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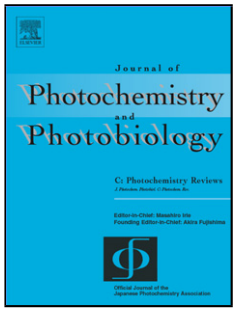

The upsurge of photocatalysts in antibiotic micropollutants treatment: Materials design, recovery, toxicity and bioanalysis

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The Upsurge of Photocatalysts in Antibiotic Micropollutants Treatment: Materials Design, Recovery, Toxicity and Bioanalysis

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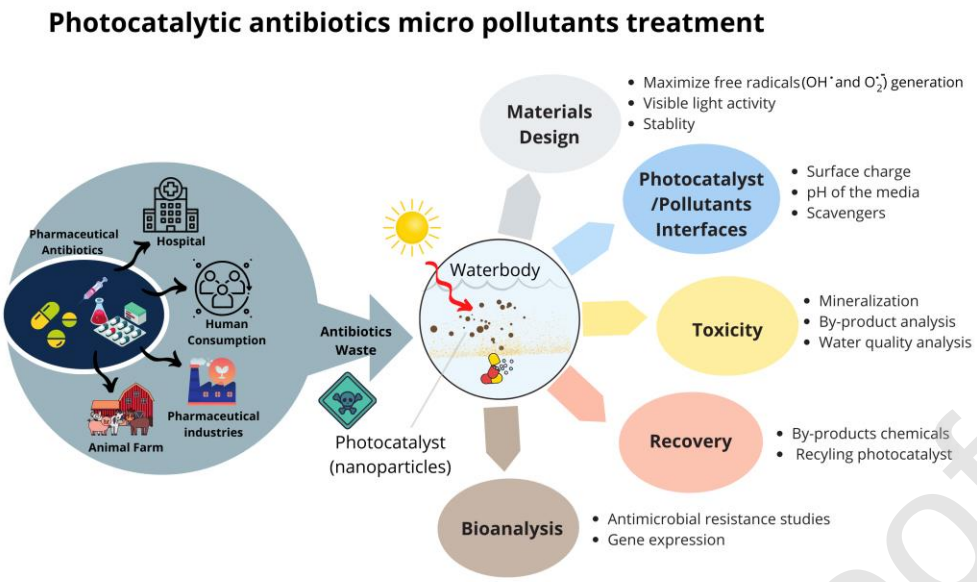
Graphical abstract



Highlights

- Discussing fundamentals, and recent progress on photocatalytic antibiotic treatment
- Critical issues on accelerating free radical generation by photocatalysis route
- Opportunities of recovering value-added chemicals during water treatment
- Importance of material's toxicity and water quality after treatment highlighted
- Materials choice, and influence of processing parameters are outlined

Abstract

The excessive use of antimicrobial agents such as antibiotics and disinfectants for domestic purposes and industries polluted the water bodies severely in the recent past. Thus released antimicrobial agents negatively impact the environment and human health as it induce antimicrobial resistance (AMR) to microbes in the environment. Conventional biodegradation routes showed feasible antibiotics pollutants degradation. Nonetheless, they often demand a long time of operation (usually in days) and a major portion of the antimicrobial agents is left untreated unlike the complete oxidation with advanced oxidation processes. The residues of antibiotics left in the water bodies accelerate growth of microorganisms (bacterial, fungal, and viral) with AMR. In virtue of avoiding the catastrophe of widespread AMR,

photocatalysis assisted antibiotic pollutant treatment is recently gaining a great popularity as an advanced oxidation process and has shown to be useful for the removal of antimicrobial compounds, mainly antibiotics. Recent review reports on photocatalytic antibiotic degradation focus on summarizing materials progress and antibiotics pollutants in chronological viewpoints. However, the relationship between photocatalytic materials and antibiotics oxidation reaction pathways and the toxicity of by-products are needed to be shown with better clarity to transfer the photocatalysis technique from lab to market in a safe way. This review critically analyzes the insights of energetic semiconductor structure lacking to achieve hydroxyl and superoxide radicals mediated antibiotics degradation, recommends new materials design (Z scheme) and standardization in the experimental designs, and also informs the influencing parameters on antibiotic degradation. It further assesses the possibility of recovering value-added chemicals from the photocatalytic treatment process and highlights the importance of environmental toxicity analysis. Overall, this review will be a resourceful guide for interdisciplinary researchers working on advanced photocatalysis and pharmaceutical pollutant treatment for achieving a sustainable ecology and initiating a circular economy in chemical industries.

Keywords: photocatalyst, solar, antibiotics, water pollutants, nanomaterial, antimicrobial resistance

1. Introduction

Antimicrobial agents such as disinfectants and antibiotics kill microorganisms (bacteria, fungi, viruses, and parasites) either on fomite surfaces or in living organisms. In particular, the antibiotics prescribed in medicinal treatments for humans

and the disinfectants used in the farming industries and aquaculture plants. A recent analysis by Klein et al. (1) on the daily doses (D.D.D.) of antibiotic consumption between 2000 to 2015 investigated in 76 countries was found to be increased by 65% (21.1–34.8 billion D.D.D.s), and the antibiotic consumption rate was increased by 39% (11.3–15.7 DDDs per 1,000 inhabitants per day). Mostly, the antibiotic consumption has increased in low- and middle-income countries and in the case of high-income countries, it was found to be modest. Though antibiotics have many benefits such as great effectiveness, low-cost and constant availability, its overuse in the recent past has caused a serious pollution in water bodies and are unfortunately left behind by the inherently incapable wastewater treatment technologies that are already in operation. Recent studies have found that various water sources, including sewage effluents, sludge, ground and surface water, soil, and manure, were containing antibiotics residues (2-4). In general, pharmaceutical antibiotics are poorly metabolized and absorbed by both humans and animals. The discharge of faecal, urinal, and contaminated water wastes from the above contact points, with a very high antibiotics residues are potential threats to the ecosystem (Figure 1). These antibiotic pollutants in the surface and groundwater accelerate antimicrobial resistance (AMR) to various microorganisms such as bacteria, fungi, viruses, and parasites as they get exposed to these pollutants almost constantly (5, 6). Microorganisms that are resistant to several classes of antimicrobials agents are referred to as “superbugs”. In many places, antibiotics are unnecessarily used in people and animals, and often given without professional oversight. In developing countries, these antimicrobial agents are available to the public without the prescriptions from qualified authorities which has been the primary cause of their inappropriate use. Antimicrobial agents are taken by people for viral infections like common cold and flu. In aquaculture and animal feeds,

antimicrobial agents are used as growth promoters to antibiotic-resistant bacteria (ARB) and antibiotic resistance genes (ARGs) (7). Such an extensive, unsupervised, and unethical use of antimicrobial agents have made the water bodies as significant reservoirs of antibiotics pollutants that could either increase pathogens to become antibiotic-resistant or contaminate our food chain (8, 9).

World Health Organization (WHO) raised severe concern on AMR being developed by the microorganisms that live in antimicrobial agents polluted wastewater that lowers the effectiveness of antimicrobial agents used currently. It is a significant concern for human health because this AMR developed by pathogens is very likely to turn minor illness into life-threatening ones as they cannot be treated any more with the antibiotics that we have today and for which the are resistant (10-15). European Union's recent Joint Research Centre report (JRC 2018) explored the scenario of antibiotic residuals found in water resources (wastewater treatment plants-WWTP), surface waters, agricultural runoff, and drinking waters) from 13 countries around the world. The survey stated that nearly 45 antibiotics were found in those water bodies. Among the surveyed countries, major antibiotic pollutants existed in the Europe (79.2%) where the concentrations of antimicrobial agents had reached as high as 1 µg/L. Domestic wastewater on the other hand is also severely contaminated by the improper disposal of antibiotics and excretions that are still rich in antibiotics.

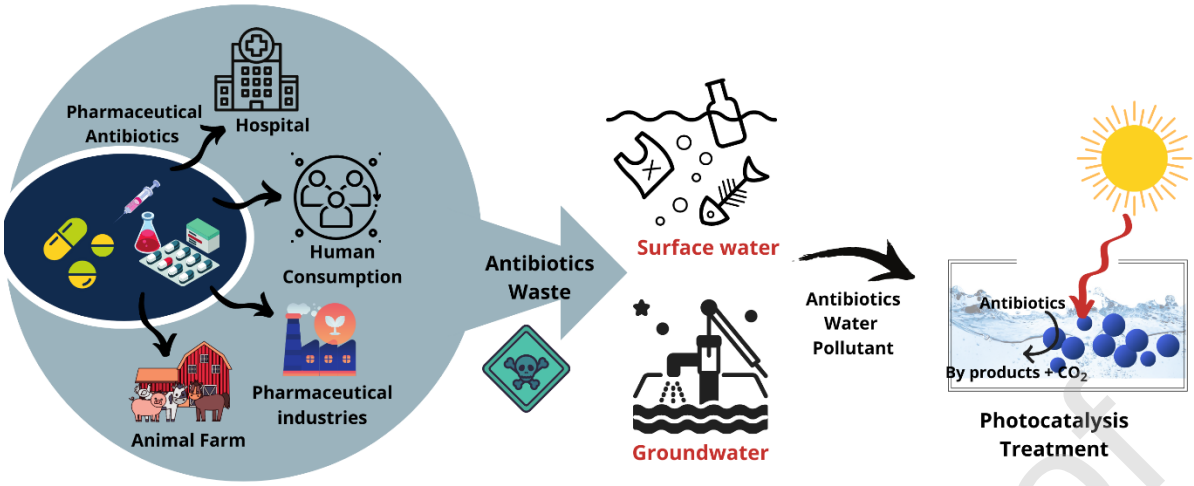


Figure 1. Schematic illustration of pharmaceutical antibiotics consumption routes and impact on water bodies and the proposal of treating the same with solar energy-driven photocatalysis technique.

Aydin et al. (11) found that existing wastewater treatment plants (WWTPs) by utilizing conventional physical and biological treatment had shown inadequate removal of antibiotics. The current efficiencies of removing antibiotics by the existing water-treatment plants are 76 and 36%, respectively in summer and winter seasons at Turkey. Though antibiotics concentration after discharging from WWTPs was reduced substantially, the concentration of antibiotics residues was still traceably higher (ng/L - µg/L level) and at this level, they are often called as the "micropollutants" which are still a serious threat to the environment and healthcare (16-18). Figure 2 shows the concentration of a few commonly used antibiotics such as ciprofloxacin, enrofloxacin, norfloxacin, ofloxacin, roxithromycin, sulfadiazine, sulfamethazine, sulfamethoxazole, and trimethoprim in the range of 100- 40,000 ng/L in the water bodies. Notably, the antibiotic pollutants are in a relatively comparable concentrations to other organic water pollutants including NSAI drugs, Estrogen, herbicide and pesticide.

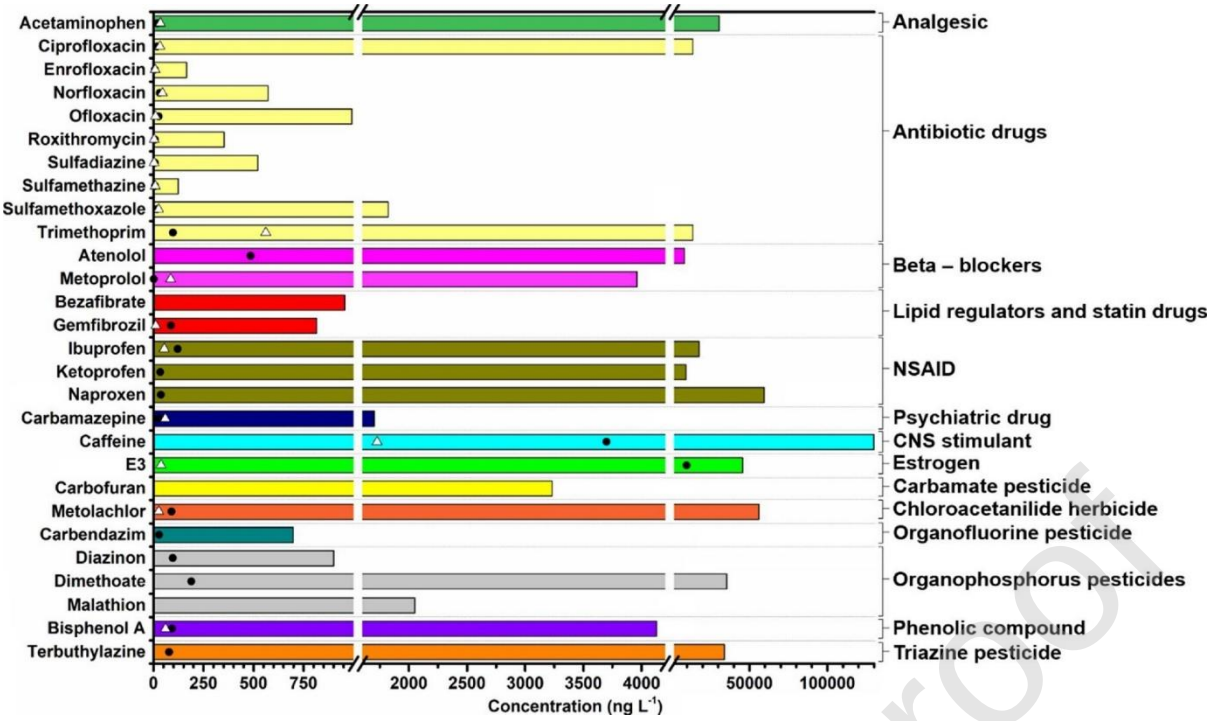


Figure 2. Concentration ranges of a few commonly used antibiotic drugs that were found in the water bodies compared with a few common organic contaminants. Reproduced from (17) with permission from Elsevier Publishers.

The existing water treatment technologies are efficiently removing the organic contaminants from water based mainly on their physiochemical behaviours such as (a) hydrophobicity, (b) absorbability, (c) volatility, (d) biodegradability, (e) charge, and (f) molecular weight and size (19). Ever since the discovery of photoelectrocatalytic water splitting by Honda and Fujishima, the light-driven oxidation process received profound attention in photocatalytic applications particularly in organic pollutants degradation (20). Many studies focused on the utilization of photocatalysis for water treatment while a handful of them are showing their prominent successes (21). In this line, a light-driven photocatalysis is a promising advanced oxidation process (AOP) technology that is capable of degrading hazardous organic water pollutants present in waterbodies and converting them into toxins-free minerals and carbon dioxide(22-27). Since 2010, the light-driven photocatalytic degradation of antibiotic contamination

(**Figure 2b**) geared up in an exponential rate owing to several advantages that it possesses. To name a few, economic viability, eco-friendly nature, ability to recycle the photocatalysts, and sludge-free post-treatment waters which is the thorn in the flesh with conventional WWTPs (28-32).

The photocatalytic antibiotic degradation efficiency relies on several factors including semiconductor properties (optical, electrical conductivity, etc.,), photo charge carrier separation (33) and recombination kinetics, the stability of the photocatalyst against photo corrosion (34), and poisoning effect by electrolyte (35) or pollutants being treated. In addition to these parameters, photocatalyst loading quantity, pH of the reaction medium, and concentration of the contaminants are also influencing the rate of antibiotics degradation. It is explicit at this point that this field requires the wisdom of different research areas such as semiconductor physics, photo/electrochemistry, pharmaceutical and environmental toxicology and is purely an interdisciplinary field. Most of the review reports published in this field (36-43) summarize either materials used or the drugs treated with monotonous perspectives and severely lack in bridging the aforementioned interdisciplinary topics that form the heart of this research field. However, the readers are still appreciated to explore the recent review reports (44-48) for the basic understanding of the contemporary practices on photocatalytic materials in antibiotic degradation and to get a comprehensive view of antibiotic pollutants. However, connecting the dots among the photocatalysis parameters, antibiotic degradation, importance of post-treatment analysis, and mechanistic pathways of drug degradation is equally inevitable. Hence, this review is consigned to critically analyse the recent research works on photocatalytic antibiotics degradation and to discuss the future perspectives (materials,

recovery and toxicity analysis) with a much-needed objective of accelerating interdisciplinary approach in this field.

2. Theory- Photocatalysis:

The interaction of light energy (hν) with matter is a crucial step in the photocatalysis process. When a semiconductor (usually TiO_2 due to its high photocatalytic characteristics), is irradiated by light, this leads to the absorption of photons and generates photo charge carriers (electrons and holes). The excited photoelectrons from the valance band to the conduction band generates an unpaired photo hole in the valance band, which can undergo interfacial electron transfer and induce useful redox reactions and this has been the core of all photocatalysis based pollutant removal techniques

$$\text{Semiconductor} + h\nu \rightarrow \text{Semiconductor}\ (e^-_{CB}, h^+_{VB}) \quad (1)$$

$$O_2 + e^-_{CB} \rightarrow O_2^{\bullet -} \quad (2)$$

$$O_2^{\bullet -} + H^+ + e^-_{CB} \rightarrow HO_2^{\bullet -} \quad (3)$$

$$HO_2^{\bullet -} + HO_2^{\bullet -} \rightarrow H_2O_2 + O_2 \quad (4)$$

$$H_2O_2 + e^-_{CB} \rightarrow OH^{\bullet} + OH^- \quad (5)$$

The photoelectrons at the conduction band (e^-_{CB}) of a semiconductor can reduce oxygen to superoxide radical ($O_2^{\bullet -}$) anion (equation 2), which in turn can produce hydroxyl radicals (equations 3–5). The superoxide radicals are energetic to disintegrate the targeted organic substances/pollutants into minerals and CO_2 and possibly to other by-products based on the substance being treated (49). When the photo holes reach the TiO_2 surface, they react with the water molecules and produce hydroxyl radicals ($OH^{\bullet}$) which are non-selective oxidants and exhibit a high oxidation potential of 2.72 V depending on the experimental conditions (50).

$H_2O + h^+_{VB} \rightarrow [H_2O]^+ \rightarrow OH^\bullet + H^+$ (6)

A typical photocatalytic reactor practiced in lab-scale antibiotic degradation is illustrated in **Figure 3 (a)**. A UV (<400 nm) or a white light source or natural sunlight can be employed as the desired light source to irradiate the semiconductor photocatalyst. A target antibiotic pollutant dispersed in the aqueous or non-aqueous media along with the photocatalyst materials are let to continuously circulate in the reactor. To avoid the transfer of heat energy from the light source to the reaction media, cold water is distributed in the reactor in a steady rate. **Figure 3(b)** depicts the schematic of photocatalytic antibiotic treatment through photoelectron and holes. As discussed in equations (2-6), $OH^\bullet$ and $O_2^{\bullet-}$ free radicals play a crucial role in degrading the antibiotic pollutants and their by-products in water. A detailed free radical analysis and quantification from photocatalytic degradation process is reported elsewhere(51-53). The free radical analysis can reveal the possible degradation pathways ($OH^\bullet$, $O_2^{\bullet-}$ or $OH^\bullet$/ $O_2^{\bullet-}$) of antibiotics being treated. A vital question in the antibiotic degradation process when compared to textile dye pollutants is does it create further harm to the environment besides ensuring water quality after the photocatalytic treatment. Most of the photocatalytic antibiotic degradation research methodology displayed degradation performances but none of them answered this question ever before.

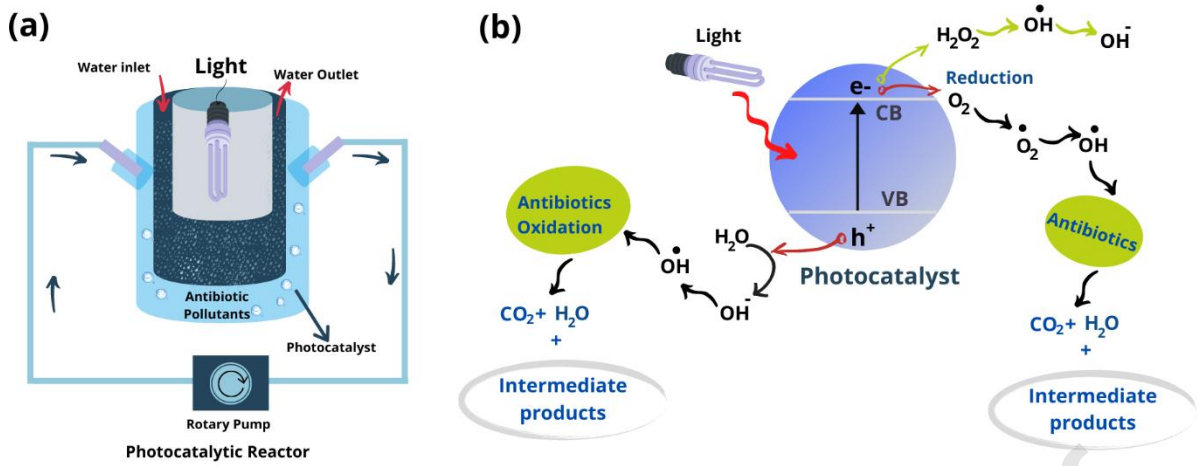


Figure 3. Schematic illustration of (a) typical flow-type photocatalytic reactor for antibiotics degradation, (b) Photocatalytic antibiotic degradation pathways.

3. Photocatalytic antibiotic degradation: recent progress

3.1 Material design:

The energy levels of semiconductors with respect to normal hydrogen electrode (NHE) are essential in determining the efficiency of the photocatalytic degradation process. A wide range of semiconductor materials including metal oxides, metal chalcogenides, metal nanoparticles, graphene, and its composites, has been demonstrated to be effective in environmental clean-up applications (54-58). The conduction band and valence band positions of potential semiconductor photocatalysts where previously established in organic pollutants degradation as summarized in **Figure 4**. As discussed above, photocatalysts with valence band position equal to or higher than +2.32 V vs. NHE were capable of producing $OH^{\bullet}$ radicals under light irradiation. Conversely, the photocatalysts with conduction band position is equal to or lesser than -0.32 V vs. NHE support the $O_2^{\bullet-}$ radicals generation. Based on the valence band and conduction band positions, a semiconductor can be chosen either for photo-oxidation and photo-reduction process (59). In **Figure 4**, the semiconductors

with valence band positions above +2.32 V vs. NHE are propitious the oxidations of antibiotic molecules by producing $OH^{\bullet}$ radicals (60). On the other hand, photocatalysts with the conduction band values more negative than -0.33 V vs. NHE are promising candidates for reducing the antibiotic molecules via $O_2^{\bullet-}$ radicals. Note that the VB and CB positions of semiconductor depends with their particle size. For instance, the WO_3 nanoparticles have different energy levels compared to bulk WO_3 (61, 62).

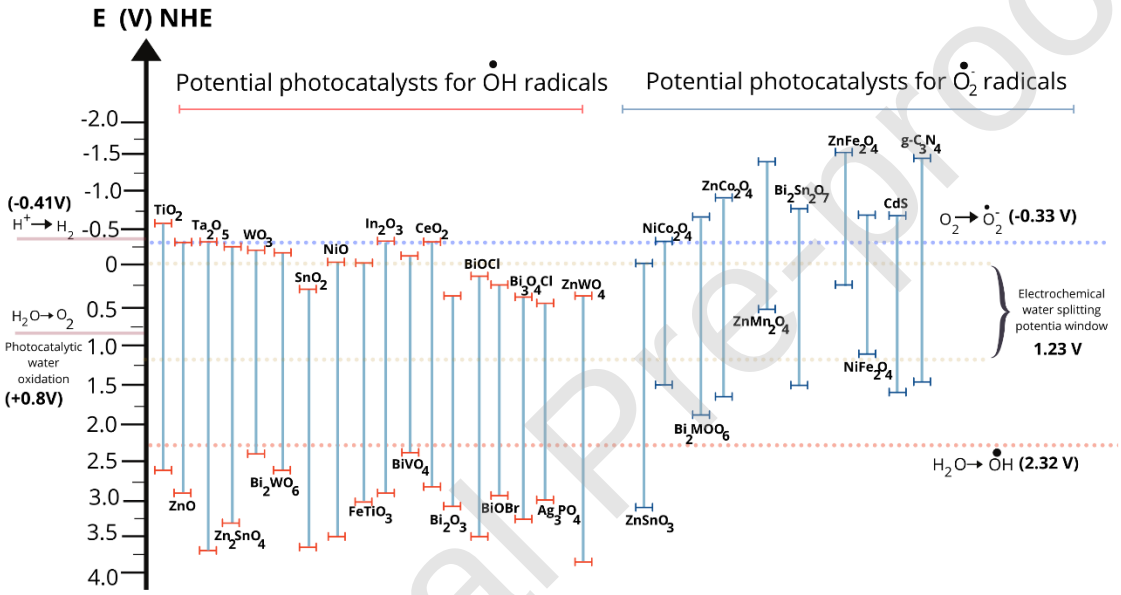


Figure 4. Energetic structure of different semiconductor photocatalysts (in V vs. NHE) that are capable of producing $OH^{\bullet}$ and $O_2^{-\bullet}$. All these values were collected from the literature for pH 7.

Figure 5 illustrates the recent survey on photocatalytic degradation of most commonly used antibiotics and highlights the high-risk candidates in the wastewater treatment plants. It seems that $OH^{\bullet}$ radical-mediated degradation is the most studied pathways compared to $O_2^{\bullet-}$ mediated degradation. The choice of a broader bandgap energy-based semiconductors (>400 nm- <800 nm) possessing favourable valence band higher than water oxidation potential (1.23 V vs. NHE) is the main reason for

demonstrating more research on $OH^{\bullet}$ radical-mediated degradation(63). But ample room is available to utilize potential semiconductors for producing $O_2^{\bullet-}$ radicals as seen in Figure 4. Mainly earth abundance (Ni, Mn and Co) (64-66) and less expensive metals (Fe, Bi and Zn) based alloys (67) (68) can be applied in photocatalytic antibiotic degradation. The Ni and Fe alloys (69) (70) have magnetic properties that can have an added advantage to recover the photocatalyst materials after the reaction. The recent invention of g-C_3N_4 materials shows promising photocatalytic performance and the desire for $O_2^{\bullet-}$ mediated degradation (71, 72). The advantage of combining these semiconductor materials as a hetero partner in association with $OH^{\bullet}$ radical producing candidates is anticipated to increase the antibiotics degradation rate. Also, heterostructured semiconductors enhance the photo charge carriers separation (73) at the semiconductor/pollutant interface and promote the degradation rate that are discussed later.

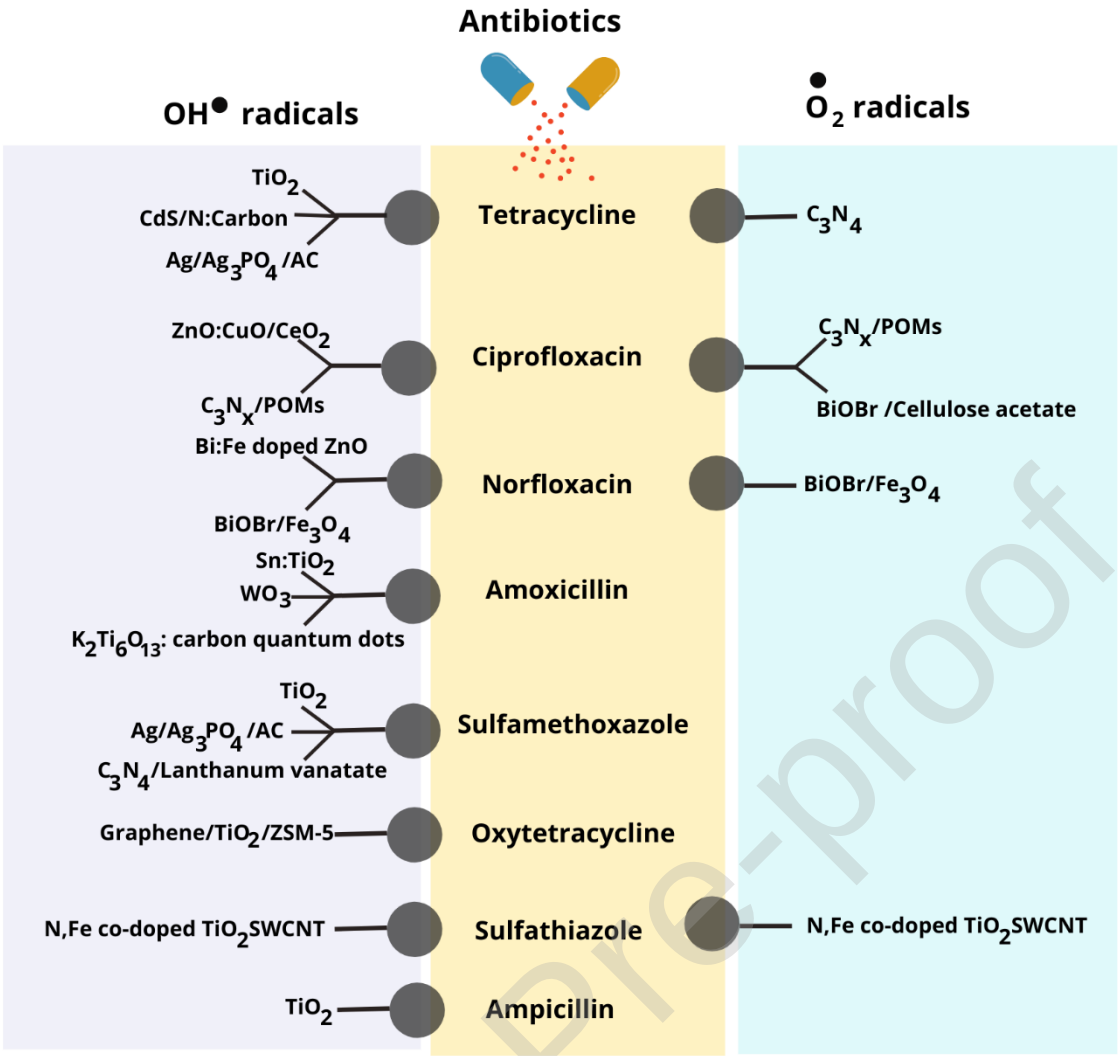


Figure 5. Commonly practiced antibiotics and their photocatalytic degradation pathways through OH• and O_2-• radicals using different photocatalyst materials. The photocatalyst materials data collected from the literature ((74) (75) (31) (76), (77) (78) (79), (80) (81) , (82) (83) (84), (32) , (85))

Figure 5 displays the recent survey on hydroxyl and superoxide radicals pathways assisted antibiotics degradation. It reflects a similar tendency that was shown in **Figure 4**, where hydroxyl radicals induced antibiotics degradation is mostly identified compared to $O_2^{\bullet-}$ radicals induced ones. Though single semiconductors such as TiO_2, ZnO, CeO_2, and Ta_2O_5 photocatalyst produce both $OH^{\bullet}$ and $O_2^{\bullet-}$ radicals, the expected self recombination process at surface require additional materials modification or decorating co-catalysts to improve charge degradation rate (86-88). Karaolia et al. (89)

showed TiO_2-rGO composite effectively removed 87% of sulfamethoxazole in 1 h than pristine TiO_2 (**Figure 6a**). This increased degradation is due to the photogenerated charges being separated at TiO_2/rGO interfaces, thus reducing charge recombination (21). The sp^2 hybridized network of the rGO facilitates electron's transport from TiO_2 conduction band towards oxygen groups to generate reactive oxygen species (ROS) which are involved in the chemical oxidation of organic microcontaminants. However, a similar experiment demonstrated by Hu et al. (90) using only TiO_2 found 100% complete removal of sulfamethoxazole with modified electrolyte media. They realized that in the absence of external electron acceptor, the rate of sulfamethoxazole degradation is greater in O_2-sparged than air-sparged suspensions (**Figure 6b**). Further, adding bromate as an alternative electron acceptor to the anoxic TiO_2 suspension accelerated photocatalytic degradation rate (91). It infers that the charge separation of photoelectron and holes enhanced antibiotic degradation while adding electron or holes scavengers in the electrolyte media, in addition to photocatalyst material modification (promoting bulk transport).

Natural sunlight is an inevitable light resource for the sustainable photocatalytic antibiotic degradation process (92) available at no cost. But traditional semiconductors (TiO_2, CeO_2, WO_3, ZnO) only perform under UV light irradiation (93-95). In the solar spectrum, only 5% of the photons fall on the earth surface. Therefore, designing narrow bandgap energy materials capable of absorbing visible light photons (>400 nm) from sunlight without sacrificing their water oxidation performance are inevitable. Referring to **Figure 4**, narrow bandgap energy materials such as CdS and C_3N_4 are appropriate for producing $O_2^{\bullet-}$ radicals under sunlight irradiation (96). The valence band position of these materials is lesser than water oxidation or OH radical generation potentials and hence, they require an additional hetero partner. Developing

visible light-driven heterostructured semiconductor photocatalyst while managing both OH• and $O_2^{\bullet-}$ radicals can promote antibiotic degradation further.

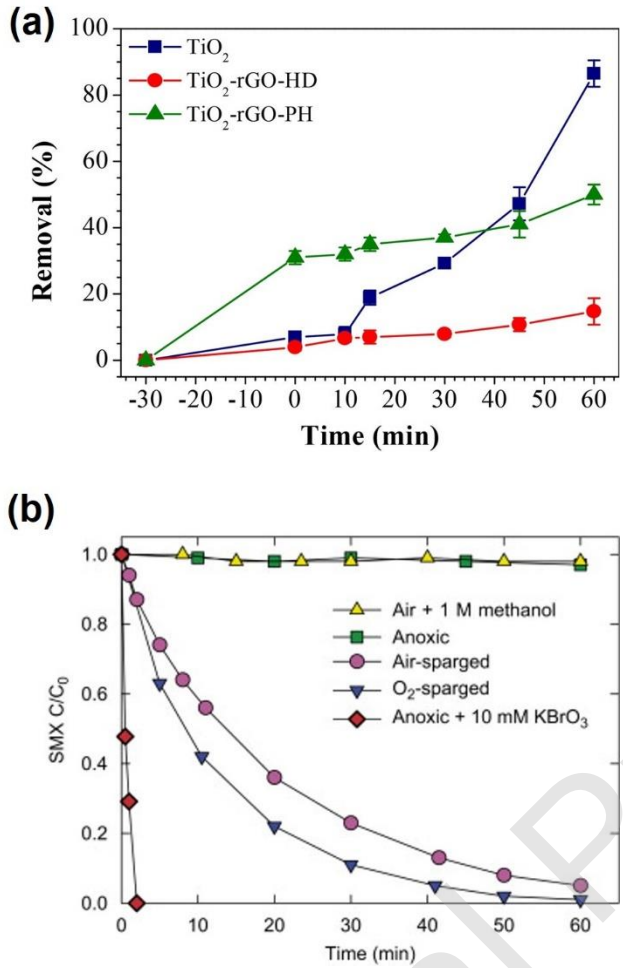


Figure 6. Photocatalytic degradation of sulfamethoxazole in different approaches (a) modified the photocatalyst and (b) modified electrolyte media (Figure 6a reprint permission from Elsevier Publishers (89)) and Figure 6b reprint permission from Elsevier Publishers (90)).

Heterostructured photocatalysts can perform water reduction or oxidation independently, either of the energetic structure favourable to these reactions. Here, scavenging the photo charge carriers generated at two photocatalyst interfaces is essential. A suitable shuttle redox mediator assisted heterojunction "Z-scheme" is successfully demonstrated in full photocatalytic water splitting process (97). Later, it inspired other researchers to develop redox-free Z scheme systems and show excellent performance in different photocatalysis applications (98-101). **Figure 5** shows the

schematic of the energetic bandgap structure of photocatalyst demonstrated in antibiotic degradation. Solid-state direct Z Scheme mechanism (101-103) offer the generation of both OH• and $O_2^{\bullet-}$ free radicals at different semiconductor surface, simultaneously. The Z-scheme-based photocatalyst showed relatively fast antibiotic degradation compared to conventional heterostructure semiconductors or single semiconductors (68, 104-106, 64). Huang et al. reported direct Z Scheme based photocatalytic degradation of tetracycline (TCY) using $SnO_2/Bi_2Sn_2O_7$ hetero semiconductors. The $SnO_2/Bi_2Sn_2O_7$ showed 88.4 % of TCY degradation though OH• and $O_2^{\bullet-}$ radicals, which was 1.4 fold higher than that of pure $Bi_2Sn_2O_7$ (62.9 %) and 12.5 times higher than pure SnO_2 (7.1%) (68). Metal nanoparticles act as Schottky junction between two semiconductors and scavenge both electrons and holes from hetero partners (**Figure 7**). Recent reports on Ag metal nanoparticles facilitated Z scheme based photocatalyst using metal nanoparticles as an interfacial layer (107-110)

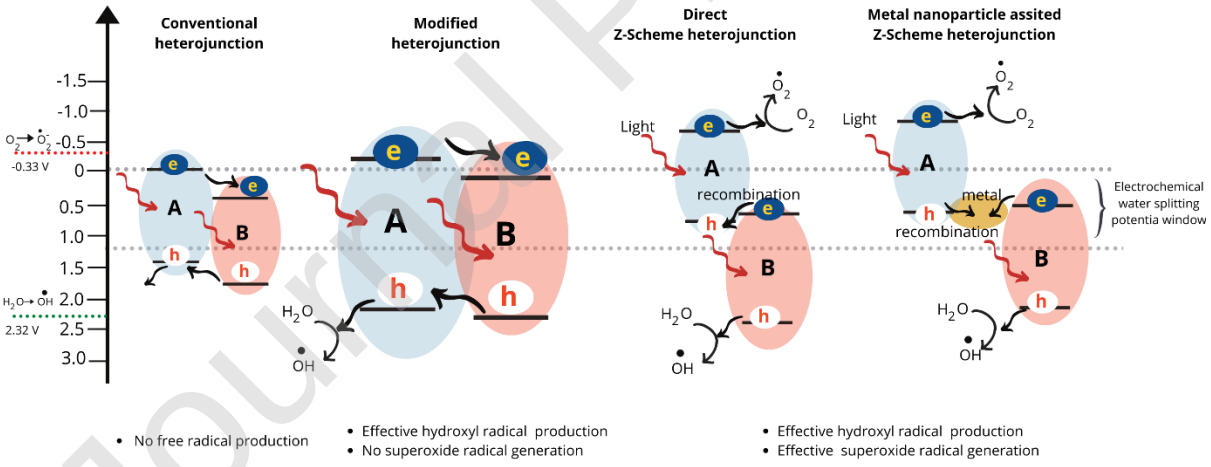


Figure 7. Schematic illustration of conventional and Z-scheme based heterojunction architecture in free radical production for antibiotic pollutants degradation. Note that A and B are semiconductor photocatalysts.

3.2 Influence of processing parameters on antibiotic degradation:

To improve photocatalysis' performance for antibiotic degradation, the factors needed to be considered are: (a) initial antibiotic concentration, (b) photocatalyst utilized and its loading, (c) light intensity, (d) electron acceptor identity and concentration, (e) pH, and (f) presence of an organic substance in the solution.

3.2.1 Initial concentration of antimicrobial compound:

Many researchers (90, 111-114) have demonstrated that increasing the initial concentration of antimicrobial pollutants causes the degradation efficiency to decrease due to the increased concentration occupying a higher number of active sites thus lowering the number of hydroxyl radicals produced. Lanhua et al. (90) showed that the reaction rates of SMX degradation decreased with increasing initial concentration from 5-500 µM. While Hapeshi et al (111) found that ofloxacin antibiotic degradation was 92%, 100% and 88% for concentrations of 5mg/L, 10mg/L and 20mg/L, respectively. The same group examined atenolol degradation by TiO_2 photocatalysis was 85%, 84% and 54% for concentrations of 5mg/L, 10mg/L and 20mg/L, respectively. It infers that increasing ofloxacin concentration above 10mg/L reduces the degradation rate. Increasing the antibiotic pollutant concentration above a certain quantity affects the solubility (mg/L), influencing the chemical kinetics (115).

$$\mathrm{Log}[q_e - q_t] = \mathrm{Log}q_e - (K_1/2.303).t \quad (7)$$

$$t/q_t = (1/k_2.q_e^2) + (t/q_e) \quad (8)$$

Where, q_e and q_t is the equilibrium concentration of the adsorbent phase [mg/g], and the antibiotic concentration at the time "t" [mg/g], respectively, and k_1 and k_2 are the rate constants of the pseudo-first-order and pseudo-second-order kinetic equations, respectively (116).

In real-time wastewater such as influents, effluents, surface water, the antibiotics molecules is found at a wide range of concentrations from a few ng L^{-1} to μg L^{-1} (117). Conventional waste water treatment techniques such as filtration, coagulation-flocculation, sedimentation, and biological (activated sludge process (ASP) and trickling filters) treatment are having challenges to remove the lower concentration in the ng/L range. But owing to the effective diffusion of antibiotic molecule transport at lower concentration favours their adsorption on photocatalyst. Therefore, photocatalysis technique can degrade even lower concentration antibiotic pollutants. Recently Biancullo et al. (118) explored that variability of antibiotic concentrations for different real urban waste water matrices from the same water treatment plants does not affect the photocatalytic degradation performance. However, the lower antibiotic concentration under the detectable limit remains a challenge to treat in the case of large-scale water treatment plants. To enhance the adsorption of these low concentrations onto photocatalyst surface has to be considered in future studies. Highly porous based photocatalyst surface modification with a metal-organic framework may solve this issue.

3.2.2. Photocatalyst Loading

Researchers have demonstrated that increasing the photocatalyst loading can enhance the reaction rates due to the increasing number of active sites available. Thus, more hydroxyl radicals produced. Landau et al. (90) increased the TiO_2 catalyst loading from 0.01 to 1g/L, which enhance the reaction rates. A similar tendency was also seen with other photocatalysts. Peres et al. (114) found adding the photocatalyst loading of TiO_2 from 4 to128 mg/L helped to improve degradation efficiency from

56.2% to 89.3% within one hour of 500ug/L ofloxacin. Hapeshi et al. (111) found that the catalyst loading increased the initial reaction rate of ofloxacin degradation until a certain point. Excess photocatalyst particles can cause several other issues such as (a) increasing the solution opacity which affects the penetration of the photon flux, (b) possibility of particle agglomeration that reduces the active surface area, and (c) light scattering induced loss in photon reception (119-122), thus affect the antibiotic degradation rate. The optimum photocatalyst loading for maximum pollutant removal depends on the target pollutant. It varies for each pollutant, for example, with ofloxacin and atenolol, the photocatalyst to substrate concentration ratio was 50 and 15, respectively (111).

3.3.3 pH of the medium:

An essential factor that varies for each target pollutant is the experiment's pH as it affects the photocatalytic reaction. The pH influences the photocatalysis reaction rate by an increase or decrease of pollutant adsorption onto the photocatalyst, thus determining the rate and the degree of photocatalytic degradation of pollutants. It is based on the ionization states of the photocatalyst surface and pollutants that influences the rate of radical and reactive species formation directly. Silva et al. (123) reported that TiO_2 has a point of zero charge (PZC) of 6. When pH is below 6, the photocatalyst surface behaves positively charged, while above 6 means it becomes negatively charged. Therefore, positively charged pollutants in pH above 6 have increased degradation due to the higher electrostatic attraction with the negatively charged TiO_2. Similarly, change in pH varies the pollutants adsorption property onto photocatalyst. Norfloxacin turned into cation when $pH < 6.2$ and behave as anion when $pH > 8.7$. At a neutral state, norfloxacin in a neutral molecular state (124). Hapeshi et al. found that decreasing the pH levels increased ofloxacin degradation efficiency

(111). It demonstrates that ofloxacin degradation is primarily caused by valance band holes rather than radicals, as the significant oxidation species are the positive holes in low pH levels (123). In contrast, hydroxyl radicals are the primary species in neutral to high pH levels. However, this is not true for all cases as Peres et al. (114) found that when pH was 3 and 10, ofloxacin's degradation was weaker than the one when pH was equal to 6 due to the charge repulsion occurring at these levels from both the surfaces being the same charges. Gad-Allah et al. (112) witnessed that the natural pH (5.8) of the ciprofloxacin solution exhibits the best degradation. Further altering the pH to acidic or alkaline solutions cause the charging of TiO_2 and ciprofloxacin surfaces and lower the degradation performance.

Photocatalytic degradation of carbamazepine (CBZ) at antimony trioxide (Sb_2O_3)/lead oxide (PbO) hetero-photocatalyst showed pH dependence, where the pollutants were effectively degraded at pH 2.0 and found to be exhibit lowered efficiencies while increasing the pH value above 2.0 (125). In this context, acid-base dissociation constants (pK_a values) are helpful to understand the chemical, environmental and toxicological properties of molecules (126). Mainly, to shed more light on predicting the interrelationship between pH and surface functional property of pollutants. For instance, ofloxacin has a pK_{a1} of 6.05 and pK_{a2} of 8.11 means that it is positively and negatively charged in alkaline and acidic solutions, respectively. It is indicating that the pH variation alone does not favour pollutants adsorption onto the photocatalyst surface. Atenolol showed the best degradation at neutral pH, but with the acidic (pH 3) and alkaline (pH 10) solutions of atenolol, the degradation efficiency decreased to 42 and 69%, respectively. It is due to the pKa value equalling 9.6, where pH between 6 and 9.6 causes an increased electrostatic attraction between the negatively charged TiO_2 surface and the positively charged atenolol. Increasing the pH

above 9.6 causes the atenolol to become negatively charged, causing a repulsion with the negatively charged TiO_2 (123). Note that pKa value varies with the antimicrobial pollutant. Oxacillin [OXA] has a pKa value of 2.8, means that it is negatively charged in neutral and basic pH levels, causing a repulsion effect with TiO_2 photocatalyst (negatively charged). It shows that changing the pH from its natural level alone does not improve the degradation and is determined with pKa value (113). Therefore, optimizing the reactions' pH value and knowing the pKa values of antibiotic pollutants helps to achieve effective adsorption of antibiotics on to photocatalyst and facilitating complete degradation with a higher rate. The influence of photocatalyst's surface functional behaviour on adsorption property is discussed below.

3.3.4. Surface functional property:

Modification of photocatalyst surface improves in tackling persistent behavioural complex chemical structured antibiotics. Mainly surface functional property tuned photocatalyst can degrade complex antibiotics. The TiO_2 photocatalyst is not effective for erythromycin degradation with which the degradation efficiencies were as low as 10% (89), and 31.6% (127). But it showed complete degradation of sulfamethoxazole antibiotics. Another example is that clarithromycin is a highly hydrophobic compound with a recalcitrant character that has only had 19% of the parent compound removed on the TiO_2 surface as it possesses hydrophilic behaviour. A modified TiO_2 with rGO (89) results in high degradation of clarithromycin (65%) and erythromycin (74%) but decreased the removal of sulfamethoxazole (37%) (89). It shows that choosing the right photocatalyst material with appropriate surface functional property helps to remove antibiotics that are recalcitrant compounds and cannot be removed by conventional biological processes. Coupling high surface area or pore structured platform is an ideal approach to improve the antibiotics loading onto photocatalyst. In

this line, a high surface area and tuneable pore structure (128) metal-organic framework (MOF) encourages to revisit the photocatalyst structures for enhanced antibiotic pollutants adsorption (129). The desired metal precursor mixed with organic frameworks (metal–MOF) through a facile in situ carbonization method yields highly ordered pore structure that showed high adsorption of antibiotics and effective photocharge carriers separation results in enhanced photocatalytic antibiotics degradation (129, 119, 130). A review by Wang et al. (131) on MOF based photocatalysis topic provide recent progress in this area.

3.3.5 Mineralization Process:

By-products formation is an inherent part of antibiotic degradation and has to be taken into account. For example, triclosan is a famous antimicrobial agent widely found in waste and drinking water resources, potentially photochemically converted to toxic 2,8-dichlorodibenzo-p-dioxin (2,8-Cl2DD) in the environment under natural sunlight. Therefore, it is necessary to develop environmentally friendly methods to degrade triclosan without producing any harmful by-products. It is recognized that mineralization (132) is a long process due to intermediates' production, which takes longer than parent antibiotic molecules degradation.

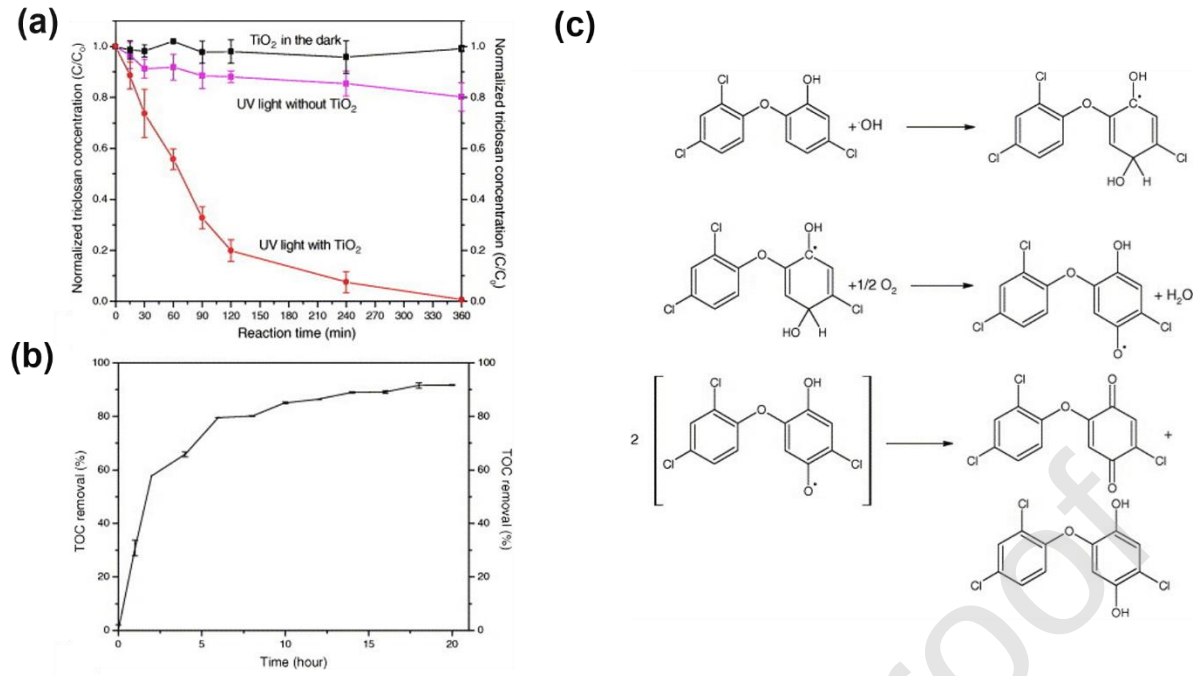


Figure 8. (a) Photocatalytic oxidation of triclosan (λmax = 365 nm); (b) TOC removal of triclosan during photocatalytic degradation; (c) Formation of quinone of triclosan and hydroquinone of triclosan during photocatalytic degradation of triclosan. Figure 8 (a-c) reused with permission from Elsevier publishers (133).

In contrast, some intermediates produced, such as carboxylic acids are resistant to the advanced oxidation process, thus preventing complete mineralization. It shows that photocatalysis can utilize a wide range of antibiotic removal, but some by-products can still be present and therefore require a post-treatment. Adamek et al. (123) found that the derivatives that are still present can be biodegradable which means a biological wastewater treatment plant could help treat this photocatalytically treated water without promoting antibiotic resistance of the wastewater plant. Yu et al. (133) examined TiO_2 with UV (<365nm) light irradiation on triclosan antibiotic degradation and evaluated the possibility of toxic by-product formation through total organic carbon (TOC) analysis (**Figure 8 (a)**). They found approximately 80% of triclosan antibiotic removed within 2 hours and took at least 6 hours for complete removal (**Figure 8 (b)**). **Figure 8 (c),** the TOC results indicated that triclosan was mineralized to carbon dioxide.

It showed that the TOC rate increased gradually with triclosan antibiotic degradation. After 6 h, around 79% of TOC was removed which implies that TOC removal was much slower than the initial degradation of the parent compound. **Figure 8 (c)** shows the intermediates formation, such as quinone and hydroquinone during triclosan photocatalytic degradation. It suggested that photocatalysis process was successful for removing triclosan antibiotics however complete mineralization not achieved in a short period. This is because the intermediate degradation is dependent on their adsorption onto TiO_2 particles, which is why the degradation of triclosan is faster than TOC removal. It is worth mentioning that intermediates' low adsorption ability would increase the time for complete mineralization (134). Therefore, ensuring complete mineralization during antibiotic degradation is mandatory for avoiding unintended toxic by-product disposal into water bodies.

3.3.6. Light Intensity:

Light intensity directly dictates the number of photons emitted and control the number of hydroxyl radicals or electronic vacancies from increased electron excitation (112). It results in higher degradation of target pollutant. Varying light intensity from 30-150 W increased the degradation of oxacillin from approximately 20% to 60% (113). Moreover, incident light energy (hν) should be higher than the photocatalyst's bandgap to facilitate charge transfer process between the photocatalyst and water molecules. Therefore, the choice of light source and intensity need more attention.

3.3.7. Addition of Electron Scavengers:

Both photoelectron and holes present on the TiO_2 photocatalyst surface lead charge recombination and lower the degradation efficiency. Addition of electron scavengers to the reaction media will hunt down the electrons in the conduction band, increasing the lifetime of holes in the valance band which in turn produce more hydroxyl radicals

through the reaction given in equation (6). Hydrogen peroxide is a well-known oxidant utilized in dye colour removal as well as in disinfection. According to equations (5) and (6), hydrogen peroxide reacts with photoelectrons and produce OH• radicals. Therefore, hydrogen peroxide can act as efficient electron scavenger in the photocatalytic process and promote antibiotics degradation by generating OH• radicals. The degradation of tetracycline improved from 44.2% to 95% and the total organic carbon removal increased from 38.4% to 52.6% within one hour of irradiation with the addition of 0.005% of H_2O_2, (112). The addition of 0.07mM of H_2O_2 promoted the TOC reduction of ofloxacin and atenolol, respectively, a 10% and 3% improvement compared to without H_2O_2 (111). The removal of ofloxacin with a degradation efficiency of 97.8% was achieved by adding 1.68 mmol of H_2O_2 to the TiO_2 photocatalysis system, thus showing the importance of electron scavengers improving degradation by preventing charge recombination (114). Though the addition of hydrogen peroxide helps to increase degradation efficiency, it does work only up to a particular concentration. Beyond this concentration, hydrogen peroxide becomes a hole and hydroxyl radical scavenger instead, which lowers the number of pollutants reacting with the holes and hydroxyl radicals, thus reducing degradation efficiency (111).

3.3.8. Presence of Other Matter:

Most of the studies discussed in this review were done with only pollutants in the reaction media that are generally obtained by spiking ultrapure water and no other matters present together. In fact, it has been the main factor that helps us to achieve high removal rates due to no/minimal competition for the photocatalyst's active sites or the radicals produced by the reaction of photo holes with water molecules. Hapeshi et al.(111) evaluated ofloxacin and atenolol in ultrapure water, groundwater, and

wastewater treatment plant effluent (WWTPef). The results showed that the amount of mineralization decreased by 51 and 23% for ofloxacin and atenolol, respectively in groundwater, 63 and 42% for ofloxacin and atenolol in WWTPef when compared to ultrapure (111). Due to the increased presence of organic carbon content in the groundwater and WWTPef that compete with the target pollutants for the photogenerated holes and hydroxyl radicals caused such a great lowering in degradation efficiencies (111). Giraldo-Aguirre et al. (113) demonstrated that iron (Fe^{2+}) above the pollutant concentration in the mineral water spiked with oxacillin caused the degradation percentage to decrease by 6% due to the lower adsorption that resulted from the increasing competition for active sites. Bicarbonate ion is a non-target compound present in most wastewater and is expected to decrease the photocatalysis performance by scavenging hydroxyl radicals via the reactions given below (135).

$$CO_3^{2-} + OH^{\bullet} \rightarrow CO_3^{\bullet-} + OH^- \quad (9)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{\bullet-} + H_2O \quad (10)$$

The carbonate radical ($CO_3^{\bullet-}$) anion considered to be a weak oxidizing agent that hardly reacts with other molecules but reduce photocatalysis degradation. In contrast, bicarbonate ions sometimes were shown to promote degradation when the concentrations of HCO_3^- and CO_3^{2-} were higher than pollutants concentration (sulfamethoxazole) they were found to react with pollutants in the bulk aqueous phase (90). Natural organic matter is present in most wastewater and natural water, affecting the photocatalysis degradation process due to interference that it could cause to the adsorption of target pollutants by reacting with the hydroxyl radicals and producing intermediates that react with target pollutants. These natural organic matters can be managed by varying pH of the reaction medium. It shows that adjusting the pH will

influence the effects of the non-target pollutants in the degradation process. It explains why most laboratory experiments result in high removal rates. The presence of only the target pollutant in the solution having no competitors for hydroxyl radical reactions is obviously the reason for the witnessed better efficiency in lab-scale studies. Based on the above discussion, the influencing parameters on antibiotic pollutants degradation summarized in **Figure 9**.

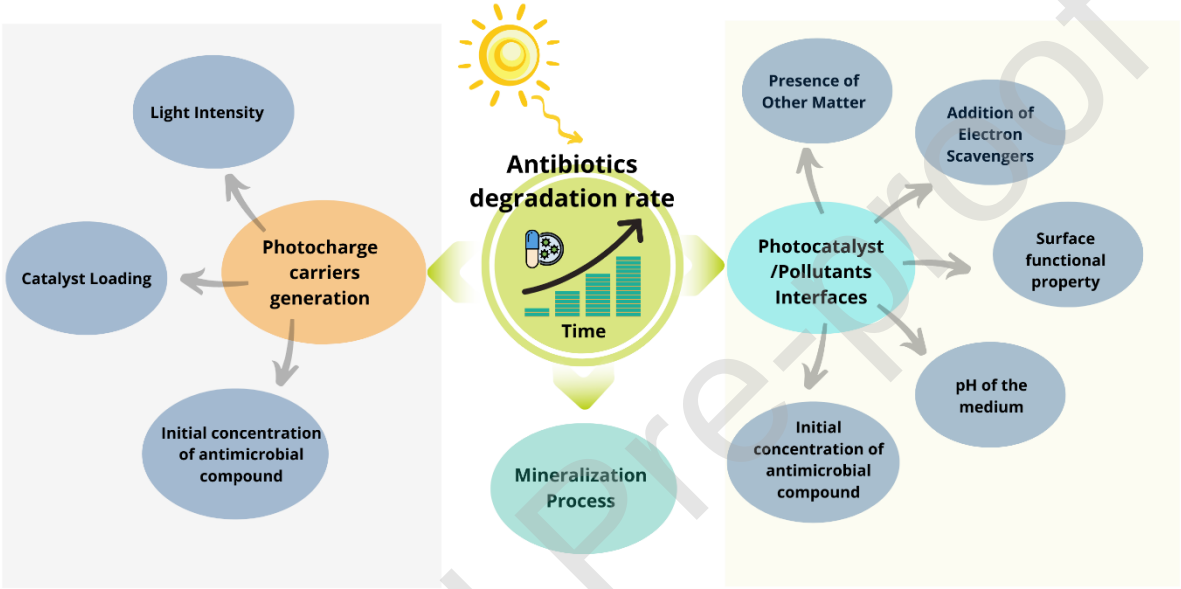


Figure 9. Processing parameters of photocatalytic antibiotic pollutants degradation.

4. Photocatalytic degradation of the pharmaceutical pollutants: pros and cons

The fundamental mechanism of photocatalytic degradation is simple, but the by-products formed after degradation of the pharmaceutical drug have both positive and negative environmental impacts. For instance, the acetaminophen or paracetamol is one of the most used common medicines ranked 9th in the top 200 most prescribed drugs in the United States (136). Due to its prominent use as an analgesic and antipyretic drug, many researchers worked on its degradation but only a few on recovering value-added product of its degradation. Chang et al.(137) degraded

paracetamol using TiO_2/ZSM-5 photocatalyst with 254 nm UV lamp on which the best TiO_2 loading was 40 wt%. The acetaminophen's degradation results in two primary intermediates, hydroquinone and 1-4-benzoquinone. The hydroquinone has a commercial value in depigmentation of the skin spots, and 1-4-benzoquinone can be utilized as a proton acceptor as well as an oxidizing agent. It indicates that the by-products formed after photocatalytic degradation can also be used for accessing other value-added chemicals that find use in other industries. Ronghua et al. (138) and Abdel-Wahab et al. (139) showed that $Bi_4O_5I_2$ and Fe_2O_3 with TiO_2 based nanocomposites were able to degrade acetaminophen under visible light. In this case, they obtained 1,2,4-benzentriol, which is used for hair dyeing and has a cosmetic value. However, not all by-products of acetaminophen degradation have a beneficial use. For example, Moctezuma et al.(140) found p-nitrophenol in the reaction mixture using Titania under UV light. This p-nitrophenol is considered as an air pollutant which imparts negative environment impacts. Hence, the post-treatment by-product analysis after photocatalytic antibiotic degradation experiment is essential to ensure the environmental safety.

5. Challenges and opportunities:

A continuous increment of research works on photocatalytic antibiotic degradation is appreciable (Figure 2b). However, repeating the trends of practices followed for photocatalytic dye pollutants degradation will not help to bring this technique from lab to industry. As pointed out in the above discussion, acquiring fundamental knowledge on photocatalysis from the previous reports and interdisciplinary research works is mandatory to move forward to the future roadmap on photocatalytic antibiotic degradation research as illustrated in Figure 10.

5.1 Materials design:

Photocatalysis has shown many advantages when compared to other AOP's due to the low energy demand, renewable nature, low chemical requirements, simple and effective removal of microbial pollutants. There are a few drawbacks which have been witnessed by various researchers, one being the water which requires treatment must be transparent or partly transparent for the light to be absorbed by photocatalyst. An increase in the opacity of reaction media occurs due to several factors such as the increased concentration of pollutants, photocatalyst loading, and presence of other contaminants (natural organic matters). Photocatalysis usually utilizes TiO_2 photocatalyst due to its low cost, excellent stability, and attractive photocatalytic characteristics. However, they can only absorb photons in the UV Light region due to the comparatively larger bandgap energy, which translates to only 5% of solar light that limits its usage. On the other hand, narrow bandgap energy-based (1.5-2.8 eV) photocatalytic materials can help to overcome this issue which allow a relatively higher number of photons get absorbed. Typically, they could help us to utilize 45% of photons at a visible wavelength at natural sunlight irradiation. Thus, a broader range of wavelengths at solar spectrum can utilize compared to UV. Another issue is that charge recombination that occurs due to the presence of photo-generated charges (electrons and holes) on the same surface. Designing heterostructured semiconductors capable of absorbing both UV and visible photons as shown in Figure 4 is appreciable for high charge separation and producing both OH• and $O_2^{\bullet-}$ radicals and can have significant improvement in degradation efficiencies.

Photocatalysis can degrade many antimicrobial compounds. However, there are still some undesired compounds (contaminants) that are usually degraded only in a small amount. This inadequate mineralization infers that the intermediates produced are

resistant to the photocatalysis process. In this case, the addition of electron scavengers (hydrogen peroxide) does increase the degradation and mineralization of the photocatalysis process. However, it increasing chemical storage cost at the water treatment site. If hydrogen peroxide can produce at in-situ mode within the reactor will complement photocatalytic antibiotic pollutants degradation and convenient compared to adding hydrogen peroxide externally (141-143). Recovering photocatalyst after the reaction is another crucial step for sustainable operation and to preserve cost efficiency. Mostly, the powder-type photocatalysis process requires a post-treatment filtration step to separate the photocatalyst particles from the treated water which is further making the process more expensive. Immobilization of photocatalyst onto a solid substrate is an alternate solution for effective recovery of photocatalyst. However, such supported photocatalyst were always shown to have reduced degradation efficiencies as they ought to sacrifice a significant proportion of the photocatalyst's surface area. This lowering of active surface area lowers the pollutant's adsorption. Therefore, the use of powder type or supported photocatalysis is a trade-off between efficiency and recoverability. Also, the light scattering effect between the particles enhances the optical pathlength (144, 145) which is beneficial to promote pollutants degradation rate. In contrast, the aggregation of the particles may reduce the optical pathlength, as well as reduce the pollutants adsorption. A continuous stirring of the reaction media helps avoiding these issues in powder-type photocatalysis route. For maintaining constant interaction between pollutants and photocatalyst, a flow type reactor is recommended which mimics the kinetic condition of water flow in currently industrialized wastewater treatment plants. A recent review article by Loeb et al. (144) pointed out the importance of flow cell type reactors,

designing light sources, need of revisiting the ways in which a high quantum yield of photocatalytic pollutants degradation can be achieved.

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5.2 Value-added products from photodegradation of antibiotics towards a circular economy:

Many research reports on photocatalytic antibiotic degradation focusing only on efficiency and analysing degradation pathways but a few researchers are also working on resource recovery (by-product) analysis. Unlike photocatalytic textile dye pollutants degradation, antibiotics degradation in water which could yield potential derivatives is a marketable feedstock for pharmaceutical and chemical industries. Antibiotics defragmentation by photo/chemical oxidation and electrochemical techniques can be couple with photocatalysis field. Yuan et al.(146) reported that oxytetracycline, doxycycline, and ciprofloxacin are completely detoxified in the UV/H_2O_2 process after exposure to light irradiation (11.45 J cm^{-2}), simultaneously. But their total organic carbon abatements are only about 10% which infers that it produces a high number of other intermediates probably one or all of possible non-toxic 1,4-benzene dicarboxylic acid, 4-oxopentanoic acid, propanedioic acid, hydroxymalonic acid, glycerin and some aliphatic acids. Among them, 1, 4-benzenedicarboxylic acid is mainly used as a raw material in the polyester industry (especially PET a component of some garments and plastic bottles). Propanedioic acid is also used as a precursor to different polymers. It can be a component in alkyd resins

which is used in several coating applications for protection against the damage caused by UV light and oxidation and corrosion. 4-oxopentanoic acid known as "Levulinic acid" is used as an additive in cigarettes to increase the release of nicotine in smoke and improve the binding of nicotine to neuronal receptors. Hydroxymalonic acid (Tartaric acid) is used in food as a food additive (number E334), mainly as an antioxidant, pH regulator, and sequestering agent. Glycerin is used as a moisturizer to treat or prevent dry, rough, scaly, itchy skin and minor skin irritation (for example, diaper rash, and skin burns caused by radiation therapy). It is also used in the cosmetic industry and is also an excellent natural cleansing agent. Amoxicillin is a bactericidal β-lactam antibiotic of the aminopenicillin family utilizing for the treatment of bacterial infections with susceptible germs. Hatice et al.(147) determined the degradation pathway of amoxicillin and the by-products. The reaction was carried out using Co-doped Titania under a Xe lamp with UV-C cut off filter. The total organic carbon results showed that 90.8% and 92.1% of amoxicillin was mineralized under UV-C light filter and visible light irradiation. The possible degradation product in this work was sodium formate which is used in fabric dyeing and printing processes. It is also used as a buffering agent for strong mineral acids to increase their pH, as a food additive (E237), which is not authorized in Europe, and as a de-icing agent. They also found benzene in the reaction mixture that was frequently used in the nineteenth and early twentieth centuries, as a solvent, in glues, varnishes, paints, inks, for dry cleaning, and metal degreasing. The discovery of its toxicity led to its gradual replacement, often by toluene, starting in the 1950s. Phenol is also found to be one of the amoxicillin degradation products. Two-thirds of phenol produced is used to produce plastics (polycarbonates, epoxy resins). In medicine, it is used primarily as a powerful antiseptic. Other products were also identified, such as thizolidin-2-ol, 5,5-

dimethylthiazolidin-2-one and 6-amino-4-thia-1-azabicyclo[3.2.0]heptan-7-ol that do not have any profitable use. Table 1 summarises the possible use of oxidation products that may result from the photodegradation of antibiotic pollutants. It shows excellent opportunities for recycling these by-products as feedstock to pharmaceutical, and chemical industries. It ensures supply chain in these industries and promotes waste reduction. But, new resource recovery models (148, 149), life cycle analysis (150, 151) and analytical tools for measuring contaminants in the recycled materials (152) to meet out safety regulations are required in this field. Therefore, interdisciplinary researchers ought to work with pharmaceutical and resource recovery management sectors in addition to just the photocatalytic antibiotics degradation to accelerate the transition readiness level from the lab to the pre-market stage.

Though the advanced oxidation process-based photocatalysis route offers the possibility of by-product generation, developing separation techniques necessitate collecting these products from the treatment plants. Therefore resource-recovery technologies need to be considered with photocatalytic reactors for large scale water treatment plants. Recent studies on membrane-based technology adopted in advanced oxidation process (153) are helpful to extract the products such as detergent from the water treatment process. Also, membrane-based filters effectively recover soluble organic matters from the real-time municipal wastewater treatment plants(154). Significantly the membranes-based filters can recover molecular level by-products such as proteins, polysaccharides. Therefore, it is anticipated to recover the molecules scale by-products from antibiotic molecules disintegration. The carbon activated filters effectively recover the liquid phase molecules from the water treatment plants(155, 156). A recent critical review on water reclamation and reuse technologies suggested the market supply potentials, technologies and bottlenecks (157). The new and

advanced recovery routes are appreciable for escalating the photocatalysis-based antibiotic degradation to the pre-industry level.

Table 1. Possible use of oxidation products from the photodegradation of model pharmaceutical micropollutants

Drugs	Oxidation products	Marketable or Value-added chemicals	References
Acetaminophen	Hydroquinone	In depigmentation of the skin spots	(137-140)
	1-4 Benzoquinone	Proton acceptor and oxidizing agent	(137, 140)
	1,2,4 benzentriol	Hair dyeing chemicals	(138, 139)
Diclofenac	2,6-dichloroaniline	Raw material for pesticides	(158, 159)
	Fumaric acid	Food additive	(159)
	2-aminophenol	Reuse in the pharmaceutical industry for reproducing drugs	(159)
	Pyrocatechol	Preparation of anti-oxidant for rubber and lubricating oils as well as photographic developer	(159)
	Pyrogallol	Absorption of oxygen because of its easy oxidation	(159)
Oxytetracycline,Doxycycline and Ciprofloxacin	1, 4-benzenedicarboxylic acid	Raw material in the polyester industry	(146)
	Propanedioic acid	Precursor to different polymers	(146)
	4-oxopentanoic	Additive used in cigarettes	(146)
	Hydroxymalonic acid	As a food additive, an antioxidant and pH regulator	(146)
	Glycerin	Moisturizer and cleansing agent	(146)
Amoxicillin	Sodium formate	Fabric dyeing and printing processes	(147)
	Benzene	Solvent, in glues, varnishes, paints	(147)

	Phenol	Plastic production and powerful antiseptic	(147)

5.3. Stability and standardization

The durability of photocatalyst in a wider pH range and a light irradiation for an extended period are essential prerequisite for sustainable operation. Photo and chemical corrosion are possible harmful effects on photocatalytic materials which potentially affect their sustainable function. Assembling nanoscale thick passivation layers (amorphous metal oxide) (160-162) on the photocatalyst's surface significantly protects them from corrosion issue with a small lowering of performance. Most of the research reports showed reproducibility of photocatalysts for 4-10 cycles. But an actual study needed is to answer the question how these photocatalytic materials sustain in a long duration in days or months instead few operating cycles.

Therefore, more significance must be given to evaluating photocatalytic materials in chemical and photo corrosion studies by exposing them for a substantial period of time. Recent review articles show the summary of photocatalytic performance for different antibiotic pollutants and semiconductor materials. The inconsistency of experimental conditions, such as various light sources used without mentioning light irradiation condition, variation in initial antibiotics quantity (g/L), diverse morphologies of the materials used are inadequate in standardizing photocatalytic performance in antibiotics degradation. For instance, Table 2 shows the summary of cyproplaxin antibiotics pollutants degradation using different semiconductor photocatalytic materials. It is difficult to conclude the degradation period, and degradation rate as irradiation condition, surface area, and morphology have profound influence on the overall photocatalytic degradation performance. Therefore, we couldn't directly compare these materials unless otherwise all those experiments were carried out

under identical conditions. This discrepancy arises mainly due to the lacking of standard experimental protocols in this field. Policy regulations on processing parameters have to be outlined by adhering to the ISO protocols that are being practiced in the photocatalytic air pollutants degradation. On the other hand, the hetero structured semiconductors are accelerating the antibiotics degradation rate due to (a) effective charge separation which reduce recombination rate, (b) enabling either or both $OH/O_2^{\bullet-}$ radicals generation, (c) extending the light harvesting wavelength region at different wavelength regions which promotes the photocatalysis rate. For instance, in table 2, $ZnMn_2O_4$- ZnO hetero structured nanocomposite showed higher rate of antibiotic degradation compared to single ZnO semiconductor. However, the energetic structure matching between the hetero structured semiconductors should take care as discussed in Figure 7.

Table 2. Summary of photocatalytic degradation of ciprofloxacin antibiotics using different semiconductor photocatalyst materials.

5.4 Nanotoxicity effect

The photocatalyst stability during water treatment performance is crucial as the semiconductor might possess severe chemical corrosion or photo corrosion property. It leads to metal ions or materials leaching from photocatalyst surface to water can induce potential environmental impact known as nanotoxicity affecting the aquatic environment and human health(178). Because the nanoparticle size (1- 100 nm) is less than biological cells, which have a high possibility of subcellular interaction. The recent review article by Friehas et al. (156) and other reports(179-182) narrates the toxicity and phototoxicity of nanoscale photocatalysts. Detailed in-vitro and in vivo studies have demonstrated on toxicity effect of nanoparticles by several researchers in different applications, including water treatment(183-185). Phytosynthesis (plants extract) based green synthesized photocatalyst materials having bio-friendly green organic chemicals (chlorophyll, polyphenols, etc.) helps protect the photocatalyst material, suppressing the toxicity effect (63, 186). A thin, atomic-scale layer of bio-friendly coating (187) onto photocatalyst as shell layer effectively protects the chemical or photo corrosion effect of nanoparticles during the water treatment process. Therefore, risk assessment and ensure the nanotoxicity effect originate from the photocatalyst surface should be taken to account for a safe water treatment process.

5.5. Evaluation of photocatalysis technique in AMR studies:

Photocatalyst materials	Morphology of the photocatalyst	Light source	Pollutant concentration	Degradation duration	Degradation rate	Pathways to degrade the pollutants ($OH^{\bullet}/O2^{\bullet-}$)	Reference
ZnO	Particulate	Xenon lamp (365 nm)	5mg/L	60 min	48%	$OH\cdot$	(163)
CeO_2	-	Xenon lamp (300W)	10mg/L	30 min	Superior to 90%	h+	(164)
ZnO	Nanotubes	Xenon lamp (300W)	2.10-5 mol/L	120 min	12%	-	(165)
g-C_3N_4	Irregular shapes	35W Xenon Lamp	10mg/L	240 min	60%	$OH\cdot$	(166)
$ZnWO_4$	Hexagonal plate-like morphology	UV-light	40µM	100 min	97%	$OH\cdot$	(167)
WO_3	Sheets	Xenon lamp (300W)	10mg/L	120 min	93.5%	$O_2\bullet-$	(168)
$ZnSnO_3$	Cubic	Xenon lamp (300W)	10mg/L	100 min	85.9%	$OH\cdot$	(169)
α- Fe_2O_3	Particulate	11W, 395nm	3.3mg/L	60 min	59%	-	(170)
Zinc ferrite/graphitic carbon nitride	layered and sheet-like structure	Visible light	20mg/L	120min	90%	$\bullet O_2^-$	(171)
Ag-$AgVO_3$-g-C_3N_4	Lamellar structures and nanoribbon features	500W Halogen lamp	10mg/L	120min	82.6%	$OH^{\cdot}/O_2^{\cdot}$	(172)
CeO_2-g-C_3N_4	Nanoflakes (for g-C_3N_4)	300 W Xe lamp with 400nm cut-off filter	10mg/L	120min	73%	$h^+/ O_2^{\cdot}$	(173)
Bi_2WO_6/C_3N_4/CNT	Microflowers	500 W Xe lamp with 400nm cut-off filter	-	90min	93.4%	$OH^{\cdot}/\bullet O_2^-$	(174)
$ZnMn_2O_4$- ZnO nanocomposite	Nanospheres	300 W Xe lamp with 420nm cut-off filter	10mg/L	60min	100%	X	(175)

The water bodies contaminated with pharmaceutical micropollutants affect microbes and cause environmental stress, which in turn induces the AMR (188). Briefly, the mechanism of AMR in bacteria is because of the presence of genes

g-C_3N_4/ Ag_3PO_4 composite	Layer structure (for g-C_3N_4)	300 W Xe lamp with 420nm cut-off filter	-	15min	67%	X	(176)
Ag_3PO_4/Ag/MoO_{3-x}	Nanosheets (for MoO_{3-x})	300 W Xe lamp with 420nm cut-off filter	10mg/L	50min	~80%	$OH^{\cdot}$/$\bullet O_2^-$	(177)

encoded specifically for enzymes, drug-specific pumps that prevent the drug's interaction at the target site, and overexpression of the target site (189). These antibiotic inactivating genes may present in plasmids, integrons, or transposon and were also detected in bacteria's chromosomal systems. Bacteria can acquire these genes from reservoirs of resistomes like mobile genetic elements and bacteriophages via horizontal gene transfer (HGT) mechanism by microbial crosstalk (190). These resistome reservoirs play a significant role in acquiring, maintaining, and spreading AMR genes (ARGs) among the environment's diversified microbial communities (191). **Figure 10** illustrate how antibiotic micropollutants present in the waterbodies induce ARG transfer by damaging the microbes (bacteria).

Currently, researchers are focusing on several approaches to combat the resistance both in humans and the environment. Bioremediation and biodegradation are promising technologies for removing environmental organic contaminants (EOCs) like drugs and pharmaceuticals due to the advantages of microbes' quick adaptability to the environment, and least or no side effects. Microalgal has been recently demonstrated to remove EOCs by adsorption, bio-uptake, and conversion of complex compounds into smaller metabolites by enzymatic actions (192). However, ciprofloxacin was less

biodegradable and hardly fragmented in the aqueous system. This drug may be biodegraded when it is present in soil with certain minerals. Mineralization of ciprofloxacin decreases the activity of microbes and also facilitates biodegradation (193). Several taxa and genera of microbial communities like Proteobacteria and Bacteroidetes, Dechloromonas, Brevundimonas, Flavobacterium, Sphingopyxis and Bosea showed ciprofloxacin degradation (194). Co-presence of other antibiotics reduce the biodegradation performance of target antibiotics (195). Another major challenging issue in biodegradation process is the protonation of antibiotics that leads to the inactivation of antibiotics (196). In the case of photolysis (light irradiation) based antibiotic degradation, ARGs can transfer to broader microbial communities by conjugative or mobile genetic elements due to a higher degree of oxidative stress in bacteria and up-regulation of target genes (197). Therefore, biodegradation and photolysis based antibiotic treatments need further improvement to control ARG transfer.

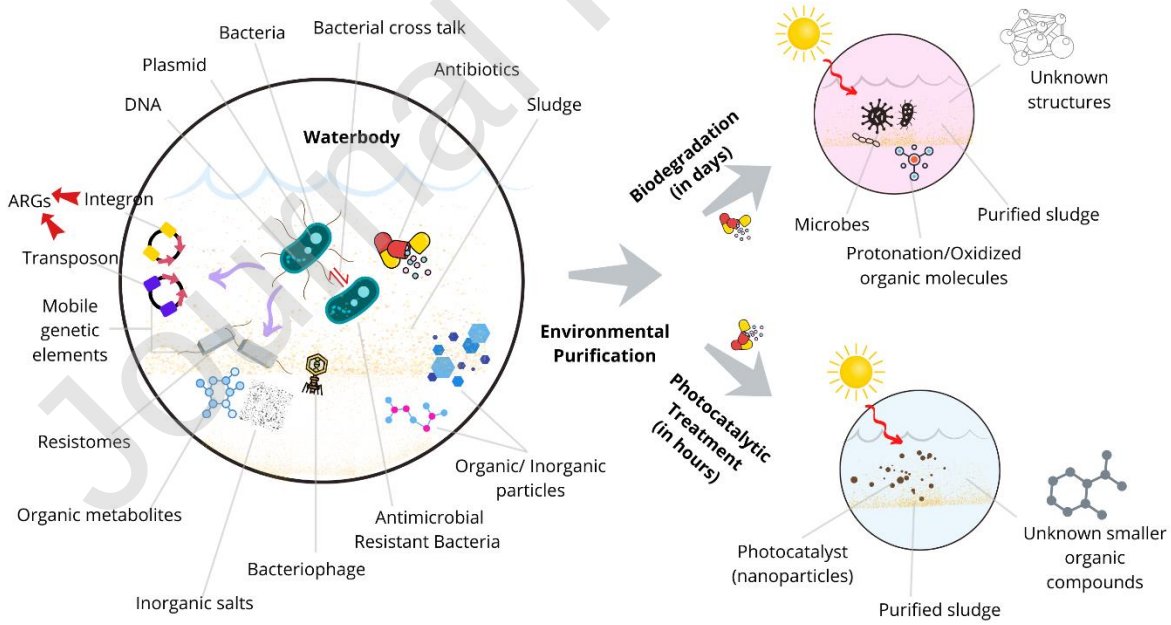

Figure 10 . Schematic illustration of polluted waterbody with antibiotic waste and other organic/inorganic contaminants (without treatment) in comparison with the antibiotic pollutants' treatments by biodegradation and photocatalysis techniques.

Figure 10 compares the feasibility of lowering ARG's through biodegradation and photocatalysis process. As discussed above, the use of bioremediation and other materials to remove ARGs and ARB from the environment have more significant challenges like finding appropriate microorganisms, availability, growth conditions, susceptibility to oxidative stress, and bacterial concentration. It mainly takes a long duration for antibiotic pollutants degradation, limiting its scale-up to the industrial level treatment. But, the use of photocatalysts for inactivation of antibiotics pollutants, typically in a few hours, and removing ARGs and ARB tested in the laboratory (198, 199, 118, 200). They have shown promising results in controlling ARGs, ARB, and inactivating drugs. Many reports endorse that hydroxyl radical ($OH^{\bullet}$) mediated lipid peroxidation of the bacteria outer cell wall components is critical in photocatalytic disinfection (198, 197). Therefore, quantifying $OH^{\bullet}$ radicals, and examining their influence on ARGs can provide further insights. Also, investigations on comparing the viability of photocatalysis technique in ARG's management (201, 202) shed more light on understanding the merits and challenges of this technique compared to photo-Fenton process and chemical treatment. Only a few research reports are available on the interrelationship between photocatalytic antibiotic degradation and ARG transfer. Karaolia et al. (89) have shown the inactivation of several resistance genes and ARB using TiO_2-reduced graphene oxide (rGO) within 3 hours and complete growth inhibition was achieved by treating this material with bacteria for 15 hours without altering the total nucleic acid contents. Compared to the biodegradation process, photocatalytic process potentially inactivates antibiotics, antimicrobial-resistant bacteria, and antimicrobial resistance genes within a short duration of time without affecting the total nucleic acid. However, photocatalyst's environmental safety and

toxicity are needed to be established before their use in sterilizing microbes, deactivating pharmaceutical drugs to avoid the spreading of drug resistance, particularly in the environment. When tested on organic and pharmaceutical substances, how a drug or organic substances are converted into a new chemical species, their chemical nature, and microbes' action are needed to be investigated explicitly. In addition to this, the inactivated organic chemical residues and their small fragments are yet precisely to be identified while also finding how organic fragments change the environment's microbial diversity. New ARG's examination protocols have to adapt to understand the injury effect (sub-lethal stress) of photocatalytic process on re-growth of antibiotic-resistant bacteria (198).

6. Future Outlook:

The current practices on photocatalytic antibiotic degradation and the challenges involved in this route has been discussed elaborately in sessions 3, 4 and 5. But one can question that which protocol is effective to degrade the antibiotic pollutants addressed in **Figure 9**. We should understand the priority of materials choice from a functional view point. Most of the photocatalyst reports focus on morphology dependence surface area, which is expected to promote active photocatalytic sites and light absorbance characteristics. Though these parameters are primarily helpful to support the photocatalyst performance, the bandgap position (**Figure 7**) concerning normal hydrogen electrode (NHE) is crucial to accelerate the hydroxyl and superoxide radicals generation thus directly dictates the antibiotics degradation rate. Secondly, the photocharge carrier separation (e^-/h^+) at photocatalyst is another necessary parameter to enhance the photocatalysis rate. Recent reviews (203) (204) (205, 206) report successful photocatalyst architectures such as hetero structure, co-catalyst decoration,

etc., for promoting the charge carrier separation. However, ensuring particle size of co-catalyst, and decoration concentration, bandgap matching between heterostructure should be taken into account. For instance, the higher loading of the co-catalyst above the optimized level might block the light photons to the primary photocatalyst layer. The stability of the photocatalyst against photo or chemical corrosion issue is critical to sustaining the performance. Post experimental analysis of photocatalyst material using X-ray photoelectron spectroscopy, scanning electron microscopy, and x-ray diffractogram are insightful to understand photocatalyst modification by corrosion. Recent in-operando(206-208), and in-situ tools(209-212), and electrochemical methods will be insightful to understand the origin of corrosion issue, the influence of electrolyte environment, and light irradiation. Designing an appropriate photocatalytic reactor helps to make use of the material advantages. The intrinsic kinetics of mass transfer, management of light scattering are of paramount importance in photocatalysis performance(213, 43). Also, as discussed in the opportunities session, including the technical provision such as membrane filter to recover the by-products during antibiotics degradation process will be added value to increase the industrial visibility of this technique. Therefore, materials design alone is not enough, but the reactor design should also consider the antibiotic degradation process. Table 2 indicates the inadequate standard protocol practices in this field. In particular, the photocatalysis experimental data derived from different light sources with various intensity does not compare with others. Therefore, a standardization in the experimental protocol required to benchmarking the photocatalyst performance. The conventional environmental toxicity analysis routes for examining the quality of water and ensuring trace level antibiotic presence before and after photocatalysis treatment needs to be revisited. The gene expression studies will shed more light on the AMR based issues

as antibiotics pollutants have a high potential to create resistance pathogens in the waterbody. The future roadmap of photocatalytic antibiotics is illustrated in **Figure 11.**

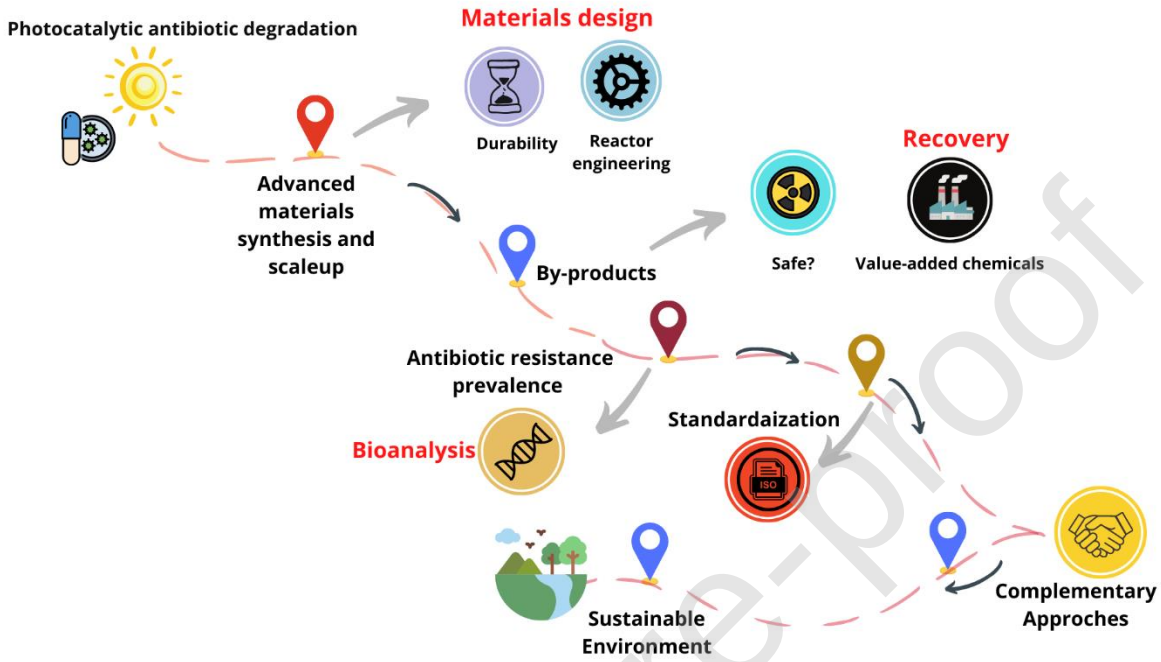

Figure 11. The future roadmap of photocatalytic antibiotic degradation.

7. Conclusions:

Photocatalysis is recently getting a thrust in antibiotic micropollutants treatment. The flexibility of selecting light sources permits us to opt for this technology for both indoor and outdoor water treatment systems. In addition, the feasibility of deploying natural sunlight makes it an industry-friendly technique. Relatively less space requirement and low maintenance than biodegradation process foster photocatalysis technique as an economical route. However, many experimental parameters of current practices have to revisited, and new opportunities beyond water treatment should be developed. This review provides a fundamental viewpoint in the photocatalytic process of water treatment and critically analyses photocatalytic antibiotic

degradation's current practices. It identifies the need for more attention in designing advanced photocatalysts to maximize the visible light photons harvesting with capabilities of generating both $OH^{\bullet}$ and $O_2^{\bullet-}$ free radicals via solid-state Z scheme heterostructures. These are expected to enhance the antibiotics degradation efficiency to a newer height. By-product analysis is a critical component that informs toxicity level and open pathways to new opportunities of recycling the derivatives of antibiotics photodegradation which can be used in other related chemical and energy industries. Significantly, interdisciplinary partners from pharmaceutical, microbiology, biotechnology should be added to the existing researchers of photocatalysis that are majorly physicists and chemists. It is also complementary to understand the unrevealed topics on antibiotics degradation induced antibiotics resistant gene and antibiotic-resistant bacteria. Standardizing the photocatalytic experiments on antibiotics degradation is by far the most significant thing that needs immediate attention. It could help to move this field forward from the lab to the pre-market stage soon.

Conflicts of interest

There are no conflicts to declare

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