of these, treatment plants for sewage and industrial wastewater were found to be the largest

sources of PPCP (Jiang et al., 2013; Lester et al., 2013). Previous studies found that concentrations of diclofenac as low as  $5 \mu\text{g L}^{-1}$  can accumulate inside the bodies of rainbow trout (Schwaiger et al., 2004) and a mixture of acetaminophen, carbamazepine, gemfibrozil, and venlafaxine at concentration 0.5 and  $10 \mu\text{g L}^{-1}$  can cause significant effects to zebrafish including tissue degeneration, a decline in embryo production, and increased in embryo mortalities (Galus et al., 2013). It is therefore extremely troublesome that PPCP can be found in surface and ground waters at concentrations ranging up to  $10,000 \mu\text{g L}^{-1}$  and  $100 \mu\text{g L}^{-1}$  for pharmaceuticals and personal care products respectively (Yang et al., 2017a).

Numerous techniques for removing PPCP from water have been reported including activated sludge (Jewell et al., 2016), fungi (Li et al., 2016), microalgae (Bai and Acharya, 2016; Matamoros et al., 2016), wetlands (Rühmland et al., 2015; Zhang et al., 2013a, 2013b, 2016), adsorption (Ali et al., 2016; Baghdadi et al., 2016; Lerman et al., 2013; Mailler et al., 2016; Nielsen and Bandosz, 2016; Wei et al., 2013), and membranes (Jin et al., 2012; Sheng et al., 2016; Wang et al., 2016). Conventional wastewater treatment plants use biological processes (e.g., activated sludge and wetlands) with removal efficiencies for PPCP, in the range of 50–90% (Ibáñez et al., 2013; Zhang et al., 2013b). While PPCP removal becomes relatively high in some cases, many of the PPCP are antimicrobial agents and designed to be persistent (McClellan and Halden, 2010). Thus, PPCP can be and are detected in the effluent of conventional wastewater treatment plants in many countries around the world (Yang et al., 2017b). There is therefore a need for improved physical treatment methods (e.g., adsorption-based systems and membranes) for PPCP removal. Adsorption and membrane filtration have shown high removal efficiencies, over 90% (Ali et al., 2016; Baghdadi et al., 2016; Jin et al., 2012; Sheng et al., 2016). However, adsorption-based systems and membranes only trap PPCP, they do not destroy them. Moreover, the spent adsorbents and rejected water from the membrane processes are classified as secondary contaminants (Ateia et al., 2018; Xu et al., 2017).

Several reviews have examined photocatalyst performance, and the limitations and advanced modification of TiO<sub>2</sub> (Chong et al.,



**Fig. 1.** Sources and pathways of pharmaceuticals and personal care products in the environment.

2010; Dong et al., 2015; Leary and Westwood, 2011; Melchionna et al., 2016; Woan et al., 2009). Daghrir et al. (2013) reviewed some modified forms of  $\text{TiO}_2$  including anion and cation doping, and coupling with narrow band gap semiconductors ( $\text{M}_x\text{O}_y/\text{TiO}_2$  or  $\text{M}_5\text{S}_y/\text{TiO}_2$ ). In addition, Khalid et al. (2017) reviewed the modification of  $\text{TiO}_2$  with carbonaceous nanomaterials as an alternative and innovative approach for the enhancement of photocatalytic activity. All of these reviews suggest that, intentionally modified  $\text{TiO}_2$  have better photocatalytic activity than pristine  $\text{TiO}_2$ . One modified form in particular, carbonaceous- $\text{TiO}_2$ ; has attracted a lot of attention for environmental applications. However, in the case of PPCP photodegradation, most reviews have focused on the use of  $\text{TiO}_2$ . Tong et al. (2012) reviewed the parameters governing  $\text{TiO}_2$  photocatalysis for the removal of pharmaceuticals and the ecotoxicity of photoproducts. In the recent years, Mahmoud et al. (2017) also reviewed  $\text{TiO}_2$  photocatalysis for removing pharmaceuticals, and the possible formation of photodegradation by-products. Kanakaraju et al. (2014) presented an overview of  $\text{TiO}_2$  photocatalysis for treatment of pharmaceuticals in wastewater. Lee et al. (2017) reviewed the occurrence of pharmaceuticals in the aquatic environment, and the application of  $\text{TiO}_2$  photocatalysis. Sarkar et al. (2014) presented an in-depth review of the application and process parameters that affect  $\text{TiO}_2$  photocatalysis for the removal of pharmaceuticals. In Fig. 2, we illustrate the compilation of all studies in the literature and the current trends for PPCP photocatalysis by carbonaceous- $\text{TiO}_2$ . PPCP even with the same molecular weight and under the same light conditions showed variations of half-life, which can be caused by the differences in the chemical backbone (Romão et al., 2017) as well as in operating

conditions. To the best of our knowledge, there is currently no review considering the use of carbonaceous- $\text{TiO}_2$  composites for removing PPCP from contaminated water. Thus, a comprehensive understanding of the use of carbonaceous- $\text{TiO}_2$  for the remediation of PPCP would help optimize the development and implementation of this composite. In this paper, we present a critical review of recent developments and applications of carbonaceous- $\text{TiO}_2$  composite photocatalysts for removing PPCP from water, and the key water chemistry and operational parameters.

## 2. Pharmaceuticals and personal care products

Pharmaceuticals and personal care products (PPCP) are a class of compounds that mainly consists of polar molecules with molecular weights ranging from 150 to 1000 Daltons (DA) and a wide variety of physicochemical properties (Barceló and Petrovic, 2007; Kim and Tanaka, 2009; Rahman et al., 2009; Suárez et al., 2008). In the last decade, the global annual consumption of PPCP has increased and top countries consumers include Brazil, Russia, India, China, and South Africa (Tijani et al., 2016). To date, more than 3000 PPCP have been produced and the constant development of new chemical compounds has led to an increasing abundance and variety of PPCP in the environment (Chen et al., 2016; Of et al., 2009). Previous investigations showed that sewage treatment plants are the main source of PPCP into aquatic environments (Brunsch et al., 2018). Accordingly, PPCP can be found in lakes (Bonvin et al., 2011; Ferguson et al., 2013; Subedi et al., 2014; Zhang et al., 2018; Zhu et al., 2013), rivers (Carmona et al., 2014; Dai et al., 2015; Hanamoto et al., 2018; Hughes et al., 2013), ground water (Del Rosario et al., 2014; Gottschall et al., 2012; Peng et al., 2014; Sui et al., 2015; Yang et al., 2017b), marine and coastal areas (Ali et al., 2018; Arpin-Pont et al., 2016; Benotti and Brownawell, 2009; Dsikowitzky et al., 2015; Pereira et al., 2016), and in drinking water (Aristizabal-Ciro et al., 2017; Batt et al., 2017; Benotti et al., 2009; T. Lin et al., 2016a). Currently, the main methods for removing PPCP in conventional wastewater treatment plants are biotransformation/biodegradation and/or adsorption on conventional adsorbents (e.g., activated carbon) (Alvarino et al., 2018). However, conventional wastewater treatment plants are inefficient at removing PPCP due to their low biodegradability (Coelho et al., 2009; Lagesson et al., 2016; Mirzaei et al., 2016). The continuous input of PPCP into the environment is a serious concern. For instance, wastewater containing a mix of pharmaceuticals caused significant reproductive and other health impacts for fish (Al-Salhi et al., 2012). Moreover, PPCP (e.g., acetaminophen, caffeine, 1,7-Dimethylxanthine, dehydronifedine, tetracycline, oxytetracycline, sulfonamides, macrolides, and ormetoprim) have been detected in fruits, vegetables, fish, meat and milk due to uptake from an environment contaminated by PPCP (Baron et al., 2014; Done and Halden, 2015; Pan et al., 2014). Alternative solutions, such as advanced treatment processes, should be implemented to diminish the release of PPCP into environment. Heterogeneous photocatalysis is considered as a sustainable technique.

## 3. Heterogeneous photocatalysis

Heterogeneous photocatalysis is an oxidation process occurring on semiconductor solid catalysts illuminated at suitable wavelengths (Ahmad et al., 2016; Sudha and Sivakumar, 2015; Venkata Laxma Reddy et al., 2011). Among frequently used semiconductor materials,  $\text{TiO}_2$  shows the greatest potential among developing green chemistry technologies. There are three different polymorphs of  $\text{TiO}_2$  crystals, namely anatase, rutile and brookite (Friedmann et al., 2010). When Zhang et al. (2014a) compared the photocatalytic activity of the three polymorphs, anatase  $\text{TiO}_2$  was

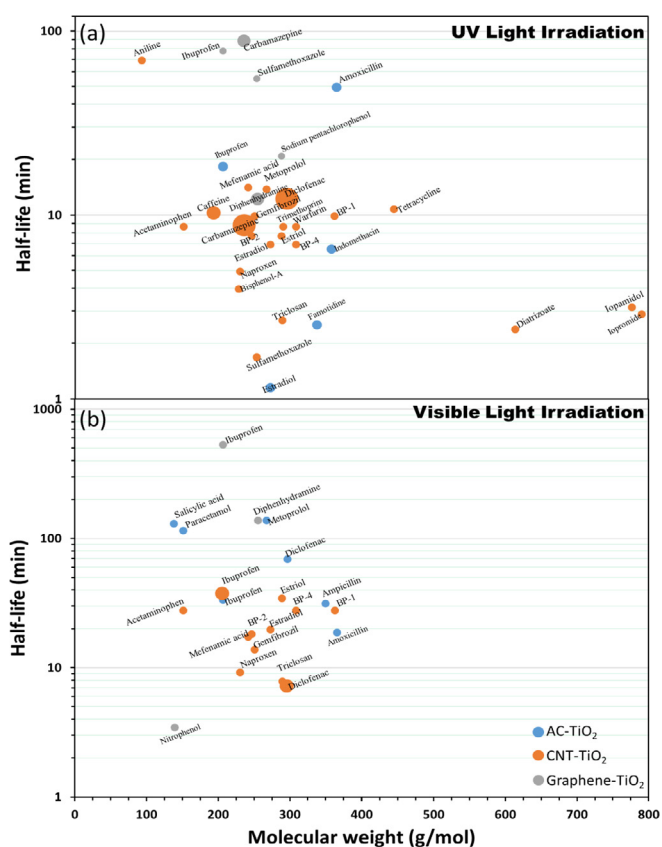


Fig. 2. Meteor rain chart of the literature review on the photocatalysis data of PPCP by carbonaceous- $\text{TiO}_2$  under (a) UV irradiation and (b) visible light irradiation. Half-life ( $t_{1/2} = \ln 2/k_{app}$  ( $k_{app}$  is pseudo-first order kinetic rate of photocatalysis)). The size of each circle represents the number of studies in the literature.

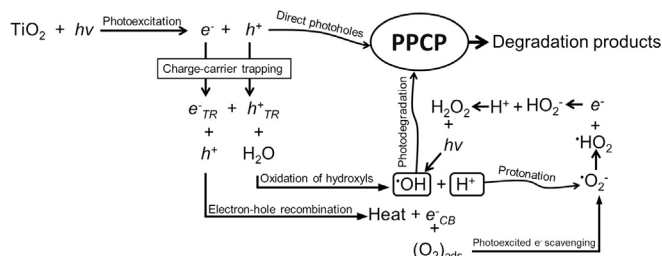
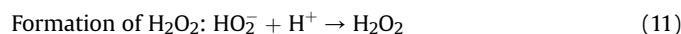
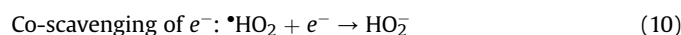
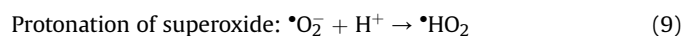
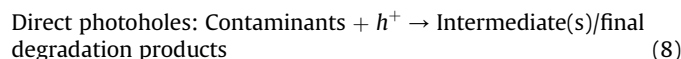
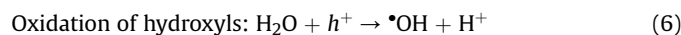
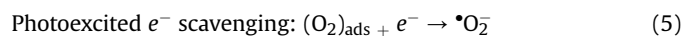
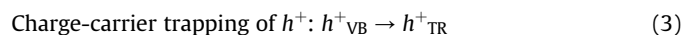
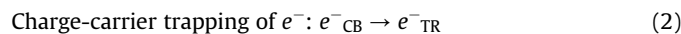
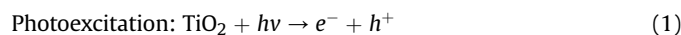


Fig. 3. The key components of photocatalytic oxidation and reduction mechanism.

found to exhibited the highest photocatalytic activity, the longest lifetime of the photoexcited electron, and the fastest migration of photogenerated electrons. Therefore, anatase is the preferred polymorph of  $\text{TiO}_2$  in photocatalysis. Basically, light with a certain energy ( $\lambda < 380 \text{ nm}$ ), an energy that is greater than the band gap (i.e., the energy difference between the valence band and the conduction band in semiconductors) of  $\text{TiO}_2$  (3.2 eV), excites the electron from the valence band to the conduction band and creates an electron-hole pair ( $e^-$  and  $h^+$ ). Electrons and holes on the surface of a semiconductor participate in redox reactions that produce reactive species such as hydroxyl radicals ( $^*\text{OH}$ ) and superoxide anion radicals ( $^*\text{O}_2^-$ ). The key reactions in the photocatalytic oxidation and reduction mechanism are summarized in Fig. 3.



The surface trapped valence band electron ( $e^-_{\text{TR}}$ ) and conduction band hole ( $h^+_{\text{TR}}$ ) are formed by the processes shown in Eqs. (2) and Eq. (3), respectively. These trapped carriers on the  $\text{TiO}_2$  surface do not recombine immediately after photoexcitation (Chong et al., 2010). In parallel, in the absence of an electron scavenger, the photoexcited electron recombines with the valence band hole in nanoseconds (Eq. (4)) (Schneider et al., 2014). Therefore, the presence of electron scavengers is very important in photocatalysis to retard recombination. The presence of oxygen prevents the recombination of the electron-hole pair (electron scavenger), and allows the formation of superoxide ( $^*\text{O}_2^-$ ) (Eq. (5)). Superoxide radicals can be protonated to form hydroperoxyl radicals ( $^*\text{HO}_2$ ) that can react further to form  $\text{H}_2\text{O}_2$  (Eqs. (9)–(11)). It should be noted that all of these reactions to produce reactive  $^*\text{OH}$  occurred

due to the presence of both dissolved oxygen and water.

The overall process of heterogeneous photocatalysis can be decomposed into five steps (Herrmann, 1999). First, PPCP move from the fluid phase to the interface region of the catalyst by diffusion. Second, PPCP are adsorbed onto the surface of the photocatalyst. Third, a chemical reaction occurs with oxidizing and/or reducing species in the vicinity of the surface. Fourth, by-products desorb. Finally, products are removed from the interface region into the bulk fluid. Previous studies showed that the photocatalytic degradation of PPCP using  $\text{TiO}_2$  could reach up to 99% within one to three hours (Czech and Buda, 2016; Lin et al., 2016a; Murgolo et al., 2015). However, the use of bare  $\text{TiO}_2$  has critical limitations such as lower activity under solar irradiation than UV light ( $\lambda > 400 \text{ nm}$ ), low adsorption capability and the difficulty of recovering it from the treated water (Dong et al., 2015). Various techniques (e.g., cation-doped, anion-doped, coupled semiconductor) have been tested in the development of  $\text{TiO}_2$ -based systems (Daghrir et al., 2013). Despite significant efforts, carbonaceous materials offer unique advantages (e.g., chemical inertness, stability, electrical properties, and tunable structure) that have not been adequately tested. Combining  $\text{TiO}_2$  with carbonaceous materials has attracted a lot of attention as a strategy for enhancing the performance of  $\text{TiO}_2$  photocatalysts, as described in the following section.

#### 4. Carbonaceous- $\text{TiO}_2$ photocatalysis

Activated carbon (AC), carbon nanotubes (CNTs) and graphene are the main carbonaceous materials that have been tested for use in water and wastewater treatment (Santhosh et al., 2016). These materials have large specific surface areas, and high charge carrier mobility (Leary and Westwood, 2011). Table 1 shows a summary of 29 studies on PPCP removal using three different carbonaceous- $\text{TiO}_2$  composites published over the past seven years. Overall, the composites of carbonaceous materials with  $\text{TiO}_2$  have higher photocatalytic activity, adsorption capacity, electron scavenging and sensitization ability, and extended visible light absorption relative to bare  $\text{TiO}_2$  (Khalid et al., 2017). Table 1 summarizes studies of the ability of photocatalytic carbonaceous- $\text{TiO}_2$  to degrade personal care products. Such studies are very limited compared for example to pharmaceuticals. Further, studies of using photocatalytic carbonaceous- $\text{TiO}_2$  for PPCP photodegradation in complex water matrices are limited. Overall, CNT- $\text{TiO}_2$  and graphene- $\text{TiO}_2$  showed better response to visible light irradiation than AC- $\text{TiO}_2$  due to better heterojunction interaction. However, synthesis methods affected the characteristics of carbonaceous- $\text{TiO}_2$  as well as their photocatalytic activity. Table 2 presents a comparison among the common synthesis methods of carbonaceous- $\text{TiO}_2$  composites.

The degradation of PPCP is enhanced when using composites of carbonaceous materials with  $\text{TiO}_2$  because of four main mechanisms. First, the affinity and the mobility of PPCP on carbonaceous materials and the high specific surface areas of carbonaceous materials help to harvest the PPCP and concentrate them close to the  $\text{TiO}_2$  active site for enhanced photodegradation (Kuvarega and Mamba, 2016; Li Puma et al., 2008). Carbonaceous material is well known as an effective adsorbent due to hydrophobic interaction,  $\pi$ - $\pi$  interactions, hydrogen-bonding interactions, and electrostatic and dispersion interactions (Ateia et al., 2017a). Second, carbonaceous materials acts as electron scavengers due to their large electron storage capacity; this property which hinders electron recombination is known as the Hoffmann mechanism (Woan et al., 2009). Simply, when a photon with sufficient energy excites an electron from the valence band to the conduction band of  $\text{TiO}_2$ , a hole is created in the valence band ( $h^+$ ). Instead of returning to the valence band, in carbonaceous materials the excited electrons are transferred into the graphitic  $\pi$  electron band, retarding

**Table 1**  
The photocatalysis of PPCP using carbonaceous-TiO<sub>2</sub> composites.

Compounds	Categories	Catalysts (g L <sup>-1</sup> )	Initial concentrations (mg L <sup>-1</sup> )	Light wavelengths (nm)	Water matrices	Irradiation Time (min)	Removal (%)	Kinetics	Light intensity (W m <sup>-2</sup> )	pH	Ref.
<b>Activated carbon -TiO<sub>2</sub> (AC - TiO<sub>2</sub>)</b>											
Amoxicillin	Pharmaceuticals	AC-TiO <sub>2</sub> (1.0–2.5)	150	366	Ultrapure water	240	75–90	Langmuir-Hinshelwood	NA	3–9	(Basha et al., 2011)
Amoxicillin	Pharmaceuticals	AC-TiO <sub>2</sub> (0.4–1.6)	50	Sunlight	Ultrapure water	180	60–100	Langmuir-Hinshelwood	NA	3	(Gar Alalm et al., 2016)
Ampicillin	Pharmaceuticals	AC-TiO <sub>2</sub> (0.4–1.6)	50	Sunlight	Ultrapure water	180	50–100	Langmuir-Hinshelwood	NA	3	(Gar Alalm et al., 2016)
Paracetamol	Pharmaceuticals	AC-TiO <sub>2</sub> (0.4–1.6)	50	Sunlight	Ultrapure water	180	40–70	Langmuir-Hinshelwood	NA	3	(Gar Alalm et al., 2016)
Diclofenac	Pharmaceuticals	AC-TiO <sub>2</sub> (0.4–1.6)	50	Sunlight	Ultrapure water	180	40–85	Langmuir-Hinshelwood	NA	3	(Gar Alalm et al., 2016)
Metoprolol	Pharmaceuticals	Magnetic AC-TiO <sub>2</sub> (0.25–0.375)	10	>300	Ultrapure water	120	50	<sup>a</sup> Pseudo-first order	550	NA	(Rey et al., 2012)
Metoprolol	Pharmaceuticals	Magnetic AC-TiO <sub>2</sub> (0.28)	50	300–800, 320–800, 390–800	Ultrapure water	300	20–60	Pseudo-first order	550	NA	(Quiñones et al., 2014)
Carbamazepine	Pharmaceuticals	AC-TiO <sub>2</sub> (120)	10	254	Ultrapure water	60	80–98	NA	105	7	(Khraisheh et al., 2013)
Ibuprofen	Pharmaceuticals	AC-TiO <sub>2</sub> co-doping N (0.5)	20	254 & 420	Ultrapure water	120	11–100	Langmuir-Hinshelwood	NA	NA	(El-Sheikh et al., 2017)
Indomethacin	Pharmaceuticals	AC-TiO <sub>2</sub> (1.2)	35.8–537	366	Ultrapure water	240	60–80	First-order, second-order, and Langmuir-Hinshelwood	NA	NA	(Basha et al., 2010)
Famotidine	Pharmaceuticals	AC-TiO <sub>2</sub> (1.5)	1000	366	Ultrapure water	180	60–80	Langmuir-Hinshelwood	NA	NA	(Keane et al., 2011)
Estrogen	Pharmaceuticals	AC-TiO <sub>2</sub> (0.25)	1	320–400	Ultrapure water	10	>90	Pseudo-first order	NA	6	(Rosa et al., 2017)
Salicylic acid	Personal care products	Magnetic AC- TiO <sub>2</sub> co-doping F-N (0.1)	30	>420 nm	Ultrapure water	180	60–80	Pseudo-first order	NA	4.95	(Ma et al., 2017)
<b>Carbon nanotubes - TiO<sub>2</sub> (CNT-TiO<sub>2</sub>)</b>											
BP-1	Personal care products	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
BP-2	Personal care products	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
BP-4	Personal care products	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Warfarin	Pharmaceuticals	CNTs-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Diclofenac	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Mefenamic acid	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Triclosan	Personal care products	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Metoprolol	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Estradiol	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Estriol	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Acetaminophen	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Carbamazepine	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Gemfibrozil	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320–700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)

Iopamidol	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320-700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Naproxen	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320-700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Iopromide	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320-700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Trimethoprim	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320-700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Diatrizoate	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320-700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Sulfamethoxazole	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1)	0.2–0.5	254 and 320-700	Ultrapure water and wastewater	200	NA	Langmuir-Hinshelwood	1000	NA	(Murgolo et al., 2015)
Ibuprofen	Pharmaceuticals	CNT-TiO <sub>2</sub> co-doping Urea (0.4)	5	410 nm	Ultrapure water	120	50–90	Pseudo-first order	183	2	(Yuan et al., 2016)
Diclofenac	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1–2)	8	254 and 366	Ultrapure water	60	>90	Pseudo-first order	NA	6	(Martínez et al., 2011a)
Tetracycline	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1–0.4)	0.5–30	240	Ultrapure water and wastewater	120	20–100	Pseudo-first order	NA	3	(Ahmadi et al., 2016)
Carbamazepine	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.1–2)	8	254 and 366	Ultrapure water	60	>95	Pseudo-first order	NA	6	(Martínez et al., 2011b)
Caffeine	Pharmaceuticals	CNT-TiO <sub>2</sub> (1)	50	>350	Ultrapure water	180	100	Pseudo-first order	500	NA	(Marques et al., 2013)
Caffeine	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.05)	50	>350	Ultrapure water	120	100	Pseudo-first order	430	NA	(Miranda et al., 2014)
Bisphenol-A	Pharmaceuticals	CNT-TiO <sub>2</sub> -SiO <sub>2</sub> (0.5)	10	366	Ultrapure water	60	>50	Pseudo-first order	10	NA	(Czech and Buda, 2015)
Carbamazepine	Pharmaceuticals	CNT-TiO <sub>2</sub> -SiO <sub>2</sub> (0.5)	10	366	Ultrapure water	60	>50	Pseudo-first order	10	NA	(Czech and Buda, 2015)
Diclofenac	Pharmaceuticals	CNT-TiO <sub>2</sub> -SiO <sub>2</sub> (0.5)	10	365 and 500-550	Ultrapure water	60	>99	Pseudo-first order	NA	6	(Czech and Buda, 2016)
4-chlorophenol	Pharmaceuticals	Immobilized CNT-TiO <sub>2</sub> layer	15	365	Ultrapure water	300	70	First order	10	9	(Zouzelka et al., 2016)
Aniline	Pharmaceuticals	CNT-TiO <sub>2</sub> (0.125)	93	366, 436, 546	Ultrapure water	15	>95	Langmuir-Hinshelwood	430	5.6	(Orge et al., 2016)
<b>Graphene-TiO<sub>2</sub></b> Sulfamethoxazole	Pharmaceuticals	Immobilized rGO-TiO <sub>2</sub> on optical fiber	5	254, 365, and >400	Ultrapure water	180	50–92	Langmuir-Hinshelwood	NA	6	(Lin et al., 2016a)
Ibuprofen	Pharmaceuticals	Immobilized rGO-TiO <sub>2</sub> on optical fiber	5	254, 365, and >400	Ultrapure water	180	20–81	Langmuir-Hinshelwood	NA	6	(Lin et al., 2016a)
Carbamazepine	Pharmaceuticals	Immobilized rGO-TiO <sub>2</sub> on optical fiber	5	254, 365, and >400	Ultrapure water	180	10–54	Langmuir-Hinshelwood	NA	6	(Lin et al., 2016b)
Carbamazepine	Pharmaceuticals	3D rGO-TiO <sub>2</sub> (0.5)	10	365	Ultrapure water	90	>99	Langmuir-Hinshelwood	13.5	NA	(Nawaz et al., 2017)
Nitrophenol	Pharmaceuticals	Graphene oxide-TiO <sub>2</sub> -Pd nanowires (0.05)	70	Visible light	Ultrapure water	90	7–85	Pseudo-first order	NA	4	(Lee et al., 2015)
2-4-dichlorophenol	Personal care products	2D interface Graphene oxide-TiO <sub>2</sub> (0.04)	10	365	Ultrapure water	60	>99	Pseudo-first order	NA	NA	(Sun et al., 2013)
Sodium pentachlorophenol	Personal care products	Graphene oxide-TiO <sub>2</sub> (0.1)	50	249	Ultrapure water	120	>95	Pseudo-first order	NA	NA	(Zhang et al., 2014b)
4-chlorophenol	Pharmaceuticals	Graphene oxide-TiO <sub>2</sub> nanofibers (0.1)	20	>420	Ultrapure water	240	60–90	Pseudo-first order	NA	NA	(Zhang et al., 2017a)
Diphenhydramine	Pharmaceuticals	rGO-TiO <sub>2</sub> (1)	100	>350 and > 430	Ultrapure water	60	>95	Pseudo-first order	60 and 500	NA	(Pastrana-Martinez et al., 2012)
Diphenhydramine	Pharmaceuticals	Graphene oxide-TiO <sub>2</sub> (1)	100	>350	Ultrapure water	60	>95	Pseudo-first order	500	NA	(Morales-Torres et al., 2013)

NA refers to not available.

<sup>a</sup> Generally, photocatalysis kinetic follows Langmuir-Hinshelwood model which then simplified as pseudo-first order model. However, at very high concentrations of pollutants ( $>5 \times 10^{-3}$  M), the reaction rate is maximum and followed the zero order kinetic model (Herrmann, 1999).

**Table 2**  
Comparison of common carbonaceous-TiO<sub>2</sub> composites synthesis techniques.

Synthesis Techniques	Advantages	Disadvantage	Ref.
Sol-gel	<ul style="list-style-type: none"> <li>● Homogeneous distribution and strong adhesion (i.e. chemical bonding) of TiO<sub>2</sub> on the surface of carbonaceous materials.</li> <li>● Control over the stoichiometry of process.</li> <li>● High purity of nano-sized crystallized powder of TiO<sub>2</sub>.</li> </ul>	<ul style="list-style-type: none"> <li>○ High calcination temperature.</li> <li>○ High consumption of various and costly reagents.</li> <li>○ Long synthesis time.</li> </ul>	(Azizi, 2017; Gao et al., 2009; Koli et al., 2017)
Chemical vapor deposition	<ul style="list-style-type: none"> <li>● Simultaneous reduction and activation of the catalyst.</li> <li>● Continuous process which is relatively easy for industrial scale applications.</li> </ul>	<ul style="list-style-type: none"> <li>○ High requirement of temperature and pressure.</li> <li>○ The need for inert gas supply with high purity.</li> <li>○ Production of by-products gas from the process.</li> </ul>	(Li Puma et al., 2008; Ma et al., 2012)
Electrophoretic deposition	<ul style="list-style-type: none"> <li>● Quick deposition of TiO<sub>2</sub> on the surface of carbonaceous materials.</li> <li>● Control over the thickness and morphology of TiO<sub>2</sub> on the surface of carbonaceous materials.</li> <li>● Can be carried out at room temperature.</li> <li>● Continuous process which is relatively easy for industrial scale applications.</li> </ul>	<ul style="list-style-type: none"> <li>○ The need of electric field to deposit TiO<sub>2</sub> on the surface of carbonaceous materials.</li> </ul>	(Bordbar et al., 2015)
Impregnation	<ul style="list-style-type: none"> <li>● Uniform coating of TiO<sub>2</sub> on the surface of carbonaceous materials.</li> <li>● Control over the crystal structure and surface morphology of the composite.</li> <li>● Continuous process which is relatively easy for industrial scale applications.</li> </ul>	<ul style="list-style-type: none"> <li>○ High calcination temperature.</li> <li>○ Long synthesis time.</li> </ul>	(Gar Alalm et al., 2016; Xu et al., 2010)
Pyrolysis	<ul style="list-style-type: none"> <li>● High purity of nano-sized powder composites.</li> <li>● Control over the stoichiometry of process in multi-component system.</li> <li>● Continuous process which is relatively easy for industrial scale applications.</li> </ul>	<ul style="list-style-type: none"> <li>○ High energy requirement to produce flame in the combustion chamber.</li> <li>○ High temperature requirement.</li> </ul>	(Lara-López et al., 2017)
Evaporation and drying (simple mixing)	<ul style="list-style-type: none"> <li>● The simplest preparation techniques.</li> <li>● Low calcination temperature.</li> <li>● Using water as a solvent.</li> <li>● Short synthesis time.</li> </ul>	<ul style="list-style-type: none"> <li>○ Non-homogeneous distribution of TiO<sub>2</sub> on the surface of carbonaceous materials.</li> <li>○ Physisorption of TiO<sub>2</sub> on carbonaceous materials which might provide insufficient bonding for electron transfer.</li> </ul>	(Yao et al., 2008)
Electrostatic attraction	<ul style="list-style-type: none"> <li>● The improvement method of simple mixing technique by providing sufficient electrostatic attraction between TiO<sub>2</sub> and carbonaceous materials.</li> <li>● Low calcination temperature.</li> <li>● Short synthesis time.</li> </ul>	<ul style="list-style-type: none"> <li>○ The needs to adjust the pH to provide optimal condition for electrostatic attraction between TiO<sub>2</sub> and carbonaceous materials.</li> <li>○ Using ethanol as a solvent.</li> </ul>	(Daneshvar Tarigh et al., 2015)
Hydrothermal	<ul style="list-style-type: none"> <li>● Possibility to control crystal structure, size and surface morphology of the composite.</li> <li>● Using water as a solvent.</li> </ul>	<ul style="list-style-type: none"> <li>○ High calcination temperature and pressure.</li> <li>○ Long synthesis time.</li> <li>○ The needs of highly concentrated NaOH (basic condition) in the synthesis process.</li> </ul>	(Liu et al., 2007; Wu et al., 2015; Yuan et al., 2016)
Solvothermal	<ul style="list-style-type: none"> <li>● Possibility to control crystal structure, size and surface morphology of the composite.</li> <li>● Calcination temperature relatively lower than hydrothermal process.</li> </ul>	<ul style="list-style-type: none"> <li>○ Using ethanol or methanol as a solvent.</li> <li>○ High calcination temperature and pressure.</li> <li>○ Long synthesis time.</li> <li>○ The needs of highly concentrated NaOH (basic condition) in the synthesis process.</li> </ul>	(Zhou et al., 2010)
Microwave assisted	<ul style="list-style-type: none"> <li>● Rapid heating than conventional thermal method.</li> <li>● Stable calcination temperature.</li> </ul>	<ul style="list-style-type: none"> <li>○ The needs of energy to provide microwave irradiation.</li> </ul>	(Orha et al., 2017)
Sonochemical treatment	<ul style="list-style-type: none"> <li>● Can work at room temperature and atmosphere pressure.</li> <li>● No need any post-thermal treatment (no need for calcination).</li> </ul>	<ul style="list-style-type: none"> <li>○ The needs of energy and sonicator machine to provide ultrasound irradiation.</li> <li>○ Long synthesis time.</li> </ul>	(Tan et al., 2013)
Dip-coating	<ul style="list-style-type: none"> <li>● Method for generating thin film layer of composite.</li> </ul>	<ul style="list-style-type: none"> <li>○ High calcination temperature.</li> <li>○ Consumes various and costly reagents.</li> <li>○ Long synthesis time.</li> <li>○ Lower photocatalytic activity of thin film composite rather than powder composites.</li> </ul>	(Omri and Benzina, 2015)
Molecular self-assembly	<ul style="list-style-type: none"> <li>● Strong chemical bonding between TiO<sub>2</sub> and carbonaceous materials (chemisorption).</li> <li>● Possibility to create complex multicomponent system composites.</li> </ul>	<ul style="list-style-type: none"> <li>○ Consumes various and costly reagents.</li> <li>○ Long synthesis time.</li> <li>○ High calcination temperature.</li> </ul>	(Sun et al., 2016)
Electrospinning	<ul style="list-style-type: none"> <li>● Method for generating ultrathin fiber composites.</li> <li>● Possibility to create various form, shape, and size of the fiber composite.</li> </ul>	<ul style="list-style-type: none"> <li>○ The needs of energy to provide electrostatic field.</li> <li>○ High calcination temperature.</li> <li>○ High consumption of various and costly reagents.</li> <li>○ Low productivity</li> </ul>	(Peining et al., 2012; Zhang et al., 2017b)

recombination because of entropy the electron ‘becomes lost’. The holes that remain ( $h^+$ ) on the TiO<sub>2</sub> are available to take part in redox reactions. Third, carbonaceous materials act as sensitizers that provide electrons to TiO<sub>2</sub>. These electrons can be excited by photons of the light energy, thereby resulting in the generation of superoxide radicals from adsorbed molecular oxygen. In addition, the positively charged carbonaceous materials attract electrons from

TiO<sub>2</sub> and create a hole ( $h^+$ ) in the TiO<sub>2</sub> valence band, which reacts with adsorbed water to create hydroxyl radicals. Fourth, the presence of carbon-oxygen-titanium linkages in the composite system reduces the band gap and extends the absorption band into the lower energy visible range (Wang et al., 2005). The carbonaceous-TiO<sub>2</sub> photocatalysis mechanisms are summarized in Fig. 4.

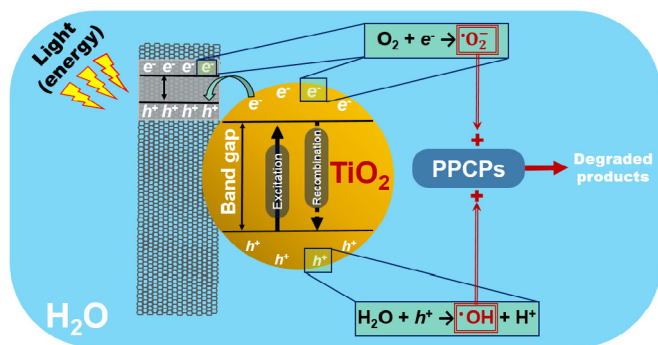


Fig. 4. The mechanism of carbonaceous-TiO<sub>2</sub> photocatalysis.

#### 4.1. Activated carbon-TiO<sub>2</sub> composites

Activated carbon (AC) is a porous and amorphous solid carbon material which can be derived from coal or plants and is the most common carbonaceous material used for water or wastewater treatment. AC is typically prepared in two stages: carbonization (i.e., heating at temperature between 400 and 600 °C to drive off volatile components) and activation (i.e., increase surface area using an activating agent such as steam or CO<sub>2</sub>) (Li Puma et al., 2008). AC has a rigid porosity on the macro (>50 nm), meso (2–50 nm) and micro (<2 nm) scale pore range, with a specific surface area ranging up to 1250 m<sup>2</sup> g<sup>-1</sup> (Leary and Westwood, 2011; Maillier et al., 2016; Park et al., 2015; Patiño et al., 2015). Further, AC has wide range of functional groups on its surface including carboxyl, carbonyl, phenol, lactone and quinone groups that enhance the affinity of AC for PPCP (Bhatnagar et al., 2013). For these reasons, researchers have used AC as a supporting material in photocatalysis applications using methods such as sol-gel (Rey et al., 2012), chemical vapor deposition (Li Puma et al., 2008), impregnation (Gar Alalm et al., 2016), pyrolysis (Lara-López et al., 2017), precipitation (Otiño et al., 2017), hydrothermal preparation (Liu et al., 2007), microwave assisted synthesis (Orha et al., 2017), sonochemical treatment (Tan et al., 2013), dip-coating (Omri and Benzina, 2015), and molecular self-assembly (Sun et al., 2016).

AC-TiO<sub>2</sub> composites have been extensively studied for PPCP degradation (Basha et al., 2011, 2010; El-Sheikh et al., 2017; Gar Alalm et al., 2016; Keane et al., 2011; Khraisheh et al., 2013; Ma et al., 2017; Quiñones et al., 2014; Rey et al., 2012; Rosa et al., 2017). They are effective due to their uniform pore structure that enhances photocatalytic activity, and their high ability to adsorb and concentrate contaminants (Ma et al., 2017). For instance, Khraisheh et al. (2013) prepared activated charcoal from coconut shell material, an inexpensive source of carbon known to also have superior quality, and prepared a TiO<sub>2</sub> composite material. AC-TiO<sub>2</sub> had a highest removal efficiency, and the composite removed carbamazepine up to 98% (UVC intensity of 10.5 mW cm<sup>-2</sup> for 40 min). In addition, response surface methodology (RSM) and a central composite design model (CCD) were used to evaluate the optimum parameters (e.g., calcination temperature and AC loading amount) for preparing AC-TiO<sub>2</sub> composite. This group of researchers demonstrated that surface area, pore-size distribution, TiO<sub>2</sub> crystal structure and composite size have significant influences on the adsorption and photocatalytic activities of AC-TiO<sub>2</sub> composites. The complete removal of pharmaceuticals (e.g., amoxicillin, ampicillin, paracetamol and diclofenac) can be achieved using AC-TiO<sub>2</sub> composites after 180 min of sunlight irradiation, while using only TiO<sub>2</sub> could not match this performance (Gar Alalm et al., 2016). The enhanced performance is due to the transfer of sorbates on AC to photoactive TiO<sub>2</sub> through the common interface between them

(Leary and Westwood, 2011). Moreover, in this study, the total costs of AC-TiO<sub>2</sub> was estimated to be around 2.3–3.19 € per m<sup>3</sup> of treated water which is similar to the total cost for TiO<sub>2</sub>. Therefore, using AC-TiO<sub>2</sub> rather than TiO<sub>2</sub> is recommended. Another study of AC-TiO<sub>2</sub> composites showed higher adsorption and photodegradation of amoxicillin, a β-lactam antibiotic, than for pure AC or TiO<sub>2</sub> (Basha et al., 2011). This may occur due to chemisorption between amoxicillin and functional groups on the AC-TiO<sub>2</sub> surface involving valence bond sharing or electron exchange (Basha et al., 2010). Moreover, this AC-TiO<sub>2</sub> maintained its photocatalytic activity over four consecutive cycles of treatment and cleaning. This work shows that TiO<sub>2</sub> loadings and substrate adsorption are important factors affecting photocatalysis by AC-TiO<sub>2</sub> composites. Meanwhile, Quiñones et al. (2014) reported enhanced photocatalytic activity and reusability of magnetic AC-TiO<sub>2</sub>-Fe by adding ozone (i.e., photocatalytic ozonation). Photocatalytic ozonation of magnetic AC-TiO<sub>2</sub>-Fe showed a high degree of mineralization of metoprolol (>80%) at 5 h reaction times. Moreover, this material can be easily separated and the photocatalytic ozonation of this material exhibited no significant loss, retaining the overall TOC removal at 75%–85% over 10 consecutive cycles. The higher removal in this system could be attributed to the synergies of direct ozonation, ozone photolytic decomposition, heterogeneous photocatalysis, Fenton reaction, and the photo-Fenton reaction.

The surface chemistry of AC plays an important role in the production of oxidants such as super oxide and hydroxyl radicals (Velo-Gala et al., 2017). AC itself can act as a photocatalyst by promoting electrons from the valence band into the conduction band and increasing the generation of •OH in the solution under UV or solar irradiation (Velo-Gala et al., 2013). Studies of the correlation between the surface chemistry of AC and the concentration of oxidants shows that: 1) while an increase in lactone and anhydride surface groups leads to more •OH under UV irradiation, generation of •OH decreased with increasing surface oxygen content (e.g., carboxyl groups); 2) an increase in physisorbed water enhanced production of superoxide (•O<sub>2</sub><sup>-</sup>) during UV irradiation; 3) under solar irradiation, •OH concentrations increase with an increase in carboxyl surface groups but the concentration of •O<sub>2</sub><sup>-</sup> decreases as carboxyl and quinone surface groups increases; 4) in both UV and solar irradiation, aromatic ring and surface oxygen groups on AC contributed to the stabilization of photogenerated electrons; and 5) AC with the lowest energy band gap favors enhanced •OH production, while the larger energy band gap of AC preferentially enhances production of •O<sub>2</sub><sup>-</sup>.

The extension of absorption bands to longer visible wavelengths is one of the proposed synergistic processes in AC-TiO<sub>2</sub> composites. However, at present the photocatalytic activity of AC-TiO<sub>2</sub> composites is limited due to insufficient interactions between AC and TiO<sub>2</sub> (Leary and Westwood, 2011). Diffuse reflectance spectra of AC-TiO<sub>2</sub> show absorption at wavelength shorter than UV-vis 400 nm (approximately 380 nm) which is not so different with the bare TiO<sub>2</sub> (385 nm) (Omri et al., 2014; Wang et al., 2013). Thus, there is minimal shifting towards the visible light region in the AC-TiO<sub>2</sub> composite system. TiO<sub>2</sub> loaded onto an AC fiber belt felt (ACF) has a lower band gap (2.95 eV) compared to pure TiO<sub>2</sub> (3.22 eV) due to perturbation of the TiO<sub>2</sub> absorption by its interaction with ACF (Li et al., 2017a). This may be because of surface morphology; the interactions that shift and scale absorption bands are intense but only over molecular distances (Kumar et al., 2017). Another study showed that F-N codoped TiO<sub>2</sub> on magnetic AC exhibits an enhanced absorption at visible wavelengths with a significant red shift in the transition measured using UV-vis diffuse reflectance spectra (Ma et al., 2017). Codoping with F and N gave a better match for excitation with sunlight. The band gap of the magnetic AC-F-N-TiO<sub>2</sub> composite was estimated to be 2.6–3.0 eV. In addition the



small particle size of this composite yields a greater surface defect density, further increasing absorption at low band gap energies (Martins et al., 2017).

There are several studies however that show decreased photocatalytic activity for AC-TiO<sub>2</sub> composites compared to pure TiO<sub>2</sub> (Rey et al., 2012; Rosa et al., 2017). The photocatalytic activity of titania-coated magnetically activated carbon (TiFeC) was not as high as pure TiO<sub>2</sub> (Degussa 25) for photodegradation of metoprolol, very likely due to non-uniform size and TiO<sub>2</sub> concentration in the composite particles (Rey et al., 2012). However, this TiFeC composite showed continued good reactivity through five series of photocatalytic experiments, and it is easy to separate using an external magnetic field. The superiority of pristine TiO<sub>2</sub> compared to the AC-TiO<sub>2</sub> composite may be due to the higher availability of active sites and the physicochemical properties of AC (Cordero et al., 2007; Rosa et al., 2017). In addition, the incorrect use of the simplified Langmuir-Hinshelwood equation for analyzing the photocatalytic kinetics of AC-TiO<sub>2</sub> can lead to erroneous conclusions (Asenjo et al., 2013). Therefore, the development of new synthesis methods for AC-TiO<sub>2</sub> composites that are active under UV and solar irradiation is still needed. In parallel, an appropriate photocatalysis kinetics model for AC-TiO<sub>2</sub> composites needs to be developed to provide a fundamental physical mechanism describing photodegradation rates as an evaluation of synergetic interaction.

#### 4.2. Carbon nanotube-TiO<sub>2</sub> composites

Recent decades have seen greatly increased interest in photocatalysis using carbon nanotubes-TiO<sub>2</sub>. CNTs are composed of cylindrical graphene sheets and can be categorized as single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs) (Iijima, 1991). CNTs have an usually high specific surface area to mass ratio (e.g., 75–1020 m<sup>2</sup> g<sup>-1</sup>) with exceptional sorption capability (Czech and Buda, 2016; Jung et al., 2015; Lerman et al., 2013; Patiño et al., 2015; Peigney et al., 2001; Wang et al., 2015; Wei et al., 2013). In contrast to AC, CNTs are prone to aggregation because of hydrophobic interactions, van-der Waals forces, and  $\pi$ - $\pi$  stacking; these processes lead to the formation of four different types of adsorption sites: inner cavities, interstitial channels, external grooves, and outermost surfaces (Agnihotri et al., 2006; Apul and Karanfil, 2015). In addition, CNTs show superior hydrophobicity making them as a promising material (Chen et al., 2007; Jung et al., 2015; Yang and Xing, 2010). The sorption behavior of CNTs mainly depends on their surface chemistries and the nature of contaminants. Due to the rehybridized sp<sup>2</sup> C-C bonds and one dimensional microstructure, CNTs exhibit unique mechanical, thermal and semiconductor properties (Cao et al., 2013). Further, CNTs have many advantages, such as; large electron-storage capacity, superior metallic conductivity, and light absorption at a broad range of wavelengths (Woan et al., 2009). In general, CNTs are an attractive option for a supporting material to enhance photocatalytic activity due to their outstanding characteristics. Many efforts have been made to exploit CNTs as a supporting material with preparation methods including hydrothermal (Yuan et al., 2016), hydrolysis (An et al., 2007), restrained hydrolysis (Chen et al., 2011), simple evaporation and drying (Yao et al., 2008), sol-gel (Abbas et al., 2016), surfactant wrapping sol-gel (Gao et al., 2009), chemical vapor deposition (CVD) (Ma et al., 2012), physical vapor deposition (PVD) (Fan et al., 2006), electrophoretic deposition (EPD) (Bordbar et al., 2015), electrostatic attraction (Daneshvar Tarigh et al., 2015), solvothermal (Zhou et al., 2010), and impregnation (Xu et al., 2010). Common to these methods is that TiO<sub>2</sub> is attached to the CNTs by physical and chemical bonding. TiO<sub>2</sub> binds more strongly to functionalized CNTs (i.e., chemisorption)

compared to physisorption on pristine CNTs (Ayissi et al., 2015). In addition, chemical bonding provides better electron transfer than physical bonding due to proximity and chemical coupling.

The use of CNT-TiO<sub>2</sub> nanocomposites for the photodegradation of PPCP has been of considerable scientific interest. In one study, functionalized CNTs and larger TiO<sub>2</sub> crystal sizes were necessary to provide good contact between the CNTs and TiO<sub>2</sub>; this interaction lead to a better enhancement of photocatalytic activity for caffeine photodegradation (Marques et al., 2013). In another study, acid treated CNT-TiO<sub>2</sub>-SiO<sub>2</sub> showed better photodegradation of diclofenac relative to untreated CNT-TiO<sub>2</sub>-SiO<sub>2</sub> due to optimal structure and well-shaped anatase TiO<sub>2</sub> crystals (Czech and Buda, 2016). The role of SiO<sub>2</sub> in the CNT-TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite was to prevent transformation from the active anatase phase to the inactive rutile phase of TiO<sub>2</sub>, and also as an effective agent for dispersing TiO<sub>2</sub> on the surface of CNTs (Kibombo et al., 2012). Further, photodegradation decreased the toxicity of treated waters as shown by Microtox toxicity tests. In another study, the photocatalytic activity of CNT-TiO<sub>2</sub> towards diclofenac was increased with the addition of dissolved oxygen and H<sub>2</sub>O<sub>2</sub> as an electron scavenger (Martínez et al., 2011a).

Use of solar radiation for photocatalysis is promising for future photocatalytic systems. Yuan et al. (2016) showed that CNT-TiO<sub>2</sub>-N exhibited high photocatalytic activity in degrading ibuprofen under visible light irradiation. The function of N-doping in the composite system was to reduce the band gap. In addition, the occurrence of CNTs resulted in a higher adsorption capacity and increased activity because the CNTs could act as electron scavengers. This successful synergetic effect was mainly attributed to the good binding interaction between CNTs, TiO<sub>2</sub> and urea. Meanwhile, the use of an authentic wastewater matrix affected the photodegradation removal of PPCP relative to ultrapure water (Murgolo et al., 2015). These results clearly show that an idealized experiment (i.e., experiment in ultrapure water) has limited value for understanding real-world treatment operations.

Recently, increased attention has been given to the need to recover and separate nanosized photocatalysts to reduce their negative impacts on the environment. An effective method for preventing these potential impacts is immobilization of the photocatalyst on a supporting material. Two possible approaches are 1) embedding or immobilizing the photocatalyst in a matrix or layer (e.g., electrospinning nanofibers) (Woan et al., 2009) and 2) attaching magnetic particles to the photocatalyst composite (Daneshvar Tarigh et al., 2015; Singh and Sarma, 2016; Zhang et al., 2015). A thin film of CNT-TiO<sub>2</sub> showed higher photocatalytic activity for the photodegradation of 4-chlorophenol compared to the TiO<sub>2</sub> thin film because the CNTs acted as an electron sink and reduced the recombination rate (Zouzelka et al., 2016). An immobilized photocatalyst system may be preferable for several reasons, such as: 1) thin films can be easily adopted for use in continuous flow systems, 2) it can prevent photocatalyst agglomeration and 3) it does not require separation or filtration (Dong et al., 2014). Although photocatalyst immobilization provides an alternative solution to the separation problem, the photochemical reactivity of supported CNT-TiO<sub>2</sub> composites is typically reduced due to the decreased mass transfer rate, hindrance of light harvesting by the inert support and reduction of photocatalyst active surface area to volume ratio (Mascolo et al., 2007). Adding magnetic particles to nanocomposites is an alternative technique for separation and recovery. However, it should be noted that attaching magnetic particles to CNT surfaces would decrease the sites available for attaching TiO<sub>2</sub> (Fei et al., 2016; Li et al., 2015). In order to overcome this issue, Ateia et al. (2017b) explored the potential advantage of using the inherent magnetic impurities of magnetic carbon nanotubes (MCNT) which are due to magnetic particles trapped inside

the graphene cylinders, as a green and facile method of removing organic micropollutants from water.

CNT-TiO<sub>2</sub> and AC-TiO<sub>2</sub> composites show higher photocatalytic activity relative to pure TiO<sub>2</sub>. Enhancement of photocatalytic activity was correlated with surface area and the interaction between carbonaceous materials and TiO<sub>2</sub>. For AC-TiO<sub>2</sub>, better photocatalytic activity was correlated with the surface area of photocatalytically active sites. In contrast, CNTs also showed better interaction with TiO<sub>2</sub> (UV-vis diffuse reflectance spectra results) resulting in a smaller band gap (i.e., increased response to sunlight). Moreover, the inherent magnetic properties of CNTs showed good potential for use in photocatalytic applications as they would make the composites magnetic while preserving CNTs surfaces for TiO<sub>2</sub> particles.

#### 4.3. Graphene-TiO<sub>2</sub> composites

Graphene is a two dimensional sheet of carbon atoms connected by sp<sup>2</sup> bonds and with an aromatic  $\pi$  electron system (Novoselov et al., 2004). Graphene has a higher density of potential adsorption sites compared to CNTs due to the open plane structure with three main types of adsorption sites; 1) open-up surface, 2) longitudinally-parallel external surface, 3) and interstitial channels (Ersan et al., 2017). Graphene has many unique properties including a high electron mobility, high mechanical strength, high thermal conductivity and high specific surface area (Hu et al., 2013). Many efforts have been made to use graphene in diverse applications including sensors (Wang and Arash, 2014), energy conversion and storage (Bonaccorso et al., 2015), polymer composites (Mittal et al., 2015), drug delivery systems (Zhang et al., 2017b), and environmental applications (Chabot et al., 2014; Upadhyay et al., 2014). In the environmental applications, graphene nanomaterials can be used as catalysts and adsorbents or disinfectant agents. Graphene is the precursor of the graphene-family nanomaterials (e.g., graphene oxide, reduced graphene oxide, fullerene, carbon nano-onion and CNTs) (Suárez-Iglesias et al., 2017). Of these, graphene oxide (GO) and reduced graphene oxide (rGO) show high efficiency for water treatment due to the presence of several surface functional groups (e.g., hydroxyl, carboxyl and epoxy) that act as adsorption sites (Fei et al., 2016; Shen et al., 2015). Moreover, GO itself is photocatalytically active (Yeh et al., 2011). GO can be made by chemical functionalization of graphene in several ways, such as: 1) the Brodie method (B.C. Brodie, 1859), 2) the Staudenmaier method (Poh et al., 2012), 3) the Hoffman method (Poh et al., 2012), and 4) the Hummers method (Hummers and Offeman, 1958). However, GO is electrically insulating due to the chemical disruption of the  $\pi$ -network and the reduction of GO (i.e., conversion to reduced graphene oxide) has become an important reaction for restoring the electrical conductivity of the material (Gao, 2015). Moreover, reduction of GO can be achieved using chemical treatment (Stankovich et al., 2007), thermal mediation (Lin et al., 2010), and electrochemical treatment (Shao et al., 2010). Reduced graphene oxide is characterized by graphene domains with residual oxygen functionalities on their surface, and improved electrical conductivity relative to GO (Compton and Nguyen, 2010). Numerous studies using GO or rGO as a co-material with TiO<sub>2</sub> for photocatalysis have been performed. Graphene-TiO<sub>2</sub> is a robust composite and can be synthesized by several methods such as: solution mixing (Morales-Torres et al., 2013), sol-gel (Azizi, 2017), hydrothermal (Wu et al., 2015), electrostatic self-assembly (Kim et al., 2012), molecular grafting (Tang et al., 2010), chemical exfoliation (Akhavan and Ghaderi, 2009), liquid phase deposition (Pastrana-Martinez et al., 2012), and electrospinning (Peining et al., 2012). Each synthesis method can affect the graphene-TiO<sub>2</sub> characteristics and photocatalytic activity (Faraldos and Bahamonde, 2017). A

stronger interaction between graphene and TiO<sub>2</sub> would give enhance photocatalytic activity (Kamat, 2010).

TiO<sub>2</sub> nanosheet-graphene 2D-2D composite showed higher removal of 2,4-dichlorophenol than bare TiO<sub>2</sub> due to strong electronic and physical coupling in the material (Sun et al., 2013). This interaction lead to enhancement of electron transfer and, thereby, superior photocatalytic activity. Further, Minella et al. (2017) demonstrated synergy using a graphene-TiO<sub>2</sub> composite. They observed electron transfer from reduced graphene oxide to TiO<sub>2</sub>, and hole transfer from TiO<sub>2</sub> to reduced graphene oxide. The formation of Ti-O-C linkages between hydroxyl surface groups on TiO<sub>2</sub> and the oxygenated surface of GO leads to narrower band gaps for the GO-TiO<sub>2</sub> composite (e.g., 2.5–2.9 eV). The surface chemistry also changed significantly because of the GO content, with a higher GO content giving a reduced point of zero charge (PZC), and more acidic composites due to the abundance of oxygenated groups (Morales-Torres et al., 2013).

Many researchers have tried to use visible light to drive graphene-TiO<sub>2</sub> photocatalysts. Under visible irradiation, rGO-TiO<sub>2</sub> composites showed significant photodegradation of diphenhydramine relative to TiO<sub>2</sub> because rGO acted as a sensitizer (Pastrana-Martinez et al., 2012) and electron sink (Gillespie and Martsinovich, 2017). Similar synergism in graphene-TiO<sub>2</sub> has also been seen in other carbonaceous-TiO<sub>2</sub> composites (e.g., CNT-TiO<sub>2</sub>, fullerene-TiO<sub>2</sub>, and AC-TiO<sub>2</sub>) (Yang et al., 2013; Zhang et al., 2010). Although GO-TiO<sub>2</sub> has similar enhancement mechanisms, there are significant differences in the mass ratios of carbon to TiO<sub>2</sub> (Yang et al., 2013). A lower mass ratio of GO is necessary to achieve optimum photocatalytic activity compared to CNT-TiO<sub>2</sub>. The pore structure and aggregation behavior of GO vary among CNTs. GOs are composed of two-dimensional graphene sheets and are more prone to restacking compared to CNTs (Ersan et al., 2017). Thus, higher GO mass ratios (i.e., above optimum) lead to the aggregation of GO-TiO<sub>2</sub> composites, lowering photocatalytic activity.

The enhanced photocatalytic activity of graphene-TiO<sub>2</sub> composites make them an ideal material for remediating PPCP. However, one of the major obstacles to using nano-scale catalysts in water treatment is the difficulty in separating and recovering the catalysts. Recently, 3D porous rGO-TiO<sub>2</sub> aerogel was shown to remove carbamazepine by more than 99% (Nawaz et al., 2017). The macroporous 3D structure of the aerogel resulted in abundant surface sites, effective charge separation, improved mass transport of contaminants and easy separation. Immobilization of rGO-TiO<sub>2</sub> on optical fibers for degradation of three different PPCP (carbamazepine, ibuprofen, and sulfamethoxazole) resulted in excellent degradation (PPCP removal up to 80%) and high durability (45 h operation) (Lin et al., 2016b). Another method for solving the catalyst recovery issue is by using magnetic separation. In this method magnetic nanoparticles are added to the surface of the composite. A magnetically recyclable GO-TiO<sub>2</sub> composite showed up to 99% removal of carbamazepine and caffeine within 60 min under UV irradiation and this composite was fully recoverable and reusable by magnetic separation (Linley et al., 2014). These three methods (3D aerogel, immobilization and magnetic separation) demonstrate a variety of solutions supporting the application of graphene-TiO<sub>2</sub> composite.

Overall, Table 3 summarizes the advantages and shortcomings of AC-TiO<sub>2</sub>, CNT-TiO<sub>2</sub>, and graphene-TiO<sub>2</sub>. It should be emphasized that carbonaceous-TiO<sub>2</sub> composites are still in development stage and most studies have been performed at lab scale. A variety of synthesis methods and operating conditions within the studies make it hard to compare directly to determine the appropriate synthesis method (Faraldos and Bahamonde, 2017). Therefore, the establishment of a standard method for evaluating the photocatalytic activity of carbonaceous-TiO<sub>2</sub> followed by a pilot-scale

**Table 3**  
Comparison of AC-TiO<sub>2</sub>, CNT-TiO<sub>2</sub>, and graphene-TiO<sub>2</sub>.

Materials	Advantages	Shortcomings	Ref.
AC-TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>● AC initial cost is cheaper than CNT and graphene.</li> <li>● AC-TiO<sub>2</sub> has a larger particle size enabling recovery.</li> </ul>	<ul style="list-style-type: none"> <li>○ Insufficient interactions between AC and TiO<sub>2</sub> to provide extension of absorption bands to longer visible wavelengths.</li> </ul>	(Asiltürk and Şener, 2012; Leary and Westwood, 2011; Omri et al., 2014)
CNT-TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>● Interactions between CNT and TiO<sub>2</sub> extend of absorption bands to longer, visible wavelengths.</li> <li>● High mechanical strength and improved thermal stability, large electron-storage capacity, and superior metallic conductivity.</li> <li>● Potential use of inherently magnetic impurities in magnetic carbon nanotubes (MCNT)-TiO<sub>2</sub> for recovery.</li> </ul>	<ul style="list-style-type: none"> <li>○ CNT initial cost is higher than AC but cheaper than graphene.</li> <li>○ CNT is more prone to aggregate than AC.</li> </ul>	(Apul and Karanfil, 2015; Ateia et al., 2017b; Woan et al., 2009)
Graphene-TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>● Interactions between graphene and TiO<sub>2</sub> extend absorption bands to longer, visible wavelengths.</li> <li>● High mechanical strength and improved thermal stability, large electron-storage capacity, and superior metallic conductivity.</li> <li>● Possibility of high interfacial contact between graphene and TiO<sub>2</sub>, providing higher photocatalytic activity via 2D graphene sheet.</li> </ul>	<ul style="list-style-type: none"> <li>○ Graphene cost is more expensive than AC and CNT.</li> <li>○ Graphene is more prone to clumping than CNT.</li> <li>○ Separation issues for graphene-TiO<sub>2</sub>.</li> </ul>	(Ersan et al., 2017; Zhang et al., 2012)

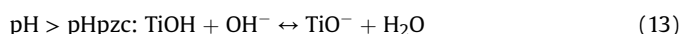
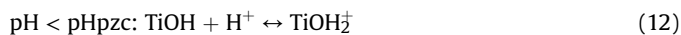
study are needed to assess the cost and support real-world applications of carbonaceous-TiO<sub>2</sub>.

## 5. The role of water chemistry in photocatalytic performance

Water chemistry (e.g., pH, temperature, contaminant concentration, dissolved oxygen, natural organic matters and inorganic species) has a significant effect on the photocatalysis of PPCP. This section discusses the significance of these parameters for the performance of carbonaceous composites of TiO<sub>2</sub>.

### 5.1. Effect of pH

Acidity affects the surface charge of the catalyst which makes it one of the most significant operating parameters in heterogeneous photocatalysis (Chong et al., 2010). The net surface charge of the catalyst can be positive or negative due to the amphoteric behavior of the metal oxide catalyst (e.g., TiO<sub>2</sub>) (Mirzaei et al., 2016). The pH of the point of zero charge (pH<sub>PZC</sub>) helps define the effect of pH on the surface charge of the catalyst. pH<sub>PZC</sub> is the pH at which the surface charge of the catalyst is zero, and it depends on the surface chemistry. Several studies found the pH<sub>PZC</sub> of TiO<sub>2</sub>, AC-TiO<sub>2</sub>, CNT-TiO<sub>2</sub> and graphene-TiO<sub>2</sub> materials to lie in the range of 6–8, 7–9, 4–6 and 4–5 respectively (Ahmadi et al., 2016; Andronic et al., 2014; Barroso-Bogeat et al., 2016; Hua et al., 2016; Malekshoar et al., 2014; Schindler and Gamsjäger, 1972). For acidic conditions (pH < pH<sub>PZC</sub>), the surface charge of the catalyst is positive and increases attraction for negatively charged contaminants, while for basic conditions (pH > pH<sub>PZC</sub>), the catalyst surface charge is negative, attracting positively charged pollutants (Chong et al., 2010). The protonation and deprotonation of TiO<sub>2</sub> with pH is shown by the following reactions (Eqs. (12) and (13)):



At low pH, photogenerated holes ( $h^+$ ) are the dominant oxidizing species, while under neutral or alkaline solutions, hydroxyl radicals play the dominant role in the contaminant oxidation (Lee et al., 2016). However, at high pH, photocatalytic reactions may be inhibited because OH<sup>-</sup> anions act as hole ( $h^+$ ) scavengers to form •OH (Yuan et al., 2016), followed by rapid scavenging of •OH by bicarbonate species to produce radical carbonate anion which is

less oxidizing than •OH (Lai et al., 2017b). Photocatalytic oxidation of ibuprofen using CNT-TiO<sub>2</sub> co-doping urea, showed that the highest removal efficiency was achieved when the pH of the solution was 5 due to the catalyst surface charge (Yuan et al., 2016). In this study, the pH<sub>PZC</sub> of the CNT-TiO<sub>2</sub> composite with co-doped urea was around 6. In this acidic conditions, ibuprofen would deprotonate to become its conjugate base which has a negative charge (Hashim and Khan, 2011). At pH 5, the surface charge of the catalyst is positive and ibuprofen would have a negative charge. In this example, changing pH was able to create electrostatic attraction between the catalyst and the contaminant. When the solution pH was greater than 5, repulsion between the catalyst and ibuprofen reduced surface affinity and therefore photocatalytic activity. In a different study, optimum photodegradation of amoxicillin using AC-TiO<sub>2</sub> was achieved at pH 9 (Basha et al., 2011). Chlorotetracycline (CTC) removal using GO-TiO<sub>2</sub> showed an increase in degradation when the pH was increased from 1 to 4 due to the net charge of chlorotetracycline and an attractive  $\pi$ - $\pi$  interaction (Li et al., 2017b). Therefore, appropriate pH control must be considered for carbonaceous-TiO<sub>2</sub> photocatalysis in order to achieve effective PPCP removal.

### 5.2. Effect of water temperature

Photocatalysis can occur at ambient temperature and atmospheric pressure, which is one of its advantage for water treatment (Lee et al., 2016). The optimum reaction temperature for photocatalysis TiO<sub>2</sub> is in the range 20–80 °C (Herrmann, 1999). Temperature effects  $e^-$  and  $h^+$  diffusion/recombination rates, and adsorption of pollutants to the photocatalyst surface (Sarkar et al., 2014). An increase in temperature >80 °C may reduce adsorption (Chong et al., 2010) and promote recombination of charge carriers (Gaya and Abdullah, 2008), resulting in lower photocatalytic activity. At very low temperatures (<0 °C), the photocatalytic activity of TiO<sub>2</sub> decreases due to the increase in activation energy needed to excite a photocatalyst (Herrmann, 1999). However, we are not aware of any studies of the influence of temperature on the activity of carbonaceous-TiO<sub>2</sub> photocatalysts. The effect of temperature and the optimum conditions for effective PPCP removal by carbonaceous-TiO<sub>2</sub> photocatalysis must be investigated.

### 5.3. Effect of initial concentration of PPCP

The initial concentration of the contaminants is an important

parameter in photocatalysis. The highest removal efficiency of tetracycline (>95%) by photocatalytic CNT-TiO<sub>2</sub> was achieved when the concentration of tetracycline was 0.5 mg L<sup>-1</sup>. However for the same CNT-TiO<sub>2</sub> dosage, increasing tetracycline to 30 mg/L decreased the removal efficiency of tetracycline from the solution (Ahmadi et al., 2016). In an AC-TiO<sub>2</sub> study, longer reaction times were needed to achieve complete removal of metoprolol when the initial concentration was 50 mg L<sup>-1</sup> than when it was 10 mg L<sup>-1</sup> (Rey et al., 2012). At high PPCP concentrations, more PPCP molecules are adsorbed on the surface of the carbonaceous-TiO<sub>2</sub>, and these adsorbed contaminants inhibit photocatalysis by absorbing light before it can reach the catalyst surface (Mirzaei et al., 2016). In addition, the competitive consumption of hydroxyl radicals by photogenerated products (Lee et al., 2016) and light scattering (Ahmad et al., 2016) can also reduce photocatalytic activity in highly concentrated solutions. Previous studies of photocatalytic remediation of PPCP have been conducted with initial concentrations up to 1000 mg L<sup>-1</sup> (Table 1). However, studies of photocatalytic oxidation of PPCP at high concentration (on the order of mg L<sup>-1</sup>) may not be relevant for predicting photocatalytic degradation of PPCP under real conditions, where PPCP concentrations are on the order of µg L<sup>-1</sup> (Gulyas et al., 2016). It is critical to study photocatalytic oxidation at realistic concentrations of up to µg L<sup>-1</sup> to avoid the inhibiting effects of high pollutant load.

#### 5.4. Effect of dissolved oxygen

Dissolved oxygen (DO) is one of the important parameters that can affect photocatalysis. DO acts as an electron acceptor and the reaction of an electron (e<sup>-</sup>) with DO results in the formation of free •OH (Hoffmann et al., 1995). •OH is unselective and mostly occurs at the photocatalyst-H<sub>2</sub>O interface; it may also diffuse into the bulk solution (Kondrakov et al., 2014). The photocatalysis rate tends to increase with higher DO because O<sub>2(aq)</sub> has a strong affinity for e<sup>-</sup>, forming •O<sub>2</sub><sup>-</sup> and reducing the electron-hole recombination rate (Martinez et al., 2011a). Referring to Eqs. (5) and (6), the contribution of DO to the formation of •OH is small and H<sub>2</sub>O is still the main source of •OH from the photocatalytic process (Kondrakov et al., 2016). For Eq. (6), the generation of •OH strongly depends on the availability of h<sup>+</sup>, instead of the availability of e<sup>-</sup> to react with (O<sub>2</sub>)<sub>ads</sub> to generate superoxide (Eq. (5)). Generally, the Henry's Law constant can be used to give an approximation of DO in an aqueous system. The Henry's Law constant for O<sub>2</sub> solvation in water is as follows:

$$C = \frac{P}{K_H} \quad (14)$$

$$k_H = k_{H0} \exp \left[ -c \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (15)$$

Where C is the concentration of O<sub>2</sub> in the water, P is the partial gas pressure of O<sub>2</sub>, and k<sub>H</sub> and k<sub>H0</sub> are the Henry's Law constant and the Henry's Law constant at 298 K, respectively, T and T<sub>0</sub> are temperature and standard state temperature (298 K) in Kelvin, and c is a constant (1700 K for O<sub>2</sub>). This equilibrium law clearly shows the reason for the decrease in DO with increasing reaction temperature (i.e., hot water). Therefore, if the photocatalyst is not a photo-thermocatalyst, it may be preferential to operate the photoreactor at ambient temperature to ensure the supply of DO.

#### 5.5. Effect of natural organic matter

Natural organic matter (NOM) is a complex mixture of organic

substances that include humic substance, hydrophilic acids, proteins, lipids, carbohydrates, carboxylic acids, amino acids, and hydrocarbon, commonly present in surface waters (Karanfil et al., 1999; Ateia et al., 2017c; Shimizu et al., 2018). The effect of organic matter on the performance of photocatalysts has been studied by using natural organic matter (NOM) (Doll and Frimmel, 2005; Drosos et al., 2015; Li and Hu, 2016; Peng et al., 2017; Van Doorslaer et al., 2015). This highly variable reagent impacts the photocatalytic activity of TiO<sub>2</sub> towards PPCP. At high concentrations (ratio of NOM/TiO<sub>2</sub> is more than 4 mg g<sup>-1</sup>), NOM can inhibit the ability of TiO<sub>2</sub> to degrade carbamazepine, while at low concentrations of NOM (ratio of NOM/TiO<sub>2</sub> < 500 µg g<sup>-1</sup>), the degradation rate of carbamazepine was higher than for the pure blank solution without NOM (Drosos et al., 2015). This enhanced degradation was caused by the formation of reactive species from NOM (i.e., singlet molecular oxygen (<sup>1</sup>O<sub>2</sub>), superoxide anion (•O<sub>2</sub><sup>-</sup>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), solvated electrons (e<sup>-</sup><sub>aq</sub>), triplet excited states of NOM (<sup>3</sup>NOM\*)) which can assist in energy transfer (Doll and Frimmel, 2003). The low degradation rate for carbamazepine at high concentrations of NOM was caused by the ability of NOM to absorb and scatter light (Frimmel, 1994). In addition, low NOM concentrations can enhance photocatalytic removal of pollutants by creating π-π interactions on the photocatalyst surface that attract contaminants, while at high concentrations of NOM, NOM will prevent PPCP from reaching the surface (Drosos et al., 2015). The inhibitory effect of NOM (e.g., humic acid) can be counteracted with phosphate, because it leads to a more negatively charged surface that is more hydrophilic, and change the adsorption bind of humic acid (Long et al., 2016). Moreover, increasing DO was seen to counteract the inhibitory effect of NOM, because it increased the generation of superoxide (Ren et al., 2018). However, the effect of NOM on the photocatalysis of PPCP by carbonaceous-TiO<sub>2</sub> is nonetheless limited.

Generally, photocatalysis is used as a tertiary treatment on effluent resulting from secondary treatment (e.g., bioremediation) (Borges et al., 2014). Effluent organic matter (EfOM) is a general term for organic matter from biologically treated wastewater (Abbt-Braun et al., 2004; Cai and Lin, 2016; Michael-Kordatou et al., 2015). The composition of EfOM is different from natural NOM. EfOM is a combination of NOM, soluble microbial products (SMPs), proteins, surfactants and trace chemicals (Barker and Stuckey, 1999; Bodhipaksha et al., 2017; Jarusutthirak and Amy, 2007; Michael-Kordatou et al., 2015; Shon et al., 2007). EfOM is relatively hydrophilic and has a high proportion of protein-like substances with molecular sizes from 10<sup>2</sup> to 10<sup>5</sup> Da (Zhou et al., 2017). Therefore, the differences between EfOM and NOM include differences in their physical and chemical behavior, leading to differences in their photodegradation (Bodhipaksha et al., 2017).

#### 5.6. Effect of inorganic species

Inorganic species in wastewater can affect the photocatalytic remediation of PPCP. Inorganic species such as H<sub>2</sub>O<sub>2</sub>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, BrO<sub>3</sub><sup>-</sup>, and SO<sub>3</sub><sup>2-</sup> have a beneficial effect, enhancing photodegradation of contaminants by acting as electron scavengers, thereby increasing the production of hydroxyl radicals and generating other oxidizing species (Lee et al., 2016). However, excessive concentrations of inorganic species can suppress photodegradation by scavenging hydroxyl radicals. The removal efficiency for clofibric acid by TiO<sub>2</sub> decreased with the presence of many inorganic species (NaCl, FeCl<sub>3</sub>, FeCl<sub>2</sub>, CaCl<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>) due to the competition for free radicals, change in the pH of the solution and blockage of catalyst active sites by adsorption of anionic or cationic species (Rioja et al., 2016). UV-light attenuation by iron solutions also plays a significant role because it gives a yellowish

color to the solution; other colored ions can have a similar effect. Radical scavenging by sulfates and carbonates appeared to be stronger than for chlorides. For the case of NaCl, photodegradation of clofibrac acid at low concentrations of NaCl (<10,000 mg L<sup>-1</sup>) inhibits photocatalysis, while at higher NaCl concentrations (>10,000 mg L<sup>-1</sup>), the photodegradation rate was almost the same as for ultrapure water. Ionic strength has been indicated as an important parameter controlling photocatalytic activity; at high ionic strength, the repulsive force of contaminants can be mitigated and enhancing adsorption (Aguedach et al., 2008). Similarly, the presence of bicarbonate and chloride increases the toxicity of ifosfamide and cyclophosphamide during photocatalysis because of photodegradation products not found in the ultrapure water reference reaction, showing that inorganic species can promote alternative photodegradation pathways (Lai et al., 2017a). Finally, we are not aware of any studies of how inorganic species affect carbonaceous-TiO<sub>2</sub> photocatalysis. The occurrence of inorganic species in water can not be excluded from the investigation of carbonaceous-TiO<sub>2</sub> photocatalysis in real-world systems and pre-treatment to remove inorganic species are essential for effective photocatalytic treatment.

## 6. Effect of system parameters on photocatalytic activity

The removal efficiency ( $\tau = (Co - Ct)/Co$  is expressed in %, where  $Co$  is initial PPCP concentration and  $Ct$  is PPCP concentration at certain time) and oxidation rate ( $\ln(Ct/Co) = -k_{app}t$  is expressed in min<sup>-1</sup>, where  $k_{app}$  is pseudo-first order rate and  $t$  is reaction time) of photocatalytic processes depend on a number of parameters including excitation wavelength, light flux at surface, catalyst loading and material composition (nature of carbonaceous material, grain size, crystal structure of TiO<sub>2</sub>, and ratio of TiO<sub>2</sub> to carbonaceous material). To achieve high photocatalytic activity, these entangled parameters need to be optimized.

### 6.1. Effect of excitation wavelength

Photon energy must exceed the bandgap to excite a photocatalyst, and the process is favored by a material's absorption and scattering coefficients. All of these properties are material dependent. For pure commercial TiO<sub>2</sub> (band gap/ $E_G = 3.2$  eV), light at wavelengths  $\lambda \leq 400$  nm is required (Herrmann, 1999). The basic equation for converting bandgap to  $\lambda$  is:

$$E = \frac{hc}{\lambda} \quad (16)$$

$$E \text{ (eV)} = \frac{1240.8}{\lambda \text{ (nm)}} \quad (17)$$

Where  $h$  is Planck's constant ( $6.626 \times 10^{-34}$  Joule s),  $c$  is the speed of light ( $3 \times 10^8$  m s<sup>-1</sup>), 1 eV is equal to  $1.602 \times 10^{-19}$  Joule, and 1 Ångström is equal to  $10^{-10}$  m. A simple equation relating wavelength to band gap is given by Eq. (13). The UV spectrum can be divided into the UV-A (315–400 nm), UV-B (280–315 nm), and UV-C (100–280 nm) regions (Rincón and Pulgarin, 2005). Recently the potential excitation of carbonaceous-TiO<sub>2</sub> with visible light has attracted a lot of attention. Carbonaceous-TiO<sub>2</sub> composites have a band gap around 2.6–3 eV (413–477 nm) (Ashkarran et al., 2013; Taleshi, 2015). Carbonaceous material as a substrate creates a carbon-oxygen-titanium linkage which can expand the absorption band into visible wavelengths (Mallakpour and Khadem, 2016). Diclofenac degradation using a CNT-TiO<sub>2</sub>-SiO<sub>2</sub> photocatalyst under UV (365 nm) and solar irradiation (550 nm) showed good performance, with removal efficiencies above 70% for UV and >90% for

solar light (Czech and Buda, 2016). GO-nanofiber TiO<sub>2</sub> composite showed a higher photodegradation rate of 4-chlorophenol under visible light irradiation relative to pristine TiO<sub>2</sub> (Zhang et al., 2017a). In contrast, AC itself did not have a sufficiently strong interaction with TiO<sub>2</sub> to induce a bandgap reduction in the visible light region (Leary and Westwood, 2011). Therefore, more work is needed to improve AC-TiO<sub>2</sub> interaction, to reduce the band gap.

### 6.2. Effect of the loading of carbonaceous-TiO<sub>2</sub>

The kinetic rates of the photocatalysis reactions are generally proportional to the mass of the catalyst inside the reactor, but the reaction rates are become independent of catalyst mass above a certain level of loading due to the full absorption of photons by the photocatalytic bed (Herrmann, 1999). Various dosages of CNT-TiO<sub>2</sub> (0.1 g L<sup>-1</sup> - 0.4 g L<sup>-1</sup>) were used in the treatment of tetracycline. The highest removal efficiency was achieved at dosage of 0.2 g L<sup>-1</sup> (Ahmadi et al., 2016). Adding CNT-TiO<sub>2</sub> above its optimum loading can cause excessive light scattering (Chong et al., 2010). Below the optimum photocatalyst loading, radical generation may be insufficient (Mirzaei et al., 2016). A similar phenomenon occurred when using AC-TiO<sub>2</sub> to treat pharmaceuticals (e.g., amoxicillin, ampicillin, paracetamol and diclofenac). Loading AC-TiO<sub>2</sub> at other than its optimum concentration will lead to compromised performance due to an insufficient abundance of active sites and increased turbidity (Gar Alalm et al., 2016). Optimal photocatalyst loading depends on the size and geometry of the reactor (Fernández-Ibáñez et al., 1999) and the hydrodynamic particle size, smaller particle sizes are better due to the higher surface to mass ratio (Carbajo et al., 2018).

### 6.3. Effect of the ratio of carbonaceous material to TiO<sub>2</sub>

The mass ratio of carbonaceous materials to TiO<sub>2</sub> is a critical factor impacting performance. The two materials have a synergistic effect on adsorption and photocatalysis. Carbonaceous material enhances total adsorption due to the enlarged surface with favorable polarizability enhancing physisorption due to the  $\pi$ -cloud, while TiO<sub>2</sub> acts as a photocatalyst (Hu et al., 2015; Rabieh et al., 2016). Increasing the ratio of carbonaceous materials to TiO<sub>2</sub> increases the amount of adsorbed PPCP available for reaction. However, at mass ratios higher than the optimum, the carbonaceous material's surface is covered, blocking light and leading to decreased photocatalytic activity (Cheng et al., 2016; Nawaz et al., 2017). Ahmadi et al. (2016) tested different mass ratios of CNT to TiO<sub>2</sub>. Mass ratios of CNTs of 1.5% enhanced tetracycline removal up to 73% relative to 0.5%, and further increases of CNTs up to 10% did not improve the removal efficiency of tetracycline. The highest degradation rate at a mass ratio of 1.5% was attributed to the uniformity of anchoring of TiO<sub>2</sub> to support the photocatalytic reaction (Nawaz et al., 2017). The decrease of tetracycline removal at high CNT mass ratios was likely due to screening of light preventing photocatalysis (Wang and Zhang, 2011). High mass ratios of TiO<sub>2</sub> inhibited CNT-TiO<sub>2</sub> activity due to the aggregation of TiO<sub>2</sub> on CNTs, leading to the restriction of CNT-TiO<sub>2</sub> contact, negating the synergistic effects (Song et al., 2012).

The ratio of rGO to TiO<sub>2</sub> was seen to affect the wettability of the composite. The water contact angle of the rGO-TiO<sub>2</sub> composite with a TiO<sub>2</sub> mass ratio of 96.7% was 0° (super-hydrophilic), while with a mass ratio of TiO<sub>2</sub> of 14.5%, the water contact angle was 157° (super-hydrophobic) (Liu et al., 2015). These results show that the surface wettability of carbonaceous-TiO<sub>2</sub> can be controlled by tuning the amount of TiO<sub>2</sub>. Therefore, an optimum ratio of carbonaceous material to TiO<sub>2</sub> must be used when designing a carbonaceous-TiO<sub>2</sub> composite to achieve maximum photodegradation of PPCP.

## 7. Conclusions and recommendations

The occurrence of PPCP in surface waters is mainly due to incomplete removal of PPCP by sewage wastewater treatment plants and industrial wastewater treatment plants. Numerous techniques for removing PPCP have been tested, including activated sludge, wetlands, adsorption, membrane and advanced oxidation processes (AOPs). As one of the AOP techniques, photocatalysis based on TiO<sub>2</sub> has shown several advantages compared to the other techniques. Photocatalysis has the ability to degrade PPCP and further, the photocatalyst can be recovered and recycled. Researchers have tried to optimize performance by combining photocatalysts with carbonaceous materials. As a supporting material, carbonaceous materials give further advantages compared to bare TiO<sub>2</sub> including high photocatalytic activity, activity under solar irradiation, and easy separation. In the application of photocatalytic carbonaceous-TiO<sub>2</sub>, several interdependent parameters of water chemistry and the process are critical. Because of the many parameters, additional studies are required to find the optimum conditions for improved photodegradation of PPCP. The review above leads us to several recommendations:

- Many methods have been developed for preparing carbonaceous-TiO<sub>2</sub> composites. However, many of them require a lot of various chemicals and are expensive, complicated, and time consuming. Therefore, the development of relatively cheap, easy, scalable and environmentally friendly method is a very high priority.
- In most cases, researchers have used TiO<sub>2</sub> for the photocatalytic degradation of PPCP; very few reports are available regarding the use of carbonaceous-TiO<sub>2</sub> for removing PPCP. Moreover, most of the investigations have used high concentrations of PPCP (mg L<sup>-1</sup> scale). Since carbonaceous-TiO<sub>2</sub> can enhance the performance of photocatalytic systems relative to TiO<sub>2</sub> itself, the performance of other PPCP photodegradation composites under more realistic concentrations (up to µg L<sup>-1</sup>) is a high priority for future work.
- The characteristics of carbonaceous-TiO<sub>2</sub> (e.g., hydrodynamic particle size, surface wettability, surface charge and chemistry, pore size distribution, specific surface area, band gap, ratio of carbonaceous material to TiO<sub>2</sub>, and TiO<sub>2</sub> crystallite structure) and background water chemistries (e.g., pH, temperature, DO, NOM, and inorganic species) can influence photocatalytic activity. Research needs to be done to understand the fundamental mechanism of photocatalytic destruction of PPCP by carbonaceous-TiO<sub>2</sub> composite under different environmentally relevant conditions.
- Practical applications of carbonaceous-TiO<sub>2</sub> composites are still limited because available studies have been conducted using artificial conditions and in batch experimental systems (i.e., lab scale). These are inadequate for evaluating the photocatalytic activity of carbonaceous-TiO<sub>2</sub> in real treatment systems. Therefore, field scale experiments must be performed to evaluate the reliability of photocatalytic carbonaceous-TiO<sub>2</sub> systems.

The present review examined the current state of knowledge as well as the limitations in the application of carbonaceous-TiO<sub>2</sub> for removing PPCP. We hope this review will help to advance the field, leading to further development of carbonaceous-TiO<sub>2</sub> applications in water treatment.

## Acknowledgements

Dion Awfa is grateful for a scholarship from Indonesia

Endowment Fund for Education (LPDP). Mohamed Ateia would like to acknowledge the support from the Vice Deanship of Research Chairs at King Saud University.

## References

- Abbas, N., Shao, G.N., Haider, M.S., Imran, S.M., Park, S.S., Jeon, S.-J., Kim, H.T., 2016. Inexpensive sol-gel synthesis of multiwalled carbon nanotube-TiO<sub>2</sub> hybrids for high performance antibacterial materials. *Mater. Sci. Eng. C* 68, 780–788. <https://doi.org/10.1016/j.msec.2016.07.036>.
- Abbt-Braun, G., Lankes, U., Frimmel, F.H., 2004. Structural characterization of aquatic humic substances - the need for a multiple method approach. *Aquat. Sci.* 66, 151–170. <https://doi.org/10.1007/s00027-004-0711-z>.
- Agnihotri, S., Mota, J.P.B., Rostam-Abadi, M., Rood, M.J., 2006. Adsorption site analysis of impurity embedded single-walled carbon nanotube bundles. *Carbon* N. Y. 44, 2376–2383. <https://doi.org/10.1016/j.carbon.2006.05.038>.
- Aguedach, A., Brosillon, S., Morvan, J., Lhadi, E.K., 2008. Influence of ionic strength in the adsorption and during photocatalysis of reactive black 5 azo dye on TiO<sub>2</sub> coated on non woven paper with SiO<sub>2</sub> as a binder. *J. Hazard Mater.* 150, 250–256. <https://doi.org/10.1016/j.jhazmat.2007.04.086>.
- Ahmad, R., Ahmad, Zaki, Khan, A.U., Mastoi, N.R., Aslam, M., Kim, J., 2016. Photocatalytic systems as an advanced environmental remediation: recent developments, limitations and new avenues for applications. *J. Environ. Chem. Eng.* 4, 4143–4164. <https://doi.org/10.1016/j.jece.2016.09.009>.
- Ahmadi, M., Ramezani Motlagh, H., Jaafarzadeh, N., Mostoufi, A., Saeedi, R., Barzegar, G., Jorfi, S., 2016. Enhanced photocatalytic degradation of tetracycline and real pharmaceutical wastewater using MWCNT/TiO<sub>2</sub> nano-composite. *J. Environ. Manage* 186, 55–63. <https://doi.org/10.1016/j.jenvman.2016.09.088>.
- Akhavan, O., Ghaderi, E., 2009. Photocatalytic reduction of graphene oxide nano-sheets on TiO<sub>2</sub> thin film for photoinactivation of bacteria in solar light irradiation. *J. Phys. Chem. C* 113, 20214–20220. <https://doi.org/10.1021/jp906325q>.
- Al-Salhi, R., Abdul-Sada, A., Lange, A., Tyler, C.R., Hill, E.M., 2012. The xenometabolome and novel contaminant markers in fish exposed to a wastewater treatment works effluent. *Environ. Sci. Technol.* 46, 9080–9088. <https://doi.org/10.1021/es3014453>.
- Ali, A.M., Rønning, H.T., Sydnes, L.K., Alarif, W.M., Kallenborn, R., Al-Lihaibi, S.S., 2018. Detection of PPCPs in marine organisms from contaminated coastal waters of the Saudi Red Sea. *Sci. Total Environ.* 621, 654–662. <https://doi.org/10.1016/j.scitotenv.2017.11.298>.
- Ali, I., Al-Othman, Z.A., Alwarthan, A., 2016. Synthesis of composite iron nano adsorbent and removal of ibuprofen drug residue from water. *J. Mol. Liq.* 219, 858–864. <https://doi.org/10.1016/j.molliq.2016.04.031>.
- Alvarino, T., Suarez, S., Lema, J., Omil, F., 2018. Understanding the sorption and biotransformation of organic micropollutants in innovative biological wastewater treatment technologies. *Sci. Total Environ.* 615, 297–306. <https://doi.org/10.1016/j.scitotenv.2017.09.278>.
- An, G., Ma, W., Sun, Z., Liu, Z., Han, B., Miao, S., Miao, Z., Ding, K., 2007. Preparation of titania/carbon nanotube composites using supercritical ethanol and their photocatalytic activity for phenol degradation under visible light irradiation. *Carbon* N. Y. 45, 1795–1801. <https://doi.org/10.1016/j.carbon.2007.04.034>.
- Andronic, L., Enesca, A., Cazan, C., Visa, M., 2014. TiO<sub>2</sub>-active carbon composites for wastewater photocatalysis. *J. Sol-Gel Sci. Technol.* 71, 396–405. <https://doi.org/10.1007/s10971-014-3393-6>.
- Apul, O.G., Karanfil, T., 2015. Adsorption of synthetic organic contaminants by carbon nanotubes: a critical review. *Water Res.* 68, 34–55. <https://doi.org/10.1016/j.watres.2014.09.032>.
- Aristizabal-Ciro, C., Botero-Coy, A.M., López, F.J., Peñuela, G.A., 2017. Monitoring pharmaceuticals and personal care products in reservoir water used for drinking water supply. *Environ. Sci. Pollut. Res.* 24, 7335–7347. <https://doi.org/10.1007/s11356-016-8253-1>.
- Arpin-Pont, L., Martínez-Bueno, M.J., Gomez, E., Fenet, H., 2016. Occurrence of PPCPs in the marine environment: a review. *Environ. Sci. Pollut. Res.* 23, 4978–4991. <https://doi.org/10.1007/s11356-014-3617-x>.
- Asenjo, N.G., Santamaría, R., Blanco, C., Granda, M., Álvarez, P., Menéndez, R., 2013. Correct use of the Langmuir-Hinshelwood equation for proving the absence of a synergy effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon. *Carbon* N. Y. 55, 62–69. <https://doi.org/10.1016/j.carbon.2012.12.010>.
- Ashkarran, A.A., Fakhari, M., Mahmoudi, M., 2013. Synthesis of a solar photo and bioactive CNT-TiO<sub>2</sub> nanocatalyst. *RSC Adv.* 3, 18529. <https://doi.org/10.1039/c3ra42991a>.
- Asiltürk, M., Şener, Ş., 2012. TiO<sub>2</sub>-activated carbon photocatalysts: preparation, characterization and photocatalytic activities. *Chem. Eng. J.* 180, 354–363. <https://doi.org/10.1016/j.cej.2011.11.045>.
- Ateia, M., Apul, O.G., Shimizu, Y., Muflihah, A., Yoshimura, C., Karanfil, T., 2017a. Elucidating adsorptive fractions of natural organic matter on carbon nanotubes. *Environ. Sci. Technol.* 51, 7101–7110. <https://doi.org/10.1021/acs.est.7b01279>.
- Ateia, M., Ceccato, M., Budi, A., Ataman, E., Yoshimura, C., Johnson, M.S., 2018. Ozone-assisted regeneration of magnetic carbon nanotubes for removing organic water pollutants. *Chem. Eng. J.* 335, 384–391. <https://doi.org/10.1016/j.cej.2017.10.166>.
- Ateia, M., Koch, C., Jelavić, S., Hirt, A., Quinson, J., Yoshimura, C., Johnson, M., 2017b. Green and facile approach for enhancing the inherent magnetic properties of

- carbon nanotubes for water treatment applications. *PLoS One* 12, e0180636. <https://doi.org/10.1371/journal.pone.0180636>.
- Atea, M., Ran, J., Fujii, M., Yoshimura, C., 2017c. The relationship between molecular composition and fluorescence properties of humic substances. *Int. J. Environ. Sci. Technol.* 14, 867–880. <https://doi.org/10.1007/s13762-016-1214-x>.
- Ayissi, S., Charpentier, P.A., Palotas, K., Farhangi, N., Schwarz, F., Hofer, W.A., 2015. Preferential adsorption of TiO<sub>2</sub> nanostructures on functionalized single-walled carbon nanotubes: a DFT study. *J. Phys. Chem. C* 119, 15085–15093. <https://doi.org/10.1021/acs.jpcc.5b01406>.
- Azizi, F., 2017. Synthesis and characterization of graphene–N-doped TiO<sub>2</sub> nanocomposites by sol–gel method and investigation of photocatalytic activity. *J. Mater. Sci. Mater. Electron.* 28, 11222–11229. <https://doi.org/10.1007/s10854-017-6911-9>.
- Brodie, B.C., 1859. On the atomic weight of graphite author (s): B. C. Brodie source. *Phil. Trans. Roy. Soc. Lond.* 149 (1859), 249. Published by: Royal Society Stable URL. <http://www.jstor.org/stable/108699>. Accessed: 27-04-. *Philos. Trans. R. Society London* 149, 249–259.
- Baghdadi, M., Ghaffari, E., Aminzadeh, B., 2016. Removal of carbamazepine from municipal wastewater effluent using optimally synthesized magnetic activated carbon: adsorption and sedimentation kinetic studies. *J. Environ. Chem. Eng.* 4, 3309–3321. <https://doi.org/10.1016/j.jece.2016.06.034>.
- Bai, X., Acharya, K., 2016. Removal of trimethoprim, sulfamethoxazole, and triclosan by the green alga *Nannochloris* sp. *J. Hazard. Mater.* 315, 70–75. <https://doi.org/10.1016/j.jhazmat.2016.04.067>.
- Barceló, D., Petrovic, M., 2007. Pharmaceuticals and personal care products (PPCPs) in the environment. *Anal. Bioanal. Chem.* 387, 1141–1142. <https://doi.org/10.1007/s00216-006-1012-2>.
- Barker, D.J., Stuckey, D.C., 1999. A review of soluble microbial products (SMP) in wastewater treatment systems. *Water Res.* 33, 3063–3082. [https://doi.org/10.1016/S0043-1354\(99\)00022-6](https://doi.org/10.1016/S0043-1354(99)00022-6).
- Baron, P.A., Love, D.C., Nachman, K.E., 2014. Pharmaceuticals and personal care products in chicken meat and other food animal products: a market-basket pilot study. *Sci. Total Environ.* 490, 296–300. <https://doi.org/10.1016/j.scitotenv.2014.04.112>.
- Barroso-Bogeat, A., Alexandre-Franco, M., Fernández-González, C., Macías-García, A., Gómez-Serrano, V., 2016. Preparation of activated carbon–SnO<sub>2</sub>, TiO<sub>2</sub>, and WO<sub>3</sub> catalysts. Study by FT-IR spectroscopy. *Ind. Eng. Chem. Res.* 55, 5200–5206. <https://doi.org/10.1021/acs.iecr.5b04563>.
- Basha, S., Barr, C., Keane, D., Nolan, K., Oelgemöller, M., Tobin, J.M., 2011. On the adsorption/photodegradation of amoxicillin in aqueous solutions by an integrated photocatalytic adsorbent (IPCA): experimental studies and kinetics analysis. *Photochem. Photobiol. Sci.* 10, 1014–1022. <https://doi.org/10.1039/c0pp00368a>.
- Basha, S., Keane, D., Morrissey, A., Nolan, K., Oelgemöller, M., Tobin, J., 2010. Studies on the adsorption and kinetics of photodegradation of pharmaceutical compound, indomethacin using novel photocatalytic adsorbents (IPCA). *Ind. Eng. Chem. Res.* 49, 11302–11309. <https://doi.org/10.1021/ie101304a>.
- Batt, A.L., Furlong, E.T., Mash, H.E., Glassmeyer, S.T., Kolpin, D.W., 2017. The importance of quality control in validating concentrations of contaminants of emerging concern in source and treated drinking water samples. *Sci. Total Environ.* 579, 1618–1628. <https://doi.org/10.1016/j.scitotenv.2016.02.127>.
- Benotti, M.J., Brownawell, B.J., 2009. Microbial degradation of pharmaceuticals in estuarine and coastal seawater. *Environ. Pollut.* 157, 994–1002. <https://doi.org/10.1016/j.envpol.2008.10.009>.
- Benotti, M.J., Trenholm, R.A., Vanderford, B.J., Holady, J.C., Stanford, B.D., Snyder, S.A., 2009. Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water. *Environ. Sci. Technol.* 43, 597–603. <https://doi.org/10.1021/es801845a>.
- Bhatnagar, A., Hogland, W., Marques, M., Sillanpää, M., 2013. An overview of the modification methods of activated carbon for its water treatment applications. *Chem. Eng. J.* 219, 499–511. <https://doi.org/10.1016/j.cej.2012.12.038>.
- Bodhipaksha, L.C., Sharpless, C.M., Chin, Y.-P., MacKay, A.A., 2017. Role of effluent organic matter in the photochemical degradation of compounds of wastewater origin. *Water Res.* 110, 170–179. <https://doi.org/10.1016/j.watres.2016.12.016>.
- Bonaccorso, F., Colombo, L., Yu, G., Stoller, M., Tozzini, V., Ferrari, A.C., Ruoff, R.S., Pellegrini, V., 2015. Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. *Science* (80) 347. <https://doi.org/10.1126/science.1246501>, 1246501–1246501.
- Bonvin, F., Rutler, R., Chavre, N., Halder, J., Kohn, T., 2011. Spatial and temporal presence of a wastewater-derived micropollutant plume in Lake Geneva. *Environ. Sci. Technol.* 45, 4702–4709. <https://doi.org/10.1021/es2003588>.
- Bordbar, M., Alimohammadi, T., Khoshnevisan, B., Khodadadi, B., Yeganeh-Faal, A., 2015. Preparation of MWCNT/TiO<sub>2</sub>-Co nanocomposite electrode by electrophoretic deposition and electrochemical study of hydrogen storage. *Int. J. Hydrogen Energy* 40, 9613–9620. <https://doi.org/10.1016/j.ijhydene.2015.05.138>.
- Borges, M.E., Hernández, T., Esparza, P., 2014. Photocatalysis as a potential tertiary treatment of urban wastewater: new photocatalytic materials. *Clean Technol. Environ. Policy* 16, 431–436. <https://doi.org/10.1007/s10098-013-0637-z>.
- Brunsch, A.F., ter Laak, T.L., Rijnaarts, H., Christoffels, E., 2018. Pharmaceutical concentration variability at sewage treatment plant outlets dominated by hydrology and other factors. *Environ. Pollut.* 235, 615–624. <https://doi.org/10.1016/j.envpol.2017.12.116>.
- Cai, M.J., Lin, Y.P., 2016. Effects of effluent organic matter (EfOM) on the removal of emerging contaminants by ozonation. *Chemosphere* 151, 332–338. <https://doi.org/10.1016/j.chemosphere.2016.02.094>.
- Cao, Q., Yu, Q., Connell, D.W., Yu, G., 2013. Titania/carbon nanotube composite (TiO<sub>2</sub>/CNT) and its application for removal of organic pollutants. *Clean Technol. Environ. Policy* 15, 871–880. <https://doi.org/10.1007/s10098-013-0581-y>.
- Carbajo, J., Tolosana-Moranchel, A., Casas, J.A., Fardalos, M., Bahamonde, A., 2018. Analysis of photoefficiency in TiO<sub>2</sub> aqueous suspensions: effect of titania hydrodynamic particle size and catalyst loading on their optical properties. *Appl. Catal. B Environ.* 221, 1–8. <https://doi.org/10.1016/j.apcatb.2017.08.032>.
- Cardoso, O., Porcher, J.M., Sanchez, W., 2014. Factory-discharged pharmaceuticals could be a relevant source of aquatic environment contamination: review of evidence and need for knowledge. *Chemosphere* 115, 20–30. <https://doi.org/10.1016/j.chemosphere.2014.02.004>.
- Carmona, E., Andreu, V., Picó, Y., 2014. Occurrence of acidic pharmaceuticals and personal care products in Turia River Basin: from waste to drinking water. *Sci. Total Environ.* 484, 53–63. <https://doi.org/10.1016/j.scitotenv.2014.02.085>.
- Chabot, V., Higgins, D., Yu, A., Xiao, X., Chen, Z., Zhang, J., 2014. A review of graphene and graphene oxide sponge: material synthesis and applications to energy and the environment. *Energy Environ. Sci.* 7, 1564. <https://doi.org/10.1039/c3ee43385d>.
- Chen, W., Duan, L., Zhu, D., 2007. Adsorption of polar and nonpolar organic chemicals to carbon nanotubes. *Environ. Sci. Technol.* 41, 8295–8300. <https://doi.org/10.1021/es071230h>.
- Chen, W., Fan, Z., Zhang, B., Ma, G., Takane, K., Zhang, X., Lai, Z., 2011. Enhanced visible-light activity of titania via confinement inside carbon nanotubes. *J. Am. Chem. Soc.* 133, 14896–14899. <https://doi.org/10.1021/ja205997x>.
- Chen, Y., Vymazal, J., Březinová, T., Koželuh, M., Kule, L., Huang, J., Chen, Z., 2016. Occurrence, removal and environmental risk assessment of pharmaceuticals and personal care products in rural wastewater treatment wetlands. *Sci. Total Environ.* 566, 1660–1669. <https://doi.org/10.1016/j.scitotenv.2016.06.069>.
- Cheng, G., Xu, F., Xiong, J., Tian, F., Ding, J., Stadler, F.J., Chen, R., 2016. Enhanced adsorption and photocatalysis capability of generally synthesized TiO<sub>2</sub>-carbon materials hybrids. *Adv. Powder Technol.* 27, 1949–1962. <https://doi.org/10.1016/j.apt.2016.06.026>.
- Chong, M.N., Jin, B., Chow, C.W.K., Saint, C., 2010. Recent developments in photocatalytic water treatment technology: a review. *Water Res.* 44, 2997–3027. <https://doi.org/10.1016/j.watres.2010.02.039>.
- Coelho, A.D., Sans, C., Agüera, A., Gómez, M.J., Esplugas, S., Dezotti, M., 2009. Effects of ozone pre-treatment on diclofenac: intermediates, biodegradability and toxicity assessment. *Sci. Total Environ.* 407, 3572–3578. <https://doi.org/10.1016/j.scitotenv.2009.01.013>.
- Compton, O.C., Nguyen, S.T., 2010. Graphene oxide, highly reduced graphene oxide, and graphene: versatile building blocks for carbon-based materials. *Small* 6, 711–723. <https://doi.org/10.1002/sml.200901934>.
- Cordero, T., Duchamp, C., Chovelon, J.M., Ferronato, C., Matos, J., 2007. Influence of L-type activated carbons on photocatalytic activity of TiO<sub>2</sub> in 4-chlorophenol photodegradation. *J. Photochem. Photobiol. A Chem.* 191, 122–131. <https://doi.org/10.1016/j.jphotochem.2007.04.012>.
- Czech, B., Buda, W., 2016. Multicomponent nanocomposites for elimination of diclofenac in water based on an amorphous TiO<sub>2</sub> active in various light sources. *J. Photochem. Photobiol. A Chem.* 330, 64–70. <https://doi.org/10.1016/j.jphotochem.2016.07.024>.
- Czech, B., Buda, W., 2015. Photocatalytic treatment of pharmaceutical wastewater using new multiwall-carbon nanotubes/TiO<sub>2</sub>/SiO<sub>2</sub> nanocomposites. *Environ. Res.* 137, 176–184. <https://doi.org/10.1016/j.envres.2014.12.006>.
- Daghir, R., Drogué, P., Robert, D., 2013. Modified TiO<sub>2</sub> for environmental photocatalytic applications: a review. *Ind. Eng. Chem. Res.* 52, 3581–3599. <https://doi.org/10.1021/ie303468t>.
- Dai, G., Wang, B., Huang, J., Dong, R., Deng, S., Yu, G., 2015. Occurrence and source apportionment of pharmaceuticals and personal care products in the Beiyun River of Beijing, China. *Chemosphere* 119, 1033–1039. <https://doi.org/10.1016/j.chemosphere.2014.08.056>.
- Daneshvar Tarigh, G., Shemirani, F., Maz'hari, N.S., 2015. Fabrication of a reusable magnetic multi-walled carbon nanotube–TiO<sub>2</sub> nanocomposite by electrostatic adsorption: enhanced photodegradation of malachite green. *RSC Adv.* 5, 35070–35079. <https://doi.org/10.1039/C4RA15593A>.
- Del Rosario, K.L., Mitra, S., Humphrey, C.P., O'Driscoll, M.A., 2014. Detection of pharmaceuticals and other personal care products in groundwater beneath and adjacent to onsite wastewater treatment systems in a coastal plain shallow aquifer. *Sci. Total Environ.* 487, 216–223. <https://doi.org/10.1016/j.scitotenv.2014.03.135>.
- Doll, T.E., Frimmel, F.H., 2005. Photocatalytic degradation of carbamazepine, clofibrate acid, and imeprol with P25 and Hombikat UV100 in the presence of natural organic matter (NOM) and other organic water constituents. *Water Res.* 39, 403–411. <https://doi.org/10.1016/j.watres.2004.09.016>.
- Doll, T.E., Frimmel, F.H., 2003. Fate of pharmaceuticals – photodegradation by simulated solar UV-light. *Chemosphere* 52, 1757–1769. [https://doi.org/10.1016/S0045-6535\(03\)00446-6](https://doi.org/10.1016/S0045-6535(03)00446-6).
- Done, H.Y., Halden, R.U., 2015. Reconnaissance of 47 antibiotics and associated microbial risks in seafood sold in the United States. *J. Hazard. Mater.* 282, 10–17. <https://doi.org/10.1016/j.jhazmat.2014.08.075>.
- Dong, H., Zeng, G., Tang, L., Fan, C., Zhang, C., He, X., He, Y., 2015. An overview on limitations of TiO<sub>2</sub>-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures. *Water Res.* 79, 128–146. <https://doi.org/10.1016/j.watres.2015.04.038>.
- Dong, Y., Tang, D., Li, C., 2014. Photocatalytic oxidation of methyl orange in water

- phase by immobilized TiO<sub>2</sub>-carbon nanotube nanocomposite photocatalyst. *Appl. Surf. Sci.* 296, 1–7. <https://doi.org/10.1016/j.apsusc.2013.12.128>.
- Drosos, M., Ren, M., Frimmel, F.H., 2015. The effect of NOM to TiO<sub>2</sub>: interactions and photocatalytic behavior. *Appl. Catal. B Environ.* 165, 328–334. <https://doi.org/10.1016/j.apcatb.2014.10.017>.
- Dsikowitzky, L., Sträter, M., Dwyitno, R., Ariyani, F., Irianto, H.E., Schwarzbauer, J., 2015. First comprehensive screening of lipophilic organic contaminants in surface waters of the megacity Jakarta, Indonesia. *Mar. Pollut. Bull.* 110, 654–664. <https://doi.org/10.1016/j.marpolbul.2016.02.019>.
- El-Sheikh, S.M., Khedr, T.M., Hakkai, A., Ismail, A.A., Badawy, W.A., Bahnemann, D.W., 2017. Visible light activated carbon and nitrogen co-doped mesoporous TiO<sub>2</sub> as efficient photocatalyst for degradation of ibuprofen. *Sep. Purif. Technol.* 173, 258–268. <https://doi.org/10.1016/j.seppur.2016.09.034>.
- Ersan, G., Apul, O.G., Perreault, F., Karanfil, T., 2017. Adsorption of organic contaminants by graphene nanosheets: a review. *Water Res.* 126 <https://doi.org/10.1016/j.watres.2017.08.010>.
- Fan, W.G., Gao, L., Sun, J., 2006. Anatase TiO<sub>2</sub>-coated multi-wall carbon nanotubes with the vapor phase method. *J. Am. Ceram. Soc.* 89, 731–733. <https://doi.org/10.1111/j.1551-2916.2005.00755.x>.
- Faraldos, M., Bahamonde, A., 2017. Environmental applications of titania-graphene photocatalysts. *Catal. Today* 285, 13–28. <https://doi.org/10.1016/j.cattod.2017.01.029>.
- Fei, P., Wang, Q., Zhong, M., Su, B., 2016. Preparation and adsorption properties of enhanced magnetic zinc ferrite-reduced graphene oxide nanocomposites via a facile one-pot solvothermal method. *J. Alloys Compd.* 685, 411–417. <https://doi.org/10.1016/j.jallcom.2016.05.279>.
- Ferguson, P.J., Bernot, M.J., Doll, J.C., Lauer, T.E., 2013. Detection of pharmaceuticals and personal care products (PPCPs) in near-shore habitats of southern Lake Michigan. *Sci. Total Environ.* 458–460, 187–196. <https://doi.org/10.1016/j.scitotenv.2013.04.024>.
- Fernández-Ibáñez, P., Malato, S., de las Nieves, F., 1999. Relationship between TiO<sub>2</sub> particle size and reactor diameter in solar photoreactors efficiency. *Catal. Today* 54, 195–204. [https://doi.org/10.1016/S0920-5861\(99\)00182-0](https://doi.org/10.1016/S0920-5861(99)00182-0).
- Friedmann, D., Mendive, C., Bahnemann, D., 2010. TiO<sub>2</sub> for water treatment: parameters affecting the kinetics and mechanisms of photocatalysis. *Appl. Catal. B Environ.* 99, 398–406. <https://doi.org/10.1016/j.apcatb.2010.05.014>.
- Frimmel, F.H., 1994. Photochemical aspects related to humic substances. *Environ. Int.* 20, 373–385. [https://doi.org/10.1016/0160-4120\(94\)90123-6](https://doi.org/10.1016/0160-4120(94)90123-6).
- Galus, M., Jeyaranjan, J., Smith, E., Li, H., Metcalfe, C., Wilson, J.Y., 2013. Chronic effects of exposure to a pharmaceutical mixture and municipal wastewater in zebrafish. *Aquat. Toxicol.* 132–133, 212–222. <https://doi.org/10.1016/j.aquatox.2012.12.016>.
- Gao, B., Chen, G.Z., Li Puma, G., 2009. Carbon nanotubes/titanium dioxide (CNTs/TiO<sub>2</sub>) nanocomposites prepared by conventional and novel surfactant wrapping sol-gel methods exhibiting enhanced photocatalytic activity. *Appl. Catal. B Environ.* 89, 503–509. <https://doi.org/10.1016/j.apcatb.2009.01.009>.
- Gao, W., 2015. The chemistry of graphene oxide. *Graphene Oxide Reduct. Recipe. Spectrosc. Appl.* 61–95. [https://doi.org/10.1007/978-3-319-15500-5\\_3](https://doi.org/10.1007/978-3-319-15500-5_3).
- Gar Alalm, M., Tawfik, A., Ookawara, S., 2016. Enhancement of photocatalytic activity of TiO<sub>2</sub> by immobilization on activated carbon for degradation of pharmaceuticals. *J. Environ. Chem. Eng.* 4, 1929–1937. <https://doi.org/10.1016/j.jece.2016.03.023>.
- Gaya, U.I., Abdullah, A.H., 2008. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. *J. Photochem. Photobiol. C Photochem. Rev.* 9, 1–12. <https://doi.org/10.1016/j.jphotochemrev.2007.12.003>.
- Gillespie, P.N.O., Martsinovich, N., 2017. Electronic structure and charge transfer in the TiO<sub>2</sub> rutile (110)/graphene composite using hybrid DFT calculations. *J. Phys. Chem. C* <https://doi.org/10.1021/acs.jpcc.6b12506> <https://doi.org/10.1021/acs.jpcc.6b12506>.
- Gottschall, N., Topp, E., Metcalfe, C., Edwards, M., Payne, M., Kleywegt, S., Russell, P., Lapen, D.R., 2012. Pharmaceutical and personal care products in groundwater, subsurface drainage, soil, and wheat grain, following a high single application of municipal biosolids to a field. *Chemosphere* 87, 194–203. <https://doi.org/10.1016/j.chemosphere.2011.12.018>.
- Gulyas, H., Ogun, M.K., Meyer, W., Reich, M., Otterpohl, R., 2016. Inadequacy of carbamazepine-spiked model wastewaters for testing photocatalysis efficiency. *Sci. Total Environ.* 542, 612–619. <https://doi.org/10.1016/j.scitotenv.2015.10.116>.
- Hanamoto, S., Nakada, N., Yamashita, N., Hanamoto, S., 2018. Source estimation of pharmaceuticals based on catchment population and in-stream attenuation in Yodo River watershed. *Japan. Sci. Total Environ.* 615, 964–971. <https://doi.org/10.1016/j.scitotenv.2017.10.013>.
- Hashim, N.H., Khan, S.J., 2011. Enantioselective analysis of ibuprofen, ketoprofen and naproxen in wastewater and environmental water samples. *J. Chromatogr. A* 1218, 4746–4754. <https://doi.org/10.1016/j.chroma.2011.05.046>.
- Herrmann, J., 1999. Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catal. Today* 53, 115–129. [https://doi.org/10.1016/S0920-5861\(99\)00107-8](https://doi.org/10.1016/S0920-5861(99)00107-8).
- Hoffmann, M.R., Martin, S., Choi, W., Bahnemann, D.W., 1995. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* 95, 69–96. <https://doi.org/10.1021/cr00033a004>.
- Hu, C., Lu, T., Chen, F., Zhang, R., 2013. A brief review of graphene-metal oxide composites synthesis and applications in photocatalysis. *J. Chinese Adv. Mater. Soc.* 1, 21–39. <https://doi.org/10.1080/22243682.2013.771917>.
- Hu, Z.T., Liu, J., Yan, X., Oh, W., Da, Lim, T.T., 2015. Low-temperature synthesis of graphene/Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> composite for synergistic adsorption-photocatalytic degradation of hydrophobic pollutant under solar irradiation. *Chem. Eng. J.* 262, 1022–1032. <https://doi.org/10.1016/j.cej.2014.10.037>.
- Hua, Z., Zhang, J., Bai, X., Ye, Z., Tang, Z., Liang, L., Liu, Y., 2016. Aggregation of TiO<sub>2</sub>-graphene nanocomposites in aqueous environment: influence of environmental factors and UV irradiation. *Sci. Total Environ.* 539, 196–205. <https://doi.org/10.1016/j.scitotenv.2015.08.143>.
- Hughes, S.R., Kay, P., Brown, L.E., 2013. Global synthesis and critical evaluation of pharmaceutical data sets collected from river systems. *Environ. Sci. Technol.* 47, 661–677. <https://doi.org/10.1021/es3030148>.
- Hummers, W.S., Offeman, R.E., 1958. Preparation of graphitic oxide. *J. Am. Chem. Soc.* 80, 1339. <https://doi.org/10.1021/ja01539a017>.
- Ibáñez, M., Gracia-Lor, E., Bijlsma, L., Morales, E., Pastor, L., Hernández, F., 2013. Removal of emerging contaminants in sewage water subjected to advanced oxidation with ozone. *J. Hazard. Mater.* 260, 389–398. <https://doi.org/10.1016/j.jhazmat.2013.05.023>.
- Ilijima, S., 1991. Helical microtubules of graphitic carbon. *Nature*. <https://doi.org/10.1038/354056a0>.
- Jarusutthirak, C., Amy, G., 2007. Understanding soluble microbial products (SMP) as a component of effluent organic matter (EfOM). *Water Res.* 41, 2787–2793. <https://doi.org/10.1016/j.watres.2007.03.005>.
- Jewell, K.S., Falás, P., Wick, A., Joss, A., Ternes, T.A., 2016. Transformation of diclofenac in hybrid biofilm-activated sludge processes. *Water Res.* 105, 559–567. <https://doi.org/10.1016/j.watres.2016.08.002>.
- Jiang, J.Q., Zhou, Z., Sharma, V.K., 2013. Occurrence, transportation, monitoring and treatment of emerging micro-pollutants in waste water - a review from global views. *Microchem. J.* 110, 292–300. <https://doi.org/10.1016/j.microc.2013.04.014>.
- Jin, X., Shan, J., Wang, C., Wei, J., Tang, C.Y., 2012. Rejection of pharmaceuticals by forward osmosis membranes. *J. Hazard. Mater.* 227–228, 55–61. <https://doi.org/10.1016/j.jhazmat.2012.04.077>.
- Jung, C., Son, A., Her, N., Zoh, K.D., Cho, J., Yoon, Y., 2015. Removal of endocrine disrupting compounds, pharmaceuticals, and personal care products in water using carbon nanotubes: a review. *J. Ind. Eng. Chem.* 27, 1–11. <https://doi.org/10.1016/j.jiec.2014.12.035>.
- Kamat, P.V., 2010. Graphene-based nanoarchitectures. Anchoring semiconductor and metal nanoparticles on a two-dimensional carbon support. *J. Phys. Chem. Lett.* 1, 520–527. <https://doi.org/10.1021/jz900265j>.
- Kanakaraju, D., Glass, B.D., Oelgemöller, M., 2014. Titanium dioxide photocatalysis for pharmaceutical wastewater treatment. *Environ. Chem. Lett.* 12, 27–47. <https://doi.org/10.1007/s10311-013-0428-0>.
- Kapelewska, J., Kotowska, U., Wiśniewska, K., 2016. Determination of personal care products and hormones in leachate and groundwater from Polish MSW landfills by ultrasound-assisted emulsification microextraction and GC-MS. *Environ. Sci. Pollut. Res.* 23, 1642–1652. <https://doi.org/10.1007/s11356-015-5359-9>.
- Karanfil, T., Kitis, M., Kilduff, J.E., Wigton, A., 1999. Role of granular activated carbon surface chemistry on the adsorption of organic compounds. 2. Natural organic matter. *Environ. Sci. Technol.* 33, 3225–3233. <https://doi.org/10.1021/es9810179>.
- Keane, D., Basha, S., Nolan, K., Morrissey, A., Oelgemöller, M., Tobin, J.M., 2011. Photodegradation of famotidine by integrated photocatalytic adsorbent (IPCA) and kinetic study. *Catal. Lett.* 141, 300–308. <https://doi.org/10.1007/s10562-010-0485-y>.
- Khalid, N.R., Majid, A., Tahir, M.B., Niaz, N.A., Khalid, S., 2017. Carbonaceous-TiO<sub>2</sub> nanomaterials for photocatalytic degradation of pollutants: a review. *Ceram. Int.* 43, 14552–14571. <https://doi.org/10.1016/j.ceramint.2017.08.143>.
- Khraisheh, M., Kim, J., Campos, L., Al-Muhtaseb, A.H., Walker, G.M., Alghouti, M., 2013. Removal of carbamazepine from water by a novel TiO<sub>2</sub>-coconut shell powder/UV process: composite preparation and photocatalytic activity. *Environ. Eng. Sci.* 30, 515–526. <https://doi.org/10.1089/ees.2012.0056>.
- Kibombo, H.S., Peng, R., Rasalingam, S., Koodali, R.T., 2012. Versatility of heterogeneous photocatalysis: synthetic methodologies epitomizing the role of silica support in TiO<sub>2</sub> based mixed oxides. *Catal. Sci. Technol.* 2, 1737. <https://doi.org/10.1039/c2cy20247f>.
- Kim, I., Tanaka, H., 2009. Photodegradation characteristics of PPCPs in water with UV treatment. *Environ. Int.* 35, 793–802. <https://doi.org/10.1016/j.envint.2009.01.003>.
- Kim, I.Y., Lee, J.M., Kim, T.W., Kim, H.N., Kim, H., Choi, W., Hwang, S.J., 2012. A strong electronic coupling between graphene nanosheets and layered titanate nanoplates: a soft-chemical route to highly porous nanocomposites with improved photocatalytic activity. *Small* 8, 1038–1048. <https://doi.org/10.1002/sml.20110703>.
- Koli, V.B., Dhodamani, A.G., Delekar, S.D., Pawar, S.H., 2017. In situ sol-gel synthesis of anatase TiO<sub>2</sub>-MWCNTs nanocomposites and their photocatalytic applications. *J. Photochem. Photobiol. A Chem.* 333, 40–48. <https://doi.org/10.1016/j.jphotochem.2016.10.008>.
- Kondrakov, A.O., Ignatev, A.N., Frimmel, F.H., Br??se, S., Horn, H., Revelsky, A.I., 2014. Formation of genotoxic quinones during bisphenol A degradation by TiO<sub>2</sub> photocatalysis and UV photolysis: a comparative study. *Appl. Catal. B Environ.* 160–161, 106–114. <https://doi.org/10.1016/j.apcatb.2014.05.007>.
- Kondrakov, A.O., Ignatev, A.N., Lunin, V.V., Frimmel, F.H., Bräse, S., Horn, H., 2016. Roles of water and dissolved oxygen in photocatalytic generation of free OH radicals in aqueous TiO<sub>2</sub> suspensions: an isotope labeling study. *Appl. Catal. B Environ.* 182, 424–430. <https://doi.org/10.1016/j.apcatb.2015.09.038>.
- Kumar, D.P., Kumari, V.D., Karthik, M., Sathish, M., Shankar, M.V., 2017. Shape dependence structural, optical and photocatalytic properties of TiO<sub>2</sub>



- nanocrystals for enhanced hydrogen production via glycerol reforming. *Sol. Energy Mater. Sol. Cells* 163, 113–119. <https://doi.org/10.1016/j.solmat.2017.01.007>.
- Kuvarega, A.T., Mamba, B.B., 2016. TiO<sub>2</sub>-based photocatalysis: toward visible light-responsive photocatalysts through doping and fabrication of carbon-based nanocomposites. *Crit. Rev. Solid State Mater. Sci.* 0, 1–52. <https://doi.org/10.1080/10408436.2016.1211507>.
- Lagesson, A., Fahlman, J., Brodin, T., Fick, J., Jonsson, M., Byström, P., Klaminder, J., 2016. Bioaccumulation of five pharmaceuticals at multiple trophic levels in an aquatic food web - insights from a field experiment. *Sci. Total Environ.* 568, 208–215. <https://doi.org/10.1016/j.scitotenv.2016.05.206>.
- Lai, W.W.-P., Chuang, Y.-C., Lin, A.Y.-C., 2017a. The effects and the toxicity increases caused by bicarbonate, chloride, and other water components during the UV/TiO<sub>2</sub> degradation of oxazaphosphorine drugs. *Environ. Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-017-9005-6>.
- Lai, W.W.-P., Hsu, M.-H., Lin, A.Y.-C., 2017b. The role of bicarbonate anions in methotrexate degradation via UV/TiO<sub>2</sub>: mechanisms, reactivity and increased toxicity. *Water Res.* 112, 157–166. <https://doi.org/10.1016/j.watres.2017.01.040>.
- Lara-López, Y., García-Rosales, G., Jiménez-Becerril, J., 2017. Synthesis and characterization of carbon-TiO<sub>2</sub>-CeO<sub>2</sub> composites and their applications in phenol degradation. *J. Rare Earths* 35, 551–558. [https://doi.org/10.1016/S1002-0721\(17\)60947-5](https://doi.org/10.1016/S1002-0721(17)60947-5).
- Leary, R., Westwood, A., 2011. Carbonaceous nanomaterials for the enhancement of TiO<sub>2</sub> photocatalysis. *Carbon N. Y.* 49, 741–772. <https://doi.org/10.1016/j.carbon.2010.10.010>.
- Lee, C.M., Palaniandy, P., Dahlan, I., 2017. Pharmaceutical residues in aquatic environment and water remediation by TiO<sub>2</sub> heterogeneous photocatalysis: a review. *Environ. Earth Sci.* 76, 611. <https://doi.org/10.1007/s12665-017-6924-y>.
- Lee, H.G., Sai-Anand, G., Komathi, S., Gopalan, A.L., Kang, S.W., Lee, K.P., 2015. Efficient visible-light-driven photocatalytic degradation of nitrophenol by using graphene-encapsulated TiO<sub>2</sub> nanowires. *J. Hazard. Mater.* 283, 400–409. <https://doi.org/10.1016/j.jhazmat.2014.09.014>.
- Lee, K.M., Lai, C.W., Ngai, K.S., Juan, J.C., 2016. Recent developments of zinc oxide based photocatalyst in water treatment technology: a review. *Water Res.* 88, 428–448. <https://doi.org/10.1016/j.watres.2015.09.045>.
- Lerman, I., Chen, Y., Xing, B., Chefetz, B., 2013. Adsorption of carbamazepine by carbon nanotubes: effects of DOM introduction and competition with phenanthrene and bisphenol A. *Environ. Pollut.* 182, 169–176. <https://doi.org/10.1016/j.envpol.2013.07.010>.
- Lester, Y., Mamane, H., Zucker, I., Avisar, D., 2013. Treating wastewater from a pharmaceutical formulation facility by biological process and ozone. *Water Res.* 47, 4349–4356. <https://doi.org/10.1016/j.watres.2013.04.059>.
- Li, M., Lu, B., Ke, Q.F., Guo, Y.J., Guo, Y.P., 2017a. Synergetic effect between adsorption and photodegradation on nanostructured TiO<sub>2</sub>/activated carbon fiber felt porous composites for toluene removal. *J. Hazard. Mater.* 333, 88–98. <https://doi.org/10.1016/j.jhazmat.2017.03.019>.
- Li, Z., Qi, M., Tu, C., Wang, W., Chen, J., Wang, A.J., 2017b. Highly efficient removal of chlorotetracycline from aqueous solution using graphene oxide/TiO<sub>2</sub> composite: properties and mechanism. *Appl. Surf. Sci.* 425, 765–775. <https://doi.org/10.1016/j.apsusc.2017.07.027>.
- Li, S., Gong, Y., Yang, Y., He, C., Hu, L., Zhu, L., Sun, L., Shu, D., 2015. Recyclable CNTs/Fe<sub>3</sub>O<sub>4</sub> magnetic nanocomposites as adsorbents to remove bisphenol A from water and their regeneration. *Chem. Eng. J.* 260, 231–239. <https://doi.org/10.1016/j.cej.2014.09.032>.
- Li, S., Hu, J., 2016. Photolytic and photocatalytic degradation of tetracycline: effect of humic acid on degradation kinetics and mechanisms. *J. Hazard. Mater.* 318, 134–144. <https://doi.org/10.1016/j.jhazmat.2016.05.100>.
- Li, X., Xu, J., de Toledo, R.A., Shim, H., 2016. Enhanced carbamazepine removal by immobilized Phanerochaete chrysosporium in a novel rotating suspension cartridge reactor under non-sterile condition. *Int. Biodeterior. Biodegrad.* 115, 102–109. <https://doi.org/10.1016/j.ibiod.2016.08.003>.
- Li Puma, G., Bono, A., Collin, J.G., 2008. Preparation of titanium dioxide photocatalyst loaded onto activated carbon support using chemical vapor deposition: a review paper. *J. Hazard. Mater.* 157, 209–219. <https://doi.org/10.1016/j.jhazmat.2008.01.040>.
- Lin, L., Wang, H., Xu, P., 2016a. Immobilized TiO<sub>2</sub>-reduced graphene oxide nanocomposites on optical fibers as high performance photocatalysts for degradation of pharmaceuticals. *Chem. Eng. J.* <https://doi.org/10.1016/j.cej.2016.04.024>.
- Lin, T., Yu, S., Chen, W., 2016b. Occurrence, removal and risk assessment of pharmaceutical and personal care products (PPCPs) in an advanced drinking water treatment plant (ADWTP) around Taihu Lake in China. *Chemosphere* 152, 1–9. <https://doi.org/10.1016/j.chemosphere.2016.02.109>.
- Lin, Z., Yao, Y., Li, Z., Liu, Y., Li, Z., Wong, C.P., 2010. Solvent-assisted thermal reduction of graphite oxide. *J. Phys. Chem. C* 114, 14819–14825. <https://doi.org/10.1021/jp1049843>.
- Linley, S., Liu, Y., Ptacek, C.J., Blowes, D.W., Gu, F.X., 2014. Recyclable graphene oxide-supported titanium dioxide photocatalysts with tunable properties. *ACS Appl. Mater. Interfaces* 6, 4658–4668. <https://doi.org/10.1021/am4039272>.
- Liu, S.X., Chen, X.Y., Chen, X., 2007. A TiO<sub>2</sub>/AC composite photocatalyst with high activity and easy separation prepared by a hydrothermal method. *J. Hazard. Mater.* 143, 257–263. <https://doi.org/10.1016/j.jhazmat.2006.09.026>.
- Liu, W., Cai, J., Ding, Z., Li, Z., 2015. TiO<sub>2</sub>/RGO composite aerogels with controllable and continuously tunable surface wettability for varied aqueous photocatalysis. *Appl. Catal. B Environ.* 174–175, 421–426. <https://doi.org/10.1016/j.apcatb.2015.03.041>.
- Long, M., Brame, J., Qin, F., Bao, J., Li, Q., Alvarez, P.J.J., 2016. Phosphate changes effect of humic acids on TiO<sub>2</sub> photocatalysis: from inhibition to mitigation of electron–hole recombination. *Environ. Sci. Technol.* <https://doi.org/10.1021/acs.est.6b04845>.
- Lu, M.C., Chen, Y.Y., Chiou, M.R., Chen, M.Y., Fan, H.J., 2015. Occurrence and treatment efficiency of pharmaceuticals in landfill leachates. *Waste Manag.* 55, 257–264. <https://doi.org/10.1016/j.wasman.2016.03.029>.
- Ma, L., Chen, A., Zhang, Z., Lu, J., He, H., Li, C., 2012. In-situ fabrication of CNT/TiO<sub>2</sub> interpenetrating network film on nickel substrate by chemical vapour deposition and application in photoassisted water electrolysis. *Catal. Commun.* 21, 27–31. <https://doi.org/10.1016/j.catcom.2012.01.013>.
- Ma, R., Wang, X., Huang, J., Song, J., Zhang, J., Wang, X., 2017. Photocatalytic degradation of salicylic acid with magnetic activated carbon-supported F-N codoped TiO<sub>2</sub> under visible light. *Vacuum* 141, 157–165. <https://doi.org/10.1016/j.vacuum.2017.04.003>.
- Mahmoud, W.M.M., Rastogi, T., Kümmerer, K., 2017. Application of titanium dioxide nanoparticles as a photocatalyst for the removal of micropollutants such as pharmaceuticals from water. *Curr. Opin. Green Sustain. Chem.* <https://doi.org/10.1016/j.cogsc.2017.04.001>.
- Mailler, R., Gasperi, J., Coquet, Y., Derome, C., Buleté, A., Vulliet, E., Bressy, A., Varrault, G., Chebbo, G., Rocher, V., 2016. Removal of emerging micropollutants from wastewater by activated carbon adsorption: experimental study of different activated carbons and factors influencing the adsorption of micropollutants in wastewater. *J. Environ. Chem. Eng.* 4, 1102–1109. <https://doi.org/10.1016/j.jece.2016.01.018>.
- Malekshoar, G., Pal, K., He, Q., Yu, A.P., Ray, A.K., 2014. Enhanced solar photocatalytic degradation of phenol with coupled graphene-based titanium dioxide and zinc oxide. *Ind. Eng. Chem. Res.* 53, 18824–18832. <https://doi.org/10.1021/ie501673v>.
- Mallakpour, S., Khadem, E., 2016. Carbon nanotube–metal oxide nanocomposites: fabrication, properties and applications. *Chem. Eng. J.* 302, 344–367. <https://doi.org/10.1016/j.cej.2016.05.038>.
- Marques, R.R.N., Sampaio, M.J., Carrapiço, P.M., Silva, C.G., Morales-Torres, S., Dražić, G., Faria, J.L., Silva, A.M.T., 2013. Photocatalytic degradation of caffeine: developing solutions for emerging pollutants. *Catal. Today* 209, 108–115. <https://doi.org/10.1016/j.cattod.2012.10.008>.
- Martínez, C., Canle L, M., Fernández, M.I., Santaballa, J.A., Faria, J., 2011a. Aqueous degradation of diclofenac by heterogeneous photocatalysis using nanostructured materials. *Appl. Catal. B Environ.* 107, 110–118. <https://doi.org/10.1016/j.apcatb.2011.07.003>.
- Martínez, C., Canle L, M., Fernández, M.I., Santaballa, J.A., Faria, J., 2011b. Kinetics and mechanism of aqueous degradation of carbamazepine by heterogeneous photocatalysis using nanocrystalline TiO<sub>2</sub>, ZnO and multi-walled carbon nanotubes–anatase composites. *Appl. Catal. B Environ.* 102, 563–571. <https://doi.org/10.1016/j.apcatb.2010.12.039>.
- Martins, A.C., Cazzetta, A.L., Pezoti, O., Souza, J.R.B., Zhang, T., Pilau, E.J., Asefa, T., Almeida, V.C., 2017. Sol-gel synthesis of new TiO<sub>2</sub>/activated carbon photocatalyst and its application for degradation of tetracycline. *Ceram. Int.* 43, 4411–4418. <https://doi.org/10.1016/j.ceramint.2016.12.088>.
- Mascolo, G., Comparelli, R., Curri, M.L., Lovecchio, G., Lopez, A., Agostiano, A., 2007. Photocatalytic degradation of methyl red by TiO<sub>2</sub>: comparison of the efficiency of immobilized nanoparticles versus conventional suspended catalyst. *J. Hazard. Mater.* 142, 130–137. <https://doi.org/10.1016/j.jhazmat.2006.07.068>.
- Matamoros, V., Uggetti, E., García, J., Bayona, J.M., 2016. Assessment of the mechanisms involved in the removal of emerging contaminants by microalgae from wastewater: a laboratory scale study. *J. Hazard. Mater.* 301, 197–205. <https://doi.org/10.1016/j.jhazmat.2015.08.050>.
- McClellan, K., Halden, R.U., 2010. Pharmaceuticals and personal care products in archived U.S. biosolids from the 2001 EPA national sewage sludge survey. *Water Res.* 44, 658–668. <https://doi.org/10.1016/j.watres.2009.12.032>.
- Melchionna, M., Prato, M., Fornasiero, P., 2016. Mix and match metal oxides and nanocarbons for new photocatalytic frontiers. *Catal. Today* 277, 202–213. <https://doi.org/10.1016/j.cattod.2016.04.024>.
- Michael-Kordatou, I., Michael, C., Duan, X., He, X., Dionysiou, D.D., Mills, M.A., Fatta-Kassinos, D., 2015. Dissolved effluent organic matter: characteristics and potential implications in wastewater treatment and reuse applications. *Water Res.* 77, 213–248. <https://doi.org/10.1016/j.watres.2015.03.011>.
- Minella, M., Sordello, F., Minero, C., 2017. Photocatalytic process in TiO<sub>2</sub>/graphene hybrid materials. Evidence of charge separation by electron transfer from reduced graphene oxide to TiO<sub>2</sub>. *Catal. Today* 281, 29–37. <https://doi.org/10.1016/j.cattod.2016.03.040>.
- Miranda, S.M., Romanos, G.E., Likodimos, V., Marques, R.R.N., Favvas, E.P., Katsaros, F.K., Stefanopoulos, K.L., Vilar, V.J.P., Faria, J.L., Falaras, P., Silva, A.M.T., 2014. Pore structure, interface properties and photocatalytic efficiency of hydration/dehydration derived TiO<sub>2</sub>/CNT composites. *Appl. Catal. B Environ.* 147, 65–81. <https://doi.org/10.1016/j.apcatb.2013.08.013>.
- Mirzaei, A., Chen, Z., Haghghat, F., Yerushalmi, L., 2016. Removal of pharmaceuticals and endocrine disrupting compounds from water by zinc oxide-based photocatalytic degradation: a review. *Sustain. Cities Soc.* 27, 407–418. <https://doi.org/10.1016/j.scs.2016.08.004>.
- Mittal, G., Dhand, V., Rhee, K.Y., Park, S.-J., Lee, W.R., 2015. A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites. *J. Ind. Eng. Chem.* 21, 11–25. <https://doi.org/10.1016/j.jiec.2014.03.022>.
- Morales-Torres, S., Pastrana-Martínez, L.M., Figueiredo, J.L., Faria, J.L., Silva, A.M.T., 2013. Graphene oxide-P25 photocatalysts for degradation of diphenhydramine pharmaceutical and methyl orange dye. *Appl. Surf. Sci.* 275, 361–368. <https://doi.org/10.1016/j.apsusc.2013.03.041>.

- doi.org/10.1016/j.apsusc.2012.11.157.
- Murgolo, S., Petronella, F., Ciannarella, R., Comparelli, R., Agostiano, A., Curri, M.L., Mascolo, G., 2015. UV and solar-based photocatalytic degradation of organic pollutants by nano-sized TiO<sub>2</sub> grown on carbon nanotubes. *Catal. Today* 240, 114–124. <https://doi.org/10.1016/j.cattod.2014.04.021>.
- Nawaz, M., Miran, W., Jiang, J., Lee, D.S., 2017. One-step hydrothermal synthesis of porous 3D reduced graphene oxide/TiO<sub>2</sub> aerogel for carbamazepine photo-degradation in aqueous solution. *Appl. Catal. B Environ.* 203, 85–95. <https://doi.org/10.1016/j.apcatb.2016.10.007>.
- Nielsen, L., Bandosz, T.J., 2016. Analysis of sulfamethoxazole and trimethoprim adsorption on sewage sludge and fish waste derived adsorbents. *Microporous Mesoporous Mater.* 220, 58–72. <https://doi.org/10.1016/j.micromeso.2015.08.025>.
- Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Zhang, Y., Dubonos, S.V., Grigorieva, I.V., Firsov, A.A., 2004. Electric field effect in atomically thin carbon films. *Science* (80) 306, 666–669. <https://doi.org/10.1126/science.1102896>.
- Of, E., Gestagens, S., Fish, O.N., 2009. Pharmaceuticals and personal care products in the environment. *Environ. Toxicol.* 28, 2663–2670. <https://doi.org/10.1021/bk-2001-0791>.
- Omar, T.F.T., Ahmad, A., Aris, A.Z., Yusoff, F.M., 2016. Endocrine disrupting compounds (EDCs) in environmental and biota matrices: review of analytical strategies for pharmaceuticals, estrogenic hormones and alkylphenol compounds. *Trac Trends Anal. Chem.* 85, 241–259. <https://doi.org/10.1016/j.trac.2016.08.004>.
- Omri, A., Benzina, M., 2015. Influence of the origin of carbon support on the structure and properties of TiO<sub>2</sub> nanoparticles prepared by dip coating method. *Arab. J. Chem.* 1–11. <https://doi.org/10.1016/j.arabjc.2015.06.027>. <https://doi.org/10.1016/j.arabjc.2015.06.027>.
- Omri, A., Lambert, S.D., Geens, J., Bennour, F., Benzina, M., 2014. Synthesis, surface characterization and photocatalytic activity of TiO<sub>2</sub> supported on almond shell activated carbon. *J. Mater. Sci. Technol.* 30, 894–902. <https://doi.org/10.1016/j.jmst.2014.04.007>.
- Orge, C.A., Faria, J.L., Pereira, M.F.R., 2016. Photocatalytic ozonation of aniline with TiO<sub>2</sub>-carbon composite materials. *J. Environ. Manage* 195, 208–215. <https://doi.org/10.1016/j.jenvman.2016.07.091>.
- Orha, C., Pode, R., Manea, F., Lazau, C., Bandas, C., 2017. Titanium dioxide-modified activated carbon for advanced drinking water treatment. *Process Saf. Environ. Prot.* 108, 26–33. <https://doi.org/10.1016/j.psep.2016.07.013>.
- Otieno, B.O., Apollo, S.O., Naidoo, B.E., Ochieng, A., 2017. Photodecolorisation of melanoidins in vinasse with illuminated TiO<sub>2</sub>-ZnO/activated carbon composite. *J. Environ. Sci. Heal. - Part A Toxic/Hazard. Subst. Environ. Eng.* 52, 616–623. <https://doi.org/10.1080/10934529.2017.1294963>.
- Pan, M., Wong, C.K.C., Chu, L.M., 2014. Distribution of antibiotics in wastewater-irrigated soils and their accumulation in vegetable crops in the Pearl River Delta, Southern China. *J. Agric. Food Chem.* 62, 11062–11069. <https://doi.org/10.1021/jf503850v>.
- Park, J.W., Kim, I., Kim, K.W., Nam, T.H., Cho, K.K., Ahn, J.H., Ryu, H.S., Ahn, H.J., 2015. Effect of commercial activated carbons in sulfur cathodes on the electrochemical properties of lithium/sulfur batteries. *Mater. Res. Bull.* 82, 109–114. <https://doi.org/10.1016/j.materresbull.2016.03.030>.
- Pastrana-Martinez, L.M., Morales-Torres, S., Likodimos, V., Figueiredo, J.L., Faria, J.L., Falaras, P., Silva, A.M.T., 2012. Advanced nanostructured photocatalysts based on reduced graphene oxide-TiO<sub>2</sub> composites for degradation of diphenhydramine pharmaceutical and methyl orange dye. *Appl. Catal. B Environ.* 123–124, 241–256. <https://doi.org/10.1016/j.apcatb.2012.04.045>.
- Patino, Y., Diaz, E., Ordóñez, S., 2015. Performance of different carbonaceous materials for emerging pollutants adsorption. *Chemosphere* 119, S124–S130. <https://doi.org/10.1016/j.chemosphere.2014.05.025>.
- Peigney, A., Laurent, C., Flahaut, E., Bacsu, R.R., Rousset, a., 2001. Specific surface area of carbon nanotubes and bundles of carbon nanotubes. *Carbon N. Y.* 39, 507–514. [https://doi.org/10.1016/S0008-6223\(00\)00155-X](https://doi.org/10.1016/S0008-6223(00)00155-X).
- Peining, Z., Nair, A.S., Shengjie, P., Shengyuan, Y., Ramakrishna, S., 2012. Facile fabrication of TiO<sub>2</sub>-graphene composite with enhanced photovoltaic and photocatalytic properties by electrospinning. *ACS Appl. Mater. Interfaces* 4, 581–585. <https://doi.org/10.1021/am201448p>.
- Peng, H., Chen, Y., Mao, L., Zhang, X., 2017. Significant changes in the photo-reactivity of TiO<sub>2</sub> in the presence of a capped natural dissolved organic matter layer. *Water Res.* 110, 233–240. <https://doi.org/10.1016/j.watres.2016.12.025>.
- Peng, X., Ou, W., Wang, C., Wang, Z., Huang, Q., Jin, J., Tan, J., 2014. Occurrence and ecological potential of pharmaceuticals and personal care products in groundwater and reservoirs in the vicinity of municipal landfills in China. *Sci. Total Environ.* 490, 889–898. <https://doi.org/10.1016/j.scitotenv.2014.05.068>.
- Pereira, C.D.S., Maranhão, L.A., Cortez, F.S., Pusceddu, F.H., Santos, A.R., Ribeiro, D.A., Cesar, A., Guimarães, L.L., 2016. Occurrence of pharmaceuticals and cocaine in a Brazilian coastal zone. *Sci. Total Environ.* 548–549, 148–154. <https://doi.org/10.1016/j.scitotenv.2016.01.051>.
- Poh, H.L., Šaněk, F., Ambrosi, A., Zhao, G., Sofer, Z., Pumera, M., 2012. Graphenes prepared by Staudenmaier, Hofmann and Hummers methods with consequent thermal exfoliation exhibit very different electrochemical properties. *Nanoscale* 4, 3515. <https://doi.org/10.1039/c2nr30490b>.
- Quiñones, D.H., Rey, A., Alvarez, P.M., Beltrán, F.J., Plucinski, P.K., 2014. Enhanced activity and reusability of TiO<sub>2</sub> loaded magnetic activated carbon for solar photocatalytic ozonation. *Appl. Catal. B Environ.* 144, 96–106. <https://doi.org/10.1016/j.apcatb.2013.07.005>.
- Rabieh, S., Nassimi, K., Bagheri, M., 2016. Synthesis of hierarchical ZnO-reduced graphene oxide nanocomposites with enhanced adsorption-photocatalytic performance. *Mater. Lett.* 162, 28–31. <https://doi.org/10.1016/j.matlet.2015.09.111>.
- Rahman, M.F., Yanful, E.K., Jasim, S.Y., 2009. Endocrine disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs) in the aquatic environment: implications for the drinking water industry and global environmental health. *J. Water Health* 7, 224–243. <https://doi.org/10.2166/wh.2009.021>.
- Ren, M., Drosos, M., Frimmel, F.H., 2018. Inhibitory effect of NOM in photocatalysis process: explanation and resolution. *Chem. Eng. J.* 334, 968–975. <https://doi.org/10.1016/j.cej.2017.10.099>.
- Rey, A., Quiñones, D.H., Álvarez, P.M., Beltrán, F.J., Plucinski, P.K., 2012. Simulated solar-light assisted photocatalytic ozonation of metoprolol over titania-coated magnetic activated carbon. *Appl. Catal. B Environ.* 111–112, 246–253. <https://doi.org/10.1016/j.apcatb.2011.10.005>.
- Rincón, A.G., Pulgarin, C., 2005. Use of coaxial photocatalytic reactor (CAPHORE) in the TiO<sub>2</sub> photo-assisted treatment of mixed E. coli and Bacillus sp. and bacterial community present in wastewater. *Catal. Today* 101, 331–344. <https://doi.org/10.1016/j.cattod.2005.03.022>.
- Rioja, N., Zorita, S., Peñas, F.J., 2016. Effect of water matrix on photocatalytic degradation and general kinetic modeling. *Appl. Catal. B Environ.* 180, 330–335. <https://doi.org/10.1016/j.apcatb.2015.06.038>.
- Romão, J., Barata, D., Ribeiro, N., Habibovic, P., Fernandes, H., Mul, G., 2017. High throughput screening of photocatalytic conversion of pharmaceutical contaminants in water. *Environ. Pollut.* 220, 1199–1207. <https://doi.org/10.1016/j.envpol.2016.11.015>.
- Rosa, S.M.C., Nossol, A.B.S., Nossol, E., Zarbin, A.J.G., Peralta-Zamora, P.G., 2017. Non-synergistic UV-A photocatalytic degradation of estrogens by nano-TiO<sub>2</sub> supported on activated carbon. *J. Braz. Chem. Soc.* 28, 582–588. <https://doi.org/10.5935/0103-5053.20160201>.
- Rühmland, S., Wick, A., Ternes, T.A., Barjenbruch, M., 2015. Fate of pharmaceuticals in a subsurface flow constructed wetland and two ponds. *Ecol. Eng.* 80, 1–15. <https://doi.org/10.1016/j.ecoleng.2015.01.036>.
- Santhosh, C., Velmurugan, V., Jacob, G., Jeong, S.K., Grace, A.N., Bhatnagar, A., 2016. Role of nanomaterials in water treatment applications: a review. *Chem. Eng. J.* 306. <https://doi.org/10.1016/j.cej.2016.08.053>.
- Sarkar, S., Das, R., Choi, H., Bhattacharjee, C., 2014. Involvement of process parameters and various modes of application of TiO<sub>2</sub> nanoparticles in heterogeneous photocatalysis of pharmaceutical wastes – a short review. *RSC Adv.* 4, 57250–57266. <https://doi.org/10.1039/C4RA09582K>.
- Schindler, P.W., Gamsjäger, H., 1972. Acid-base reactions of the TiO<sub>2</sub> (anatase) - water interface and the point of zero charge of TiO<sub>2</sub> suspensions. *Kolloid-Zeitschrift Zeitschrift Polym.* 250, 759–763. <https://doi.org/10.1007/BF01498568>.
- Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiuchi, Y., Anpo, M., Bahnemann, D.W., 2014. Understanding TiO<sub>2</sub> photocatalysis: mechanisms and materials. *Chem. Rev.* 114, 9919–9986. <https://doi.org/10.1021/cr500189z>.
- Schwaiger, J., Ferling, H., Mallow, U., Wintermayr, H., Negele, R.D., 2004. Toxic effects of the non-steroidal anti-inflammatory drug diclofenac. Part I: histopathological alterations and bioaccumulation in rainbow trout. *Aquat. Toxicol.* 68, 141–150. <https://doi.org/10.1016/j.aquatox.2004.03.014>.
- Shao, Y., Wang, J., Engelhard, M., Wang, C., Lin, Y., 2010. Facile and controllable electrochemical reduction of graphene oxide and its applications. *J. Mater. Chem.* 20, 743–748. <https://doi.org/10.1039/B917975E>.
- Shen, J., Ma, G., Zhang, J., Quan, W., Li, L., 2015. Facile fabrication of magnetic reduced graphene oxide-ZnFe<sub>2</sub>O<sub>4</sub> composites with enhanced adsorption and photocatalytic activity. *Appl. Surf. Sci.* 359, 455–468. <https://doi.org/10.1016/j.apsusc.2015.10.101>.
- Sheng, C., Nnanna, A.G.A., Liu, Y., Vargo, J.D., 2016. Removal of trace pharmaceuticals from water using coagulation and powdered activated carbon as pretreatment to ultrafiltration membrane system. *Sci. Total Environ.* 550, 1075–1083. <https://doi.org/10.1016/j.scitotenv.2016.01.179>.
- Shimizu, Y., Ateia, M., Yoshimura, C., 2018. Natural organic matter undergoes different molecular sieving by adsorption on activated carbon and carbon nanotubes. *Chemosphere* 203, 345–352. <https://doi.org/10.1016/j.chemosphere.2018.03.197>.
- Shon, H.K., Vigneswaran, S., Kandasamy, J., Cho, J., 2007. Characteristics of effluent organic matter in wastewater. *UNESCO - Encycl. Life Support Syst. Water Wastewater Treat. Technol.* 1–17.
- Singh, K.K., Sarma, K.C., 2016. A simple and feasible approach to decorating MWCNT with Fe<sub>3</sub>O<sub>4</sub> and ZnS and their use as a magnetically separable photocatalyst in the degradation of Cr(VI) in wastewater. *Environ. Nanotechnol. Monit. Manag.* <https://doi.org/10.1016/j.enmm.2016.11.003>.
- Song, C., Chen, P., Wang, C., Zhu, L., 2012. Photodegradation of perfluorooctanoic acid by synthesized TiO<sub>2</sub>-MWCNT composites under 365 nm UV irradiation. *Chemosphere* 86, 853–859. <https://doi.org/10.1016/j.chemosphere.2011.11.034>.
- Stankovich, S., Dikin, D.A., Piner, R.D., Kohlhaas, K.A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S.B.T., Ruoff, R.S., 2007. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon N. Y.* 45, 1558–1565. <https://doi.org/10.1016/j.carbon.2007.02.034>.
- Suárez-Iglesias, O., Collado, S., Oulego, P., Díaz, M., 2017. Graphene-family Nanomaterials in Wastewater Treatment Plants, vol. 313, pp. 121–135. <https://doi.org/10.1016/j.cej.2016.12.022>.
- Suárez, S., Carballa, M., Omil, F., Lema, J.M., 2008. How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters? *Rev.*

- Environ. Sci. Biotechnol. 7, 125–138. <https://doi.org/10.1007/s11157-008-9130-2>.
- Subedi, B., Codru, N., Dzielwski, D.M., Wilson, L.R., Xue, J., Yun, S., Braun-Howland, E., Miihane, C., Kannan, K., 2014. A pilot study on the assessment of trace organic contaminants including pharmaceuticals and personal care products from on-site wastewater treatment systems along Skaneateles Lake in New York State, USA. *Water Res.* 72, 28–39. <https://doi.org/10.1016/j.watres.2014.10.049>.
- Sudha, D., Sivakumar, P., 2015. Review on the photocatalytic activity of various composite catalysts. *Chem. Eng. Process. Process Intensif.* 97, 112–133. <https://doi.org/10.1016/j.cep.2015.08.006>.
- Sui, Q., Cao, X., Lu, S., Zhao, W., Qiu, Z., Yu, G., 2015. Occurrence, sources and fate of pharmaceuticals and personal care products in the groundwater: a review. *Emerg. Contam.* 1, 14–24. <https://doi.org/10.1016/j.emcon.2015.07.001>.
- Sun, J., Zhang, H., Guo, L., Zhao, L., 2013. Two-dimensional interface engineering of a titania-graphene nanosheet composite for improved photocatalytic activity. *ACS Appl. Mater. Interfaces* 5, 13035–13041.
- Sun, Z., He, X., Du, J., Gong, W., 2016. Synergistic effect of photocatalysis and adsorption of nano-TiO<sub>2</sub> self-assembled onto sulfanyl/activated carbon composite. *Environ. Sci. Pollut. Res.* 23, 21733–21740. <https://doi.org/10.1007/s11356-016-7364-z>.
- Taleshi, F., 2015. Study of morphology and band gap energy of TiO<sub>2</sub>-carbon nanotube nanocomposite. *J. Mater. Sci. Mater. Electron.* 26, 3262–3267. <https://doi.org/10.1007/s10854-015-2825-6>.
- Tan, Q., Xu, Y., Yang, J., Qiu, L., Chen, Y., Chen, X., 2013. Preparation and electrochemical properties of the ternary nanocomposite of polyaniline/activated carbon/TiO<sub>2</sub> nanowires for supercapacitors. *Electrochim. Acta* 88, 526–529. <https://doi.org/10.1016/j.electacta.2012.10.126>.
- Tang, Y., Lee, C., Xu, J., Liu, Z., Chen, Z., He, Z., Cao, Y., Yuan, G., Song, H., Chen, L., Luo, L., Cheng, H., Zhang, W., Bello, I., Lee, S., 2010. Incorporation of graphenes in nanostructured TiO<sub>2</sub> films via molecular. *ACS Nano* 4, 3482–3488. <https://doi.org/10.1021/nn100449w>.
- Tijani, J.O., Fatoba, O.O., Babajide, O.O., Petrik, L.F., 2016. Pharmaceuticals, endocrine disruptors, personal care products, nanomaterials and perfluorinated pollutants: a review. *Environ. Chem. Lett.* 14, 27–49. <https://doi.org/10.1007/s10311-015-0537-z>.
- Tong, A.Y.C., Braund, R., Warren, D.S., Peake, B.M., 2012. TiO<sub>2</sub>-assisted photodegradation of pharmaceuticals – a review. *Cent. Eur. J. Chem.* 10, 989–1027. <https://doi.org/10.2478/s11532-012-0049-7>.
- Upadhyay, R.K., Soin, N., Roy, S.S., 2014. Role of graphene/metal oxide composites as photocatalysts, adsorbents and disinfectants in water treatment: a review. *RSC Adv.* 4, 3823–3851. <https://doi.org/10.1039/C3RA45013A>.
- Van Doorslaer, X., Dewulf, J., De Maerschalk, J., Van Langenhove, H., Demeestere, K., 2015. Heterogeneous photocatalysis of moxifloxacin in hospital effluent: effect of selected matrix constituents. *Chem. Eng. J.* 261, 9–16. <https://doi.org/10.1016/j.cej.2014.06.079>.
- Velo-Gala, I., López-Peñalver, J.J., Sánchez-Polo, M., Rivera-Utrilla, J., 2017. Role of activated carbon surface chemistry in its photocatalytic activity and the generation of oxidant radicals under UV or solar radiation. *Appl. Catal. B Environ.* 207, 412–423. <https://doi.org/10.1016/j.apcatb.2017.02.028>.
- Velo-Gala, I., López-Peñalver, J.J., Sánchez-Polo, M., Rivera-Utrilla, J., 2013. Activated carbon as photocatalyst of reactions in aqueous phase. *Appl. Catal. B Environ.* 142–143, 694–704. <https://doi.org/10.1016/j.apcatb.2013.06.003>.
- Venkata Laxma Reddy, P., Kim, K.H., Kim, Y.H., 2011. A review of photocatalytic treatment for various air pollutants. *Asian J. Atmos. Environ.* 5, 181–188. <https://doi.org/10.5572/ajae.2011.5.3.181>.
- Wang, F., Zhang, K., 2011. Reduced graphene oxide–TiO<sub>2</sub> nanocomposite with high photocatalytic activity for the degradation of rhodamine B. *J. Mol. Catal. A Chem.* 345, 101–107. <https://doi.org/10.1016/j.molcata.2011.05.026>.
- Wang, H., Li, J., Zhou, M., Guan, Q., Lu, Z., Huo, P., 2015. Journal of industrial and engineering chemistry preparation and characterization of Ag<sub>2</sub>O/SWNTs photocatalysts and its photodegradation on tetracycline. *J. Ind. Eng. Chem.* 30, 64–70. <https://doi.org/10.1016/j.jiec.2015.05.002>.
- Wang, Q., Arash, B., 2014. A review on applications of carbon nanotubes and graphenes as nano-resonator sensors. *Comput. Mater. Sci.* 82, 350–360. <https://doi.org/10.1016/j.commatsci.2013.10.010>.
- Wang, W., Serp, P., Kalck, P., Faria, J.L., 2005. Visible light photodegradation of phenol on MWNT-TiO<sub>2</sub> composite catalysts prepared by a modified sol-gel method. *J. Mol. Catal. A Chem.* 235, 194–199. <https://doi.org/10.1016/j.molcata.2005.02.027>.
- Wang, X., Wu, Z., Wang, Y., Wang, W., Wang, X., Bu, Y., Zhao, J., 2013. Adsorption-photodegradation of humic acid in water by using ZnO coupled TiO<sub>2</sub>/bamboo charcoal under visible light irradiation. *J. Hazard. Mater.* 262, 16–24. <https://doi.org/10.1016/j.jhazmat.2013.08.037>.
- Wang, Y., Ma, J., Zhu, J., Ye, N., Zhang, X., Huang, H., 2016. Multi-walled carbon nanotubes with selected properties for dynamic filtration of pharmaceuticals and personal care products. *Water Res.* 92, 104–112. <https://doi.org/10.1016/j.watres.2016.01.038>.
- Wei, H., Deng, S., Huang, Q., Nie, Y., Wang, B., Huang, J., Yu, G., 2013. Regenerable granular carbon nanotubes/alumina hybrid adsorbents for diclofenac sodium and carbamazepine removal from aqueous solution. *Water Res.* 47, 4139–4147. <https://doi.org/10.1016/j.watres.2012.11.062>.
- Woan, K., Pyrgiotakis, G., Sigmund, W., 2009. Photocatalytic carbon-nanotube-TiO<sub>2</sub> composites. *Adv. Mater.* 21, 2233–2239. <https://doi.org/10.1002/adma.200802738>.
- Wu, H., Fan, J., Yang, Y., Liu, E., Hu, X., Ma, Y., Fan, X., Tang, C., 2015. Hydrothermal synthesis of graphene-TiO<sub>2</sub> nanowire with an enhanced photocatalytic activity. *Russ. J. Phys. Chem. A* 89, 1189–1194. <https://doi.org/10.1134/S0036024415070134>.
- Xu, Y., Liu, T., Zhang, Y., Ge, F., Steel, R.M., Sun, L., 2017. Advances in technologies for pharmaceuticals and personal care products removal. *J. Mater. Chem. A* 5, 12001–12014. <https://doi.org/10.1039/C7TA03698A>.
- Xu, Y., Zhuang, Y., Fu, X., 2010. New insight for enhanced photocatalytic activity of TiO<sub>2</sub> by doping carbon nanotubes: a case study on degradation of benzene and methyl orange. *J. Phys. Chem. C* 114, 2669–2676. <https://doi.org/10.1021/jp909855p>.
- Yang, K., Xing, B., 2010. Adsorption of organic compounds by carbon nanomaterials in aqueous phase: polanyi theory and its application. *Chem. Rev.* 110, 5989–6008. <https://doi.org/10.1021/cr100059s>.
- Yang, M., Zhang, N., Xu, Y., 2013. Synthesis of fullerene -, carbon nanotube -, and graphene - TiO<sub>2</sub> nanocomposite photocatalysts for selective oxidation: a comparative study. *ACS Appl. Mater. Interfaces* 5, 1156–1164. <https://doi.org/10.1021/am3029798>.
- Yang, Y., Ok, Y.S., Kim, K.-H., Kwon, E.E., Tsang, Y.F., 2017a. Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: a review. *Sci. Total Environ.* 596–597, 303–320. <https://doi.org/10.1016/j.scitotenv.2017.04.102>.
- Yang, Y.Y., Zhao, J.L., Liu, Y.S., Liu, W.R., Zhang, Q.Q., Yao, L., Hu, L.X., Zhang, J.N., Jiang, Y.X., Ying, G.G., 2017b. Pharmaceuticals and personal care products (PPCPs) and artificial sweeteners (ASs) in surface and ground waters and their application as indication of wastewater contamination. *Sci. Total Environ.* 616–617, 816–823. <https://doi.org/10.1016/j.scitotenv.2017.10.241>.
- Yao, Y., Li, G., Ciston, S., Lueptow, R.M., Gray, K.A., 2008. Photoreactive TiO<sub>2</sub>/carbon nanotube composites: synthesis and reactivity. *Environ. Sci. Technol.* 42, 4952–4957. <https://doi.org/10.1021/es800191n>.
- Yeh, T.F., Chan, F.F., Hsieh, C. Te, Teng, H., 2011. Graphite oxide with different oxygenated levels for hydrogen and oxygen production from water under illumination: the band positions of graphite oxide. *J. Phys. Chem. C* 115, 22587–22597. <https://doi.org/10.1021/jp204856c>.
- Yuan, C., Hung, C.H., Li, H.W., Chang, W.H., 2016. Photodegradation of ibuprofen by TiO<sub>2</sub> co-doping with urea and functionalized CNT irradiated with visible light - effect of doping content and pH. *Chemosphere* 155, 471–478. <https://doi.org/10.1016/j.chemosphere.2016.04.055>.
- Zhang, D.Q., Gersberg, R.M., Hua, T., Zhu, J., Goyal, M.K., Ng, W.J., Tan, S.K., 2013a. Fate of pharmaceutical compounds in hydroponic mesocosms planted with *Scirpus validus*. *Environ. Pollut.* 181, 98–106. <https://doi.org/10.1016/j.envpol.2013.06.016>.
- Zhang, D.Q., Hua, T., Gersberg, R.M., Zhu, J., Ng, W.J., Tan, S.K., 2013b. Carbamazepine and naproxen: fate in wetland mesocosms planted with *Scirpus validus*. *Chemosphere* 91, 14–21. <https://doi.org/10.1016/j.chemosphere.2012.11.018>.
- Zhang, N., Zhang, Y., Xu, Y.-J., 2012. Recent progress on graphene-based photocatalysts: current status and future perspectives. *Nanoscale* 4, 5792. <https://doi.org/10.1039/c2nr31480k>.
- Zhang, P., Mo, Z., Han, L., Wang, Y., Zhao, G., Zhang, C., Li, Z., 2015. Magnetic recyclable TiO<sub>2</sub>/multi-walled carbon nanotube nanocomposite: synthesis, characterization and enhanced photocatalytic activity. *J. Mol. Catal. A Chem.* 402, 17–22. <https://doi.org/10.1016/j.molcata.2015.03.005>.
- Zhang, P., Zhou, H., Li, K., Zhao, X., Liu, Q., Li, D., Zhao, G., 2018. Occurrence of pharmaceuticals and personal care products, and their associated environmental risks in a large shallow lake in north China. *Environ. Geochem. Health.* <https://doi.org/10.1007/s10653-018-0069-0>.
- Zhang, L., Zhang, Q., Xie, H., Guo, J., Lyu, H., Li, Y., Sun, Z., Wang, H., Guo, Z., 2017a. Electrospun titania nanofibers segregated by graphene oxide for improved visible light photocatalysis. *Appl. Catal. B Environ.* 201, 470–478. <https://doi.org/10.1016/j.apcatb.2016.08.056>.
- Zhang, Q., Wu, Z., Li, N., Pu, Y., Wang, B., Zhang, T., Tao, J., 2017b. Advanced review of graphene-based nanomaterials in drug delivery systems: synthesis, modification, toxicity and application. *Mater. Sci. Eng. C* 77, 1363–1375. <https://doi.org/10.1016/j.msec.2017.03.196>.
- Zhang, Y., Lv, T., Carvalho, P.N., Zhang, L., Arias, C.A., Chen, Z., Brix, H., 2016. Ibuprofen and iohexol removal in saturated constructed wetland mesocosms. *Ecol. Eng.* <https://doi.org/10.1016/j.ecoleng.2016.05.077>.
- Zhang, Y., Tang, Z.-R., Fu, X., Xu, Y.-J., 2010. TiO<sub>2</sub>-graphene nanocomposites for gas-phase photocatalytic degradation of volatile aromatic pollutant: is TiO<sub>2</sub>-graphene truly different from Other TiO<sub>2</sub>-carbon composite materials? *ACS Nano* 4, 7303–7314. <https://doi.org/10.1021/nn1024219>.
- Zhang, Y., Zhou, Z., Chen, T., Wang, H., Lu, W., 2014a. Graphene TiO<sub>2</sub> nanocomposites with high photocatalytic activity for the degradation of sodium pentachlorophenol. *J. Environ. Sci. (China)* 26, 2114–2122. <https://doi.org/10.1016/j.jes.2014.08.011>.
- Zhang, J., Zhou, P., Liu, J., Yu, J., 2014b. New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO<sub>2</sub>. *Phys. Chem. Chem. Phys.* 16, 20382–20386. <https://doi.org/10.1039/C4CP02201G>.
- Zhou, H., Lian, L., Yan, S., Song, W., 2017. Insights into the photo-induced formation of reactive intermediates from effluent organic matter: the role of chemical constituents. *Water Res.* 112, 120–128. <https://doi.org/10.1016/j.watres.2017.01.048>.
- Zhou, W., Pan, K., Qu, Y., Sun, F., Tian, C., Ren, Z., Tian, G., Fu, H., 2010. Photodegradation of organic contamination in wastewaters by bonding TiO<sub>2</sub>/single-walled carbon nanotube composites with enhanced photocatalytic activity.

- Chemosphere 81, 555–561. <https://doi.org/10.1016/j.chemosphere.2010.08.059>.
- Zhu, S., Chen, H., Li, J., 2013. Sources, distribution and potential risks of pharmaceuticals and personal care products in Qingshan Lake basin, Eastern China. *Ecotoxicol. Environ. Saf.* 96, 154–159. <https://doi.org/10.1016/j.ecoenv.2013.06.033>.
- Zouzelka, R., Kusumawati, Y., Remzova, M., Rathousky, J., Pauporté, T., 2016. Photocatalytic activity of porous multiwalled carbon nanotube-TiO<sub>2</sub> composite layers for pollutant degradation. *J. Hazard. Mater.* 317, 52–59. <https://doi.org/10.1016/j.jhazmat.2016.05.056>.