Nano-Materials as Photocatalysts for Degradation of Environmental Pollutants
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Solar light-induced photocatalytic degradation of pharmaceuticals in wastewater treatment

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Abstract

The use of pharmaceutical products (PP) has increased significantly within the last decade. Many pharmaceuticals products are water-soluble and non-biodegradable and conventional wastewater, and water treatment technologies are not designed to remove them. While they provide many advantages in improving the quality of human and animal health, the potential for the release of pharmaceuticals into the environment makes them an emerging pollutant of concern. New technologies are required for the effective removal of these contaminants. This chapter presents a discussion on a number of solar light-driven catalytic materials for the degradation of pharmaceuticals, with an emphasis on the advantages of using heterocatalysts for wastewater treatment.

Keywords: Photocatalytic degradation, Water treatment, Heterocatalysts, TiO_2, Endocrine disruptors

1. Introduction

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Declining water quality for a rapidly growing population has become a global issue. An emerging concern in this area is the impact of the overuse and discharge of pharmaceuticals and personal care products (PPCP), such as birth control pills, painkillers and antibiotics, on aquatic ecosystems and human health (Jones *et al.,* 2005). Even at trace levels, these materials can have significant biological effects. Widespread use in human populations means that increasing amounts are reaching the environment through wastewater treatment discharges, and the academic literature shows increasing concern amongst scientists on the issue (WHO, 2001; Rizzo *et al*., 2013).

Antibiotics and hormones are also reaching the environment from a variety of food production sectors, including aquaculture, cattle farming, pig rearing and the poultry sector (Kemper, 2008; Landers *et al,* 2012). The potential exists for bioaccumulation in higher levels of the food chain (Chapman & Organization, 1996).

Photocatalysis is an important technology that is considered to have high potential as an effective, low cost, green and sustainable technology to remove pharmaceutical residues from effluents (Comninellis *et al,* 2008). The chapter aims to provide a comprehensive overview with a variety of semiconductor catalysts for the degradation of pharmaceutical effluents using solar light irradiation.

2. Pharmaceutical waste in water resources

Pharmaceutical products are mainly categorised based on their chemical structure, origin or by their therapeutic use. Alkaloids are pharmaceuticals usually derived from plants, such as

cocaine, quinine, morphine, etc. Other common pharmaceuticals are antibiotics, lipid regulators, non-steroidal anti-inflammatories, anti-depressants, anticonvulsants, antineoplastics, beta-blockers (Renita *et al*, 2017). These materials can be found in concentrations from nanograms per litre (ng L^{-1}) to micrograms per litre (μg L^{-1}) in the aquatic environment (Serpone *et al*, 2017).

The release of pharmaceutical residues to the aquatic environment happens *via* different routes. Figure 1 illustrates various possible pathways. Even though pharmaceuticals are present in low concentrations, when compared to other organic pollutants in the environment, potency and potential bioaccumulation are factors that lead to a concern that organisms, including humans, maybe at high risk from these discharges.

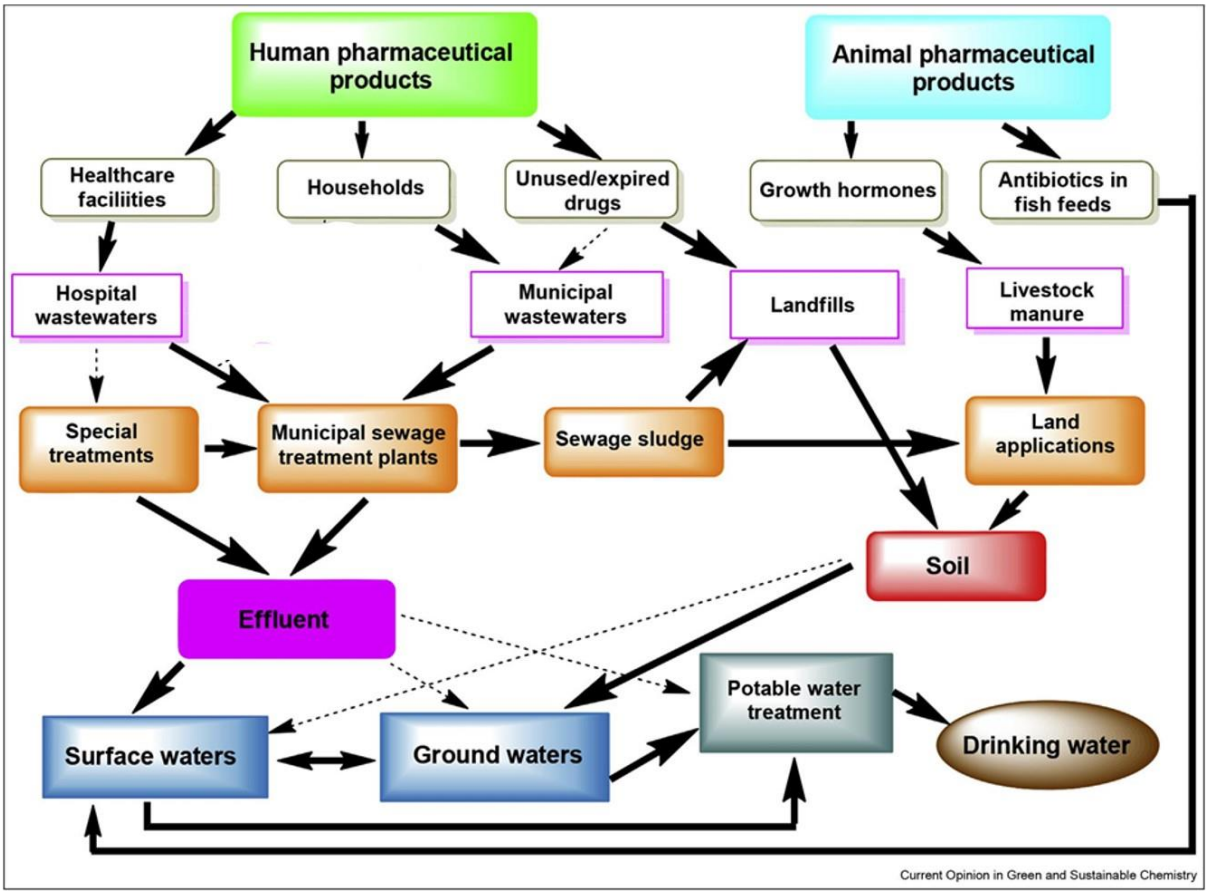

Figure 1. Pathways of human and animal pharmaceutical products to contaminate water sources. (Serpone *et al*, 2017)

3. Health effects of pharmaceutical waste

Different categories of pharmaceutical materials can have different effects when exposure occurs from environmental sources. Antibiotics, for example are a very important group of pharmaceuticals which make a considerable contribution to a wide variety of disease treatments (Dias *et al*, 2012; O'Shea & Moser, 2008); Lara *et al*., 2010; Dias *et al*., 2012; Fair & Tor, 2014; (Mathur & Hoskins, 2017)). They are consumed to mitigate any risk or infection

associated with bacterial strains (Ventola, 2015). They are an effective potential cure against several infectious diseases in humans and animals (Perumal Samy & Gopalakrishnakone, 2010). The use of antibiotics has resulted in a significant decline in mortality rates amongst humans and animals (Hawkey, 2008).

However, their action is concentration-dependent. At high concentration, antibiotics are extremely lethal to microbial cells. However, prolonged exposure to low concentrations can lead to the development of genetic and phenotypic variability, or antibiotic resistance (Whitham *et al*, 2006). Antibiotics are partially metabolised inside the human body, and several active fragments are disseminated via urine and faeces (Hsu *et al*, 2014). Thus, wastewater from municipal sewage, as well as agricultural usage, are the common routes of antibiotics discharge to the environment (Strauch, 2011). The rate of contribution from each source varies from country to country. Asian countries, particularly developing economies, such as India and China have seen an increase in pharmaceutical companies, while the European countries have seen a rise in the use of antibiotics in animal husbandry and aquaculture (Huttner *et al*, 2013). Studies have shown that the discharge of antibiotics to the environment has had a number of effects. Alterations to the pH, adsorption capacity, temperature, texture of soils are some of the environmental impact found (Sassman & Lee, 2005).

The introduction of antibiotics to soil affects the balance of microbial species in the overall microbial ecosystem. Studies have shown the loss of particular bacterial groups, such as those controlling the nitrogen fixation process (Kümmerer, 2009). Stress responses shown have

included significant growth in some bacteria (Davies & Davies, 2010). Others have led to alteration of target sites with microbial cells, production of inactivating enzymes, changes to cellular permeability and changes to transportation systems such as the efflux pumps (Wexler, 2007).

The emergence of antibiotic resistance has been the subject of many studies (Laxminarayan *et al*, 2013). It has been identified as one of the major threats to global health and food security (Berendonk *et al*, 2015). The rise in cases of antibiotic resistances impacts the overall economy of a country (Malizos & Kirketerp-Møller, 2016; Ventola, 2015). It increases the duration of medical care, which increases the average medical cost of the population (Aslam *et al*, 2018). It also jeopardises other critical treatments, such as organ transplant, chemotherapy *etc.* (Lundholm *et al*, 1992).

In response to this, the WHO has strategised a global action plan on antimicrobial resistance. It requires countries to identify the sources of antibiotic release to the environment and to develop standards to reduce the levels of discharge (Tiong *et al*, 2016). The European Commission and many North American countries have also taken similar actions (Morgan *et al*, 2011). However, conventional wastewater treatment plants are not designed for the removal of pharmaceutical products (Stackelberg *et al*, 2004). New technologies are being introduced in new treatment plants such as advanced oxidation processes (AOPs), microfiltration utilising membranes *etc.* (Pérez-González *et al*, 2012). These can lead to a significant increase in the cost of treatment.

Another category of pharmaceuticals of concern is Endocrine Disruptive Compounds. These compounds can cause significant health threat by interfering with metabolism, and hormone biosynthesis can lead to congenital disabilities or developmental disorders in infants. They have also been shown to cause cancer. (Diamanti-Kandarakis *et al*, 2009). Accumulation of such materials could interfere with the functioning of organs. Most of the pharmaceuticals can act as endocrine disruptive compounds (EDC) (Benotti *et al*, 2008).

4. Solar active photocatalytic degradation of Pharmaceuticals

4.1 Photocatalytic degradation mechanism

The development of Photocatalysis technology can be traced back to the 1960s when the landmark work was done by Honda and Fujishima (Ganguly *et al*, 2017). Initial studies investigated the use of TiO_2 for photoelectrochemical applications, and there are now many applications in energy and environmental remediation (Fujishima & Honda, 1972). In this chapter, the use of photocatalysis for the degradation of pharmaceutical effluent is discussed. The role of a semiconductor photocatalyst is to provide active sites on the surface of a material for reduction and oxidation processes that result from irradiation by solar light (Mathew *et al*, 2018). When the energy of the incident photon matches with the bandgap of the semiconductor material, it results in the excitation of the electron-hole pairs (Ganguly *et al*, 2019). In general, the valence band displays an oxidative potential of +1.0 eV to +3.5 eV versus NHE. Similarly, the conduction band show a reductive potential of +0.5 eV to -1.5 eV versus NHE (Tong *et al*, 2012). Thus, the irradiated solar energy is utilised to generate charge carriers. These charge

carriers have a minute timescale, of around few femtoseconds, to participate with the water and oxygen in the atmosphere to create potential reactive oxygen species (transform into chemical energy) (Panneri *et al*, 2017b). A significant amount of the input energy is transferred back in the form of light and thermal energy, as a large proportion of the charge carriers (electron-hole pairs) recombine (Panneri *et al*, 2016). Several structural and chemical modifications have been introduced in the semiconductor surfaces to date to delay the recombination process (Panneri *et al*, 2017a). Defect formation, the introduction of co-catalysts, the formation of different types of heterojunctions are some of the major routes investigated to enhance the photocatalytic efficiency (Mathew *et al*, 2018). These processes induce an internal electric field that causes the migration of the charge carriers from the conduction and the valence band of the semiconductor surface.

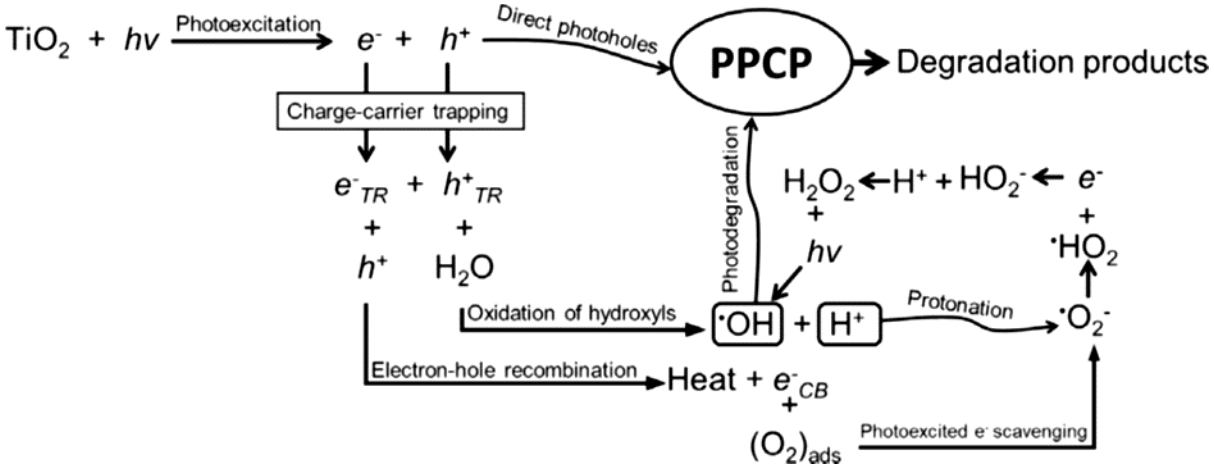

Figure 2. Schematic illustration of photocatalytic reduction and oxidation mechanism of pharmaceutical and personal care products (Awfa *et al*, 2018).

Notwithstanding the improved technologies and photocatalytic results observed, there still exists significant scope for growth and improvement. Firstly, in the case of photocatalytic

efficiency, the major challenge is scale-up to commercial scale. Secondly, the stability and the cost of these semiconductor materials is a significant concern. Thirdly, the toxicity profile and their impact on the ecosystem must be addressed. Fourthly, visible light absorption must be improved. Finally, a better understanding of the surface-interface chemistry of the semiconductor surface, which is a key factor contributing to the transfer of electrons and overpotential of the redox reactions, is required (Tong *et al*, 2012). Thus, engineering eco-friendly, cost-effective semiconductor systems with significant photocatalytic efficiency that illustrate thermal, structural and chemical stability, is a major target. (Awfa *et al*, 2018).

4.2 Titania based materials

TiO_2 is an ideal catalyst for photocatalytic degradation of waste materials because of its high photostability, non-toxicity, low cost and photoreactivity. There are three polymorphs for TiO_2, namely anatase, rutile and brookite. Among these polymorphs, anatase exhibits the highest photocatalytic activity, most extended lifetime of photo-excited electron and fastest migration of photoelectron (Malato *et al*, 2009). TiO_2 even shows catalytic activity under mild conditions with mild oxidants (Malato *et al*, 2009). However, in the presence of a high concentration of contamination, it shows low photo-efficiencies and kinetics, which could lead to catalyst inactivation and unpredictable mechanisms. This need to be addressed. Limitation of photocatalytic activity of unmodified TiO_2 within the UV range of spectra ($\lambda < 380$ nm), is another factor inhibiting its use in real-life applications. Reactor set-up with artificial lamps for use in industrial applications could increase the cost of production at a large scale. Employing visible light radiation for catalytic degradation of pharmaceutical waste will be a sustainable

solution for this. Modification of TiO_2 by doping noble metals or non-metals, or coupling with other semiconductor materials has been used in the activation of titania in the visible light region.

Doping of titania with various metals, non-metals and carbonaceous materials have been extensively studied previously. Belet *et al*, studied a comparison analysis on seven photocatalysts with TiO_2, ZnO, TiO_2+ P25, TiO_2+Ag, TiO_2+ MnO_2, TiO_2 + Zn+ and TiO_2 (aqua) for degradation of 15 different pharmaceutical products. Ag-doped TiO_2 and P25 doped TiO_2 showed better performance in pharmaceutical waste degradation (Belet *et al*, 2019). Similarly, Rabhi *et al.* reported 100% efficiency demonstrated by 1 wt% Ag-TiO_2 in the degradation of amlodipine besylate within 100 min of irradiation. This efficiency is due to the introduction of more active sites by Ag doping and the presence of polymorphism of TiO_2 crystals with 47% of anatase phase and 53% of rutile phase. Several studies of N doped TiO_2 for removal of antibiotic ciprofloxacin (CIP) have been reported. The first report of CIP degradation with N doped TiO_2 was by Shetty *et al*, (Shetty *et al*, 2017). 95% degradation of antibiotic within 90 mins of visible light irradiation at neutral pH was attained by N doped catalyst. Xing *et al.* synthesised immobilised N doped TiO_2 on glass spheres. The removal efficiency of CIP by these materials was about 90% in 90 mins under visible light irradiation. The recyclability of materials up to 5 cycles was also reported (Xing *et al*, 2018). Easy removal of these catalysts from the reactor and recyclability gives a new impetus to the use of these materials at the industrial application level. Tri-doped anatase-brookite titania heterojunction catalyst was reported for complete degradation of Ibuprofen under visible light irradiation. C,

N, S tri doped mesoporous TiO_2 exhibited 40 times more reaction rate when compared to pristine TiO_2 (Khedr *et al*, 2017).

Namshah *et al.,* (Namshah & Mohamed, 2018) reported visible light photocatalytic degradation (100%) of paracetamol, using 3 wt% WO_3-TiO_2 as a catalyst, with 30 min of irradiation time. The coupling of tungsten trioxide with titanium dioxide increased the surface area of the materials, due to the insertion of tungsten ion into titania lattice. These enhanced surface area helped in increasing the number of active sites on the surface, which could enhance the paracetamol degradation. The coupling with WO_3 also enhanced the photogenerated charge separation in TiO_2.

To enhance the photocatalytic activity of titania, N doped TiO_2 was coupled with graphene to form a 2-D heterocatalyst. Zhao *et al*. studied the photocatalytic degradation of multiple antibiotics (norfloxacin, sulfamethazine, oxytetracycline, chlortetracycline) using N-TiO_2/graphene. Inhibiting the recombination of generated electron-hole pairs is an efficient way to enhance the catalytic property of TiO_2. Graphene can work as an efficient "electron pump" for the photodegradation, which can promote the separation of carriers. (Zhao *et al*, 2018) . During UV light illumination, the electrons in the VB of TiO_2 get excited to the CB, to generate electron-hole pairs. The holes are transferred from VB of exited TiO_2 to N-TiO_2, due to the comparable energy difference between the VB of TiO_2 and N-TiO_2. These holes react with hydroxyl groups (OH^-) to form the OH• radicals. These OH radicals are responsible for the decomposition of antibiotics during the photocatalytic process. The photo-generated electrons migrate to the graphene surface, where electrons are scavenged by molecular oxygen

O_2 to yield $O_2^{\bullet-}$ superoxide radicals. This helps in decreasing the recombination of the electron-hole pairs, thus enhancing the photocatalytic efficiency of the material.

MoS_2 is a graphene-like two-dimensional (2D) transition metal dichalcogenide. MoS_2/TiO_2 composite for photocatalytic degradation for Carbamazepine, an anti-epilepsy drug was reported by Cravanzola *et al*. The MoS_2/TiO_2 was obtained by thermal treatment under H_2S atmosphere. The photocatalytic activity was compared to P-25. Even though the surface area of P25 was larger than the composite, the synthesised MoS_2/TiO_2 showed enhanced catalytic activity. Small and thin MoS_2 slabs dispersed on the surface of TiO_2 nanoparticles, here the MoS_2 is acting as a photosensitizer. By using this composite in the mineralisation of carbamazepine, the formation of a hazardous by-product (acridine derivatives), which is usually formed with other catalysts, was prevented (Cravanzola *et al*, 2018).

4.3 Graphene-based materials

Reduced graphene oxide (rGO) is a two-dimensional material which is widely explored due to its large surface area, excellent electrical and chemical stability, as well as greater carrier mobility. Dong *et al*. reported the visible light degradation of metronidazole by $ZnSnO_3$ hollow nanospheres/reduced graphene oxide (rGO). The composite $ZnSnO_3$/rGO showed better activity than other prepared samples, $ZnSnO_3$ hollow nanospheres, $ZnSnO_3$/rGO nanocomposites, pure rGO, and $ZnSnO_3$–rGO. The surface areas of the later three samples were kept to eliminate the enhancement in the photocatalytic activity due to the surface area of rGO. ZnSnO3/rGO showed 72.5% of removal of metronidazole under visible light

illumination. The addition of rGO resulted in enhanced absorption efficiency and visible light activity absorption of catalyst (Dong *et al*, 2014)

Lin *et al.* reported the removal of pharmaceutical wastes like carbamazepine, ibuprofen, and sulfamethoxazole using immobilised TiO_2- rGO on side glowing optical fibres (SOFs). The coupling of TiO_2 with rGO helped in reducing the bandgap energy, thus increasing the visible light absorption efficiency. SOF is a fibre with quartz glass as inner core and silicone rubber as the coating. Light irradiation distribution of these fibres is uniform along the fibre length. It can act as catalyst support and simultaneously provide light illumination in the reactor (Lin *et al*, 2017). As previously reported, the photocatalytic activity increased by increasing rGO concentration from 0 to 2.7%. At 2.7% rGO displayed carbamazepine (54%), ibuprofen (81%), and sulfamethoxazole (92%) degradation after 180 min of high-pressure UV irradiation. Similarly, Shinde *et al*, also reported TiO_2-rGO composite with Pt metals for the enhanced photocatalytic degradation and mineralisation of pharmaceutical pollutant b blocker propranolol under solar irradiation. Ternary composite in the ratio of 1Pt:10 rGO showed the enhanced photocatalytic degradation (94%) of propranolol using simulated solar light. In these reactions, rGO acts as an electron sink, and it provides more surface area to the catalyst to adsorb the pollutant to the catalyst surface. Pt nanoparticles help in reducing the recombination of photogenerated species and increasing the absorption in the visible spectra (Shinde *et al*, 2018).

rGO/$AgInS_8$ composite was prepared for visible light active degradation of nitrophenol (2 nitrophenols and 4 nitrophenol) by Che *et al*. (2018). 1% rGO/AIS composite exhibited higher

degradation efficiency than their parent compound. The coupling of $AgIn_5S_8$ (AIS) with rGO promoted the flow of photogenerated electrons from AIS to rGO. The catalyst showed 91% of 4NP and 93.2% of 2 NP removal efficiency within 120 min of visible light irradiation. These could be attributed to the phenomenon of rGO acting as an electron acceptor, which helps in inhibiting the electron-hole recombination by enhancing the photogenerated charge separation. Meanwhile, by increasing the concentration of rGO, they found that the photocatalytic activity declined, due to the suppression of visible light absorption of AIS by excess rGO covering on its surface (Che *et al*, 2018).

4.4 Metal-Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) are the new class of hybrid materials with inorganic and organic components. The versatile physicochemical properties of these compounds make them superior candidates for the photocatalytic treatment of pharmaceutical waste, relative to other materials. Easily modifiable structure and high porosity help to act as a filter for organic pollutants by trapping the organic molecule in the pores. Crystalline structure, chemical/ physical stability and tunable bandgap help in the degradation of adsorbed contaminants in the pores in the presence of sunlight. MOFs with a loaded catalyst is a new area where a lot of studies are being undertaken in relation to wastewater treatment. The high surface area of these networks helps in absorbing the hazardous molecules onto its surface. This peculiarity is widely exploited, especially in the degradation of pharmaceutical waste, where most of them are not biodegradable.

Liang *et al*. reported an initial study, using metal doped MOFs for the removal of pharmaceutical waste. Pd NPs @ MIL-100(Fe) nanocomposite was developed for the photocatalytic degradation of pharmaceutical contaminants like theophylline, ibuprofen and bisphenol A under visible light irradiation (Liang *et al*, 2015). 1 wt% Pd @ MIL-100(Fe) showed enhanced degradation efficiency over bare MIL-100(Fe). Pd NPs helps in minimising the recombination of photogenerated electron-hole pairs, thus leading to an increase in the photocatalytic activity. The efficiency in removing contaminants remained constant, even after an increase in the loading concentration of Pd NPs. The different contaminants behaved differently with the catalyst at varying pHs. By decreasing pH from 6 to 2, the adsorption of theophylline to the MOFs and degradation efficiency increased significantly from 65% to 100%. For ibuprofen and bisphenol A, it was observed that degradation efficiency was enhanced by increasing the pH of the system.

Tetracycline removal by a simulated solar source using a novel composite, Co-doped UiO-66 synthesised by the solvothermal method, was reported by Cao *et al*. (Cao *et al*, 2018). The CoUiO-66 with Zr:Co molar ratio of 1:1 displayed the highest photocatalytic activity (94%) and adsorption capacity. This adsorption can be ascribed due to the π-π and electrostatic interaction between the tetracycline molecule and catalyst. The doping of Co aided in the enhancement of visible light absorption, thus in an increase in photocatalytic degradation efficiency. Tc was degraded into CO_2 and H_2O.

Wang *et al.,* have done a comparative study for tetracycline degradation using Fe based MOFs (Fe-MIL-101, Fe-MIL-100, and Fe-MIL-53). Fe-MIL 101 showed the highest degradation

efficiency, with 96.6% removal, and also the highest visible light absorption efficiency. The concentration of TC stayed constant at 50 mg/L, and the efficiency was decreased relative to the increase in the TC concentration. Fe based MOFs show visible light activity due to the presence of Fe-O clusters presents in the ligand. The photogenerated electrons react with adsorbed O_2 molecules to form $\bullet O_2^-$. With Radicle, on the other hand, photogenerated holes react with an adsorbed water molecule to form hydroxyl radicles. These generated ROS help in the removal of tetracycline (Wang *et al*, 2018).

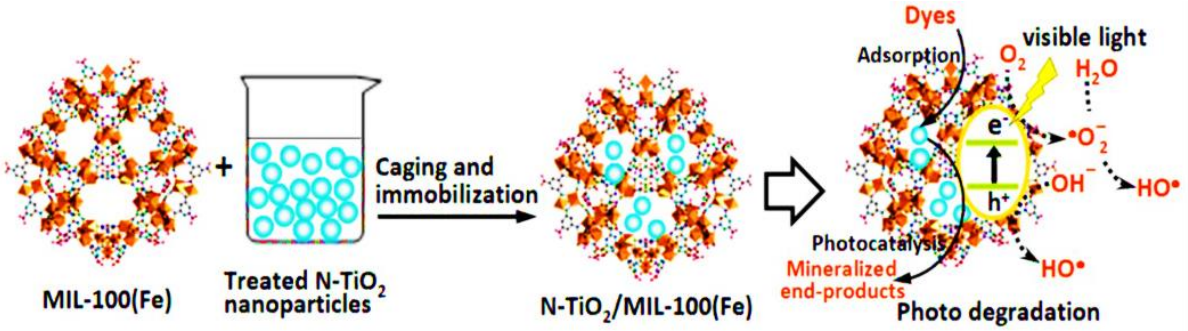

Figure 3. Schematic illustration of photocatalytic degradation mechanism using MOFs (Huang *et al*, 2017).

MIL(100)Fe loaded N-TiO_2 for dye degradation in wastewater was firstly reported by Huang *et al*. (Huang *et al,* 2017). Later, He *et al*, reported a magnetic MIL-101 (Fe)/TiO_2 for degradation of tetracycline (TC) under solar light (He *et al*, 2019). The large surface area of the MOFs and photocatalytic activity of TiO_2 helped in the enhanced adsorption and degradation of TC. 92.7 % of TC degradation was achieved by 10 mins of solar light irradiation. Additionally, due to the magnetic properties of the catalyst, it could also easily recovered from the TC solution by using a magnet.

A novel visible light photocatalyst Fe_2O_3/TiO_2@MIL-101 was synthesised by Tilgner *et al.* MIL-101(Cr) was used as the support for Fe_2O_3(hematite)/TiO_2(anatase) heterojunction. The average size of crystallites was taken as 300 nm, large enough for the separation of generated charge carriers and small enough to have high surface area for the modification of catalysts. The visible light active degradation of antibiotics of as synthesised material was compared with Fe_2O_3@MIL-101, TiO_2@MIL-101, bare Fe_2O_3, TiO_2 and commercial TiO_2 (P25). The Fe_2O_3/TiO_2@MIL-101 material showed higher photocatalytic activity than their bare parent materials. This enhanced catalytic activity is due to the support and synergy effect of Fe_2O_3 and TiO_2 with MIL-101 crystallites. Fe_2O_3 acts as the visible light absorbing component. Under illumination, the excited electrons can be transferred from Fe_2O_3 to the conduction band of TiO_2, and this ensures the efficient charge separation, which helps in the enhanced production of ROS for the degradation of organic components. (Tilgner *et al*, 2018)

4.5 Novel composites

Recently, Ray *et al.* reported AgBr-α-$NiMoO_4$ composite photocatalyst for rapid degradation and mineralisation of Naproxen (a non-steroidal anti-inflammatory drug) in wastewater. $NiMoO_4$ is a low cost and environmentally friendly photocatalyst with a bandgap of 2.8 eV, and it consists of low temperature α monoclinic structure. To increase the photocatalytic activity of $NiMoO_4$, material was coupled with AgBr with the bandgap of 2.5eV. The prepared AgBr-α-$NiMoO_4$ composite exhibited 84% degradation of the drug within 20 min and achieved 100% mineralisation after 100 min of visible light irradiation. This high photocatalytic activity

is attributed to the efficient charge separation, due to matching energy levels of $NiMoO_4$ and AgBr and as well as the surface plasmon resonance of silver particles (Ray *et al*, 2018).

$BiVO_4$ is another visible light active photocatalytic semiconductor that has been widely investigated for treating wastewater. Even though it exhibits long-term stability, low separation of photogenerated electrons and poor electrical conductivity limit its application in practical situations. To enhance the photocatalytic activity of $BiVO_4$, Regmi *et al.,* co-doped the catalyst with non-metal - Sulphur (S) and a metal - Tungsten (W), for the catalytic degradation of Naproxen. Compared to undoped and S and W single doped catalyst, co-doped samples showed significant increases in efficiency (76.5%), up to 180 mins of visible light radiation. The band gap of the semiconductor was reduced by the insertion of S 3p orbitals with Bi 6s and O *2p* states. Thus, the valence bandwidth increased, which caused the shortening of the bandgap (Regmi *et al*, 2018), increasing the surface area of the co-doped catalyst, which enhanced the visible light absorption for the activation.

For harnessing broad brand spectrum Kumar *et al*. 2018, developed a novel quaternary plasmonic core-shell nanostructured photocatalyst. These catalysts comprise of La doped $NaYF_4$@ CdS core-shell decorated with Au NPs supported on rGO nanosheets. $NaYF_4$:Yb/Er was used to obtain NIR photons and to convert them to visible light, core-shell CdS was helpful in the direct absorption visible region of the spectra. Au NPs was added to exploit the plasmonic enhancement effect. The SPR effect of NPs can be effectively used to increase the adsorbent efficiency of semiconductors due to the tunability from UV to NIR. Au NPs also act as cocatalysts to reduce the recombination of generated electron-hole pairs, while rGO O acts as

an electron acceptor, electron transporter, and also as an adsorbent of the pollutant (Kumar *et al*, 2018). Depending on the percentage of rGO incorporated, the photocatalytic degradation efficiency varied. The optimum value rGO for the highest degradation efficiency of 90% within 180 min under visible light was 4wt%.

The use of clay-based photocatalysts for pharmaceutical waste treatment is another new area that is being explored. These materials are promising alternatives for traditional photocatalysts, due to their low cost, abundant availability, chemical stability and non-toxicity. Degradation of antibiotics sulfamethoxazole and trimethoprim by UV and solar radiation using clay was recently reported by Martinez-Costa *et al.* (Martinez-Costa *et al*, 2018). They used bentonite and vermiculite as photocatalysts. Doping ions present within the structure of these materials help to enhance the generation of electrons and holes and directly react with the antibiotics. Among them, vermiculite showed better efficiency due to the presence of a high concentration of Fe, Mn, Ti and V relative to the bentonite. They reported 11.4 and 46.4 times increase in the reaction rate under UV radiation for sulfamethoxazole and trimethoprim.

5. The scope of photocatalysis for wastewater treatment

Conventional means of wastewater treatments are done by using physical, chemical and biological process. Based on the pollutant concentration in the effluent and the production cost of the process, different treatment methods can be chosen (Homem & Santos, 2011). In wastewater treatment plants (WWTP), there are three main stages of treatment, i.e., primary, secondary and tertiary treatments. The raw wastewater is pretreated/screened to remove grit, paper, plastic, fat and grease. For the primary treatment, the wastewater flows through a large

sedimentation tank, where the heavy solids are settled using gravitational force. The effluent is transferred for secondary treatment, where dissolved and suspended biological matter are removed using aerobic digestion (activated sludge bacteria). Bacteria in the effluent form flocs, excess amounts of which are removed by sedimentation, which also produces the treated wastewater. In tertiary treatment (not used in all plants), effluent is treated with a variety of physical and chemical methods, which are normally focused on disinfection (as opposed to further removal of pollutant chemicals..

Following these treatments, the treated water is released to the water bodies or, in some countries, can be used as reclaimed water. Reclaimed water or reused water is mainly used for irrigation in agricultural, for toilet flushing in households, and for replenishing the surface water or groundwater. It can be further treated to achieve the drinking water standard. Whether wastewater is disposed to surface waters (which may be a source, downstream, of water for treatment to drinking water), or it is used as reclaimed water, a significant concern is emerging that current wastewater and water treatment technologies and systems can lead to exposure PPCS from water and alteration of physicochemical and microbiological properties of the environment.

Over time, exposure to these harmful chemicals could lead to chronic diseases. A current lack of technologies for the complete removal of these substances is a significant issue today. The use of photocatalytic materials for the degradation of pharmaceutical and personal care substance could be an effective way of dealing with the issue.

Recently, many studies of photocatalytic treatment of outlet water from WWTP have been reported. Bernabeu *et al*. used solar photocatalysts for the removal of a pharmaceutical substance from treated water in WWTP in the south-east of Spain (Bernabeu *et al*, 2011). In a preliminary analysis of water from the outlet of the treatment plant, they found a significant amount of 9 emerging pollutants (trimethoprim, ofloxacin, enrofloxacin, clarithromycin, acetaminophen, diclofenac, caffeine, thiabendazole and carbamazepine). Irradiation of the wastewater with TiO_2 catalyst showed significant removal of these contaminants and 100% faecal bacteria elimination was achieved. 0.2 to 0.5 g/L of TiO_2 was used and irradiated for 3 hours. The complete removal of bacteria was achieved within 1 hr. Similarly, Prieto *et al*. reported the removal of endocrine disruptive compounds with very low concentrations of TiO_2 from tertiary treated water (Prieto-Rodriguez *et al.*, 2012). With the use of compound parabolic reactors (CPC) reactors of wide diameter under natural sunlight, 85% of these chemicals were degraded. Low concentrated TiO_2 is an effective, economical and simple alternative for the tertiary treatment of WWTP effluent.

6. Conclusions

The development of more effective strategies for the removal of pharmaceutical waste from water has become a necessity, as these pollutants pose a significant threat to humans and the wider environment. The use of solar light active materials as catalysts for removing such wastes is an effective option, but the production of toxic by-products, scale-up issues, and difficulties with separation and recycling of heterocatalysts are limitations to their use in real-world applications.

An ideal solution may be to use combined immobilised photocatalyst systems with membrane filtration or adsorption for the treatment of effluents containing pharmaceutical waste products, as well as other organic materials. Further investigation is also required into upscaling of the proposed treatment technology from bench-scale to municipal/industrial applications.

7. References

Aslam, B., Wang, W., Arshad, M. I., Khurshid, M., Muzammil, S., Rasool, M. H., Nisar, M. A., Alvi, R. F., Aslam, M. A. & Qamar, M. U. (2018) Antibiotic resistance: a rundown of a global crisis. *Infection and drug resistance*, 11, 1645.

Awfa, D., Ateia, M., Fujii, M., Johnson, M. S. & Yoshimura, C. (2018) Photodegradation of pharmaceuticals and personal care products in water treatment using carbonaceous-TiO2 composites: A critical review of recent literature. *Water Research*, 142, 26-45.

Belet, A., Wolfs, C., Mahy, J. G., Poelman, D., Vreuls, C., Gillard, N. & Lambert, S. D. (2019) Sol-gel Syntheses of Photocatalysts for the Removal of Pharmaceutical Products in Water. *Nanomaterials*, 9(1).

Benotti, M. J., Trenholm, R. A., Vanderford, B. J., Holady, J. C., Stanford, B. D. & Snyder, S. A. (2008) Pharmaceuticals and endocrine disrupting compounds in US drinking water. *Environmental science & technology*, 43(3), 597-603.

Berendonk, T. U., Manaia, C. M., Merlin, C., Fatta-Kassinos, D., Cytryn, E., Walsh, F., Bürgmann, H., Sørum, H., Norström, M. & Pons, M.-N. (2015) Tackling antibiotic resistance: the environmental framework. *Nature Reviews Microbiology*, 13(5), 310.

Bernabeu, A., Vercher, R., Santos-Juanes, L., Simón, P., Lardín, C., Martínez, M., Vicente, J., González, R., Llosá, C. & Arques, A. (2011) Solar photocatalysis as a tertiary treatment to remove emerging pollutants from wastewater treatment plant effluents. *Catalysis Today*, 161(1), 235-240.

Cao, J., Yang, Z. H., Xiong, W. P., Zhou, Y. Y., Peng, Y. R., Li, X., Zhou, C. Y., Xu, R. & Zhang, Y. R. (2018) One-step synthesis of Co-doped UiO-66 nanoparticle with enhanced removal efficiency of tetracycline: Simultaneous adsorption and photocatalysis. *Chemical Engineering Journal*, 353, 126-137.

Chapman, D. V. & Organization, W. H. (1996) Water quality assessments: a guide to the use of biota, sediments and water in environmental monitoring.

Che, W. J., Luo, Y. B., Deng, F., Zhang, A. T., Zhao, L. N., Luo, X. B. & Ruan, Q. H. (2018) Facile solvothermal fabrication of cubic-like reduced graphene oxide/AgIn5S8 nanocomposites with anti-photocorrosion and high visible-light photocatalytic performance for highly-efficient treatment of nitrophenols and real pharmaceutical wastewater. *Applied Catalysis a-General*, 565, 170-180.

Comninellis, C., Kapalka, A., Malato, S., Parsons, S. A., Poulios, I. & Mantzavinos, D. (2008) Advanced oxidation processes for water treatment: advances and trends for R&D. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, 83(6), 769-776.

Cravanzola, S., Sarro, M., Cesano, F., Calza, P. & Scarano, D. (2018) Few-Layer MoS2 Nanodomains Decorating TiO2 Nanoparticles: A Case Study for the Photodegradation of Carbamazepine. *Nanomaterials*, 8(4).

Davies, J. & Davies, D. (2010) Origins and evolution of antibiotic resistance. *Microbiol. Mol. Biol. Rev.*, 74(3), 417-433.

Diamanti-Kandarakis, E., Bourguignon, J.-P., Giudice, L. C., Hauser, R., Prins, G. S., Soto, A. M., Zoeller, R. T. & Gore, A. C. (2009) Endocrine-Disrupting Chemicals: An Endocrine Society Scientific Statement. *Endocrine Reviews*, 30(4), 293-342.

Dias, D. A., Urban, S. & Roessner, U. (2012) A historical overview of natural products in drug discovery. *Metabolites*, 2(2), 303-336.

Dong, S. Y., Sun, J. Y., Li, Y. K., Yu, C. F., Li, Y. H. & Sun, J. H. (2014) ZnSnO3 hollow nanospheres/reduced graphene oxide nanocomposites as high-performance photocatalysts for degradation of metronidazole. *Applied Catalysis B-Environmental*, 144, 386-393.

Fujishima, A. & Honda, K. (1972) Electrochemical photolysis of water at a semiconductor electrode. *nature*, 238(5358), 37.

Ganguly, P., Byrne, C., Breen, A. & Pillai, S. C. (2017) Antimicrobial Activity of Photocatalysts: Fundamentals, Mechanisms, Kinetics and Recent Advances. *Applied Catalysis B: Environmental*.

Ganguly, P., Mathew, S., Clarizia, L., R Kumar, S., Akande, A., Hinder, S., Breen, A. & Pillai, C. S. (2019) Theoretical and experimental investigation of visible light responsive AgBiS 2 -TiO 2 heterojunctions for enhanced photocatalytic applications. *Applied Catalysis B: Environmental*.

Hawkey, P. (2008) The growing burden of antimicrobial resistance. *Journal of antimicrobial chemotherapy*, 62(suppl_1), i1-i9.

He, L., Dong, Y. N., Zheng, Y. N., Jia, Q. M., Shan, S. Y. & Zhang, Y. Q. (2019) A novel magnetic MIL-101(Fe)/TiO2 composite for photo degradation of tetracycline under solar light. *Journal of Hazardous Materials*, 361, 85-94.

Homem, V. & Santos, L. (2011) Degradation and removal methods of antibiotics from aqueous matrices–a review. *Journal of environmental management*, 92(10), 2304-2347.

Hsu, J.-T., Chen, C.-Y., Young, C.-W., Chao, W.-L., Li, M.-H., Liu, Y.-H., Lin, C.-M. & Ying, C. (2014) Prevalence of sulfonamide-resistant bacteria, resistance genes and integron-associated horizontal gene transfer in natural water bodies and soils adjacent to a swine feedlot in northern Taiwan. *Journal of hazardous materials*, 277, 34-43.

Huang, J., Song, H. Y., Chen, C. X., Yang, Y., Xu, N. D., Ji, X. Z., Li, C. Y. & You, J. A. (2017) Facile synthesis of N-doped TiO2 nanoparticles caged in MIL-100(Fe) for photocatalytic degradation of

organic dyes under visible light irradiation. *Journal of Environmental Chemical Engineering*, 5(3), 2579-2585.

Huttner, A., Harbarth, S., Carlet, J., Cosgrove, S., Goossens, H., Holmes, A., Jarlier, V., Voss, A. & Pittet, D. (2013) Antimicrobial resistance: a global view from the 2013 World Healthcare-Associated Infections Forum. *Antimicrobial resistance and infection control*, 2(1), 31.

Kemper, N. (2008) Veterinary antibiotics in the aquatic and terrestrial environment. *Ecological indicators*, 8(1), 1-13.

Khedr, T. M., El-Sheikh, S. M., Hakki, A., Ismail, A. A., Badawy, W. A. & Bahnemann, D. W. (2017) Highly active non-metals doped mixed-phase TiO2 for photocatalytic oxidation of ibuprofen under visible light. *Journal of Photochemistry and Photobiology a-Chemistry*, 346, 530-540.

Kumar, A., Reddy, K. L., Kumar, S., Sharma, V. & Krishnan, V. (2018) Rational Design and Development of Lanthanide-Doped NaYF4@CdS-Au-RGO as Quaternary Plasmonic Photocatalysts for Harnessing Visible-Near-Infrared Broadband Spectrum. *Acs Applied Materials & Interfaces*, 10(18), 15565-15581.

Kümmerer, K. (2009) Antibiotics in the aquatic environment–a review–part I. *Chemosphere*, 75(4), 417-434.

Landers, T. F., Cohen, B., Wittum, T. E. & Larson, E. L. (2012) A review of antibiotic use in food animals: perspective, policy, and potential. *Public health reports*, 127(1), 4-22.

Laxminarayan, R., Duse, A., Wattal, C., Zaidi, A. K., Wertheim, H. F., Sumpradit, N., Vlieghe, E., Hara, G. L., Gould, I. M. & Goossens, H. (2013) Antibiotic resistance—the need for global solutions. *The Lancet infectious diseases*, 13(12), 1057-1098.

Liang, R. W., Luo, S. G., Jing, F. F., Shen, L. J., Qin, N. & Wu, L. (2015) A simple strategy for fabrication of Pd@MIL-100(Fe) nanocomposite as a visible-light-driven photocatalyst for the treatment

of pharmaceuticals and personal care products (PPCPs). *Applied Catalysis B-Environmental*, 176, 240-248.

Lin, L., Wang, H. Y. & Xu, P. (2017) Immobilized TiO2-reduced graphene oxide nanocomposites on optical fibers as high performance photocatalysts for degradation of pharmaceuticals. *Chemical Engineering Journal*, 310, 389-398.

Lundholm, K., Hyltander, A. & Sandström, R. (1992) Nutrition and multiple organ failure. *Nutrition research reviews*, 5(1), 97-113.

Malato, S., Fernández-Ibáñez, P., Maldonado, M. I., Blanco, J. & Gernjak, W. (2009) Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. *Catalysis Today*, 147(1), 1-59.

Malizos, K. N. & Kirketerp-Møller, K. (2016) Incidence and Socioeconomic Impact of Bone and Joint Infections (BJIs): The European Perspective, *Periprosthetic Joint Infections*Springer, 3-18.

Martinez-Costa, J. I., Rivera-Utrilla, J., Leyva-Ramos, R., Sanchez-Polo, M. & Velo-Gala, I. (2018) Individual and simultaneous degradation of antibiotics sulfamethoxazole and trimethoprim by UV and solar radiation in aqueous solution using bentonite and vermiculite as photocatalysts. *Applied Clay Science*, 160, 217-225.

Mathew, S., Ganguly, P., Rhatigan, S., Kumaravel, V., Byrne, C., Hinder, S., Bartlett, J., Nolan, M. & Pillai, S. (2018) Cu-Doped TiO2: Visible Light Assisted Photocatalytic Antimicrobial Activity. *Applied Sciences*, 8(11), 2067.

Mathur, S. & Hoskins, C. (2017) Drug development: Lessons from nature. *Biomedical reports*, 6(6), 612-614.

Morgan, D. J., Okeke, I. N., Laxminarayan, R., Perencevich, E. N. & Weisenberg, S. (2011) Non-prescription antimicrobial use worldwide: a systematic review. *The Lancet infectious diseases*, 11(9), 692-701.

Namshah, K. S. & Mohamed, R. M. (2018) WO3-TiO2 nanocomposites for paracetamol degradation under visible light. *Applied Nanoscience*, 8(8), 2021-2030.

O'Shea, R. & Moser, H. E. (2008) Physicochemical properties of antibacterial compounds: implications for drug discovery. *Journal of medicinal chemistry*, 51(10), 2871-2878.

Panneri, S., Ganguly, P., Mohan, M., Nair, B. N., Mohamed, A. A. P., Warrier, K. G. & Hareesh, U. (2017a) Photoregenerable, Bifunctional Granules of Carbon-Doped g-C3N4 as Adsorptive Photocatalyst for the Efficient Removal of Tetracycline Antibiotic. *ACS Sustainable Chemistry & Engineering*, 5(2), 1610-1618.

Panneri, S., Ganguly, P., Nair, B. N., Mohamed, A. A. P., Warrier, K. G. & Hareesh, U. N. (2016) Copyrolysed C3N4-Ag/ZnO Ternary Heterostructure Systems for Enhanced Adsorption and Photocatalytic Degradation of Tetracycline. *European Journal of Inorganic Chemistry*, 2016(31), 5068-5076.

Panneri, S., Thomas, M., Ganguly, P., Nair, B. N., Mohamed, A. P., Warrier, K. & Hareesh, U. (2017b) C 3 N 4 anchored ZIF 8 composites: photo-regenerable, high capacity sorbents as adsorptive photocatalysts for the effective removal of tetracycline from water. *Catalysis Science & Technology*.

Perumal Samy, R. & Gopalakrishnakone, P. (2010) Therapeutic potential of plants as anti-microbials for drug discovery. *Evidence-based complementary and alternative medicine*, 7(3), 283-294.

Prieto-Rodriguez, L., Miralles-Cuevas, S., Oller, I., Agüera, A., Puma, G. L. & Malato, S. (2012) Treatment of emerging contaminants in wastewater treatment plants (WWTP) effluents by solar photocatalysis using low TiO2 concentrations. *Journal of hazardous materials*, 211, 131-137.

Pérez-González, A., Urtiaga, A., Ibáñez, R. & Ortiz, I. (2012) State of the art and review on the treatment technologies of water reverse osmosis concentrates. *Water research*, 46(2), 267-283.

Ray, S. K., Dhakal, D. & Lee, S. W. (2018) Rapid degradation of naproxen by AgBr-α-NiMoO4 composite photocatalyst in visible light: Mechanism and pathways. *Chemical Engineering Journal*, 347, 836-848.

Regmi, C., Kshetri, Y. K., Pandey, R. P. & Lee, S. W. (2018) Visible-light-driven S and W co-doped dendritic BiVO4 for efficient photocatalytic degradation of naproxen and its mechanistic analysis. *Molecular Catalysis*, 453, 149-160.

Renita, A. A., Kumar, P. S., Srinivas, S., Priyadharshini, S. & Karthika, M. (2017) A review on analytical methods and treatment techniques of pharmaceutical wastewater. *DESALINATION AND WATER TREATMENT*, 87, 160-178.

Sassman, S. A. & Lee, L. S. (2005) Sorption of three tetracyclines by several soils: assessing the role of pH and cation exchange. *Environmental Science & Technology*, 39(19), 7452-7459.

Serpone, N., Artemev, Y. M., Ryabchuk, V. K., Emeline, A. V. & Horikoshi, S. (2017) Light-driven advanced oxidation processes in the disposal of emerging pharmaceutical contaminants in aqueous media: A brief review. *Current Opinion in Green and Sustainable Chemistry*, 6, 18-33.

Shetty, R., Chavan, V. B., Kulkarni, P. S., Kulkarni, B. D. & Kamble, S. P. (2017) Photocatalytic Degradation of Pharmaceuticals Pollutants Using N-Doped TiO2 Photocatalyst: Identification of CFX Degradation Intermediates. *Indian Chemical Engineer*, 59(3), 177-199.

Shinde, Y., Wadhai, S., Ponkshe, A., Kapoor, S. & Thakur, P. (2018) Decoration of Pt on the metal free RGO-TiO2 composite photocatalyst for the enhanced photocatalytic hydrogen evolution and photocatalytic degradation of pharmaceutical pollutant beta blocker. *International Journal of Hydrogen Energy*, 43(8), 4015-4027.

Stackelberg, P. E., Furlong, E. T., Meyer, M. T., Zaugg, S. D., Henderson, A. K. & Reissman, D. B. (2004) Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. *Science of the total environment*, 329(1-3), 99-113.

Strauch, K. A. (2011) Invisible pollution: the impact of pharmaceuticals in the water supply. *Aaohn Journal*, 59(12), 525-533.

Tilgner, D., Friedrich, M., Verch, A., de Jonge, N. & Kempe, R. (2018) A Metal–Organic Framework Supported Nonprecious Metal Photocatalyst for Visible-Light-Driven Wastewater Treatment. *ChemPhotoChem*, 2(4), 349-352.

Tiong, J. J., Loo, J. S. & Mai, C.-W. (2016) Global antimicrobial stewardship: A closer look at the formidable implementation challenges. *Frontiers in microbiology*, 7, 1860.

Tong, H., Ouyang, S., Bi, Y., Umezawa, N., Oshikiri, M. & Ye, J. (2012) Nano-photocatalytic materials: possibilities and challenges. *Advanced materials*, 24(2), 229-251.

Ventola, C. L. (2015) The antibiotic resistance crisis: part 1: causes and threats. *Pharmacy and therapeutics*, 40(4), 277.

Wang, D., Jia, F., Wang, H., Chen, F., Fang, Y., Dong, W., Zeng, G., Li, X., Yang, Q. & Yuan, X. (2018) Simultaneously efficient adsorption and photocatalytic degradation of tetracycline by Fe-based MOFs. *Journal of colloid and interface science*, 519, 273-284.

Wexler, H. M. (2007) Bacteroides: the good, the bad, and the nitty-gritty. *Clinical microbiology reviews*, 20(4), 593-621.

Whitham, T. G., Bailey, J. K., Schweitzer, J. A., Shuster, S. M., Bangert, R. K., LeRoy, C. J., Lonsdorf, E. V., Allan, G. J., DiFazio, S. P. & Potts, B. M. (2006) A framework for community and ecosystem genetics: from genes to ecosystems. *Nature Reviews Genetics*, 7(7), 510.

Xing, X. B., Du, Z. X., Zhuang, J. C. & Wang, D. (2018) Removal of ciprofloxacin from water by nitrogen doped TiO2 immobilized on glass spheres: Rapid screening of degradation products. *Journal of Photochemistry and Photobiology a-Chemistry*, 359, 23-32.

Zhao, W., Duan, J., Ji, B., Ma, L. & Yang, Z. (2018) Novel formation of large area N-TiO2/graphene layered materials and enhanced photocatalytic degradation of antibiotics. *Journal of Environmental Chemical Engineering*.

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