

# Pharmaceutical residues: New emerging contaminants and their mitigation by nano-photocatalysis

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**Abstract.** The steady growth in population has led to an enhanced water demand and immense pressure on water resources. Pharmaceutical residues (PRs) are unused or non-assimilated medicines found in water supplies that originate from the human and animal consumption of antibiotics, antipyretics, analgesics etc. These have been detected recently in sewage effluents, surface water, ground water and even in drinking water. Due to their toxicity and potential hazard to the environment, humans and aquatic life, PRs are now categorized as the emerging contaminants (ECs). India figures in the top five manufacturers of medicines in the world and every third pill consumed in the world is produced in India. Present day conventional wastewater treatment methods are ineffective and don't eliminate them completely. The use of nanotechnology via advanced oxidation processes (AOP) is one of the most effective methods for the removal of these PRs. Present study is aimed at reviewing the presence of various PRs in water supplies and also to describe the process of AOP to overcome their threat. This study is also very important in view of World Health Organization report confirming more than 30 million cases of COVID-19 worldwide. This will lead to an alleviated use of antibiotics, antipyretics etc. and their subsequent occurrence in water bodies. Need of the hour is to devise a proper treatment strategy and a decision thereof by the policymakers to overcome the possible threat to the environment and health of humans and aquatic life.

**Keywords:** emerging contaminants; pharmaceutical residues; wastewater treatment; nanocatalysts; conventional methods; advanced oxidation process; photocatalyst

## 1. Introduction

The steady growth in population has led to many challenges like depletion of resources, rapid industrialization, urbanization and change in agricultural practices. This has resulted in immense pressure on global environment especially the water resources. Shortage of drinking water and water pollution are among the major problems nations are currently facing. The water crisis is intensifying with each passing day and has now become an issue of global concern. The availability of water resources & quality water is essential for the sustainable development of a nation (Alcama *et al.* 2000). All these factors have resulted in generation of excess amounts of waste water containing diverse range of pollutants like heavy metals, dyes, pesticides, herbicides and pharmaceutical residues. The major sources of these pollutants are chemical, textile, steel, petroleum, agricultural and pharmaceutical industries, and effluents from hospitals and domestic sewage (Hlongwane *et al.* 2019). Pharmaceuticals are of immense importance to human health; owing to their use in prophylaxis, diagnosis and treatment (humans, veterinary) and in agriculture practices. Thus, a huge number of

different pharmaceutical drugs have been developed and their use has shown a substantial growth in the last decades.

According to World Health Organization (WHO), "any substance or pharmaceutical product for human or veterinary use that is intended to modify or explore physiological systems or pathological states for the benefit of the recipient" is termed as drug. The terms drug, medicine and pharmaceutical product are commonly used interchangeably. Pharmaceutical compounds and their residues are now recognized as emerging contaminants (ECs) as their presence in the water poses a serious threat to the environment and human health (Fekadu *et al.* 2019, Ivetic *et al.* 2014, Lee *et al.* 2017, Mirzaei *et al.* 2016, Rodriguez *et al.* 2017, Tijani *et al.* 2013). Pharmaceutical residues (PRs) are the remains of pharmaceutical drugs or products used by humans and other organisms to treat various diseases (Courtier *et al.* 2019). These ECs persist in the environment due to their recalcitrant nature and low biodegradability. This has led to a growing concern about their toxicity and potential hazard to the environment, humans and aquatic life (Solis-Casados *et al.* 2017).

PRs have been detected in sewage effluents, surface and ground water and even in drinking water (Awfa *et al.* 2018, Lee *et al.* 2017, Nikolaou *et al.* 2007, Rabiet *et al.* 2006, Stackelberg *et al.* 2004, Wu *et al.* 2012). Drinking water all over the world has been reported to contain everything from antidepressants to heart medication to birth control pills to caffeine. The main contributing sources of PRs in the environment are human (hospital/household) use, animal

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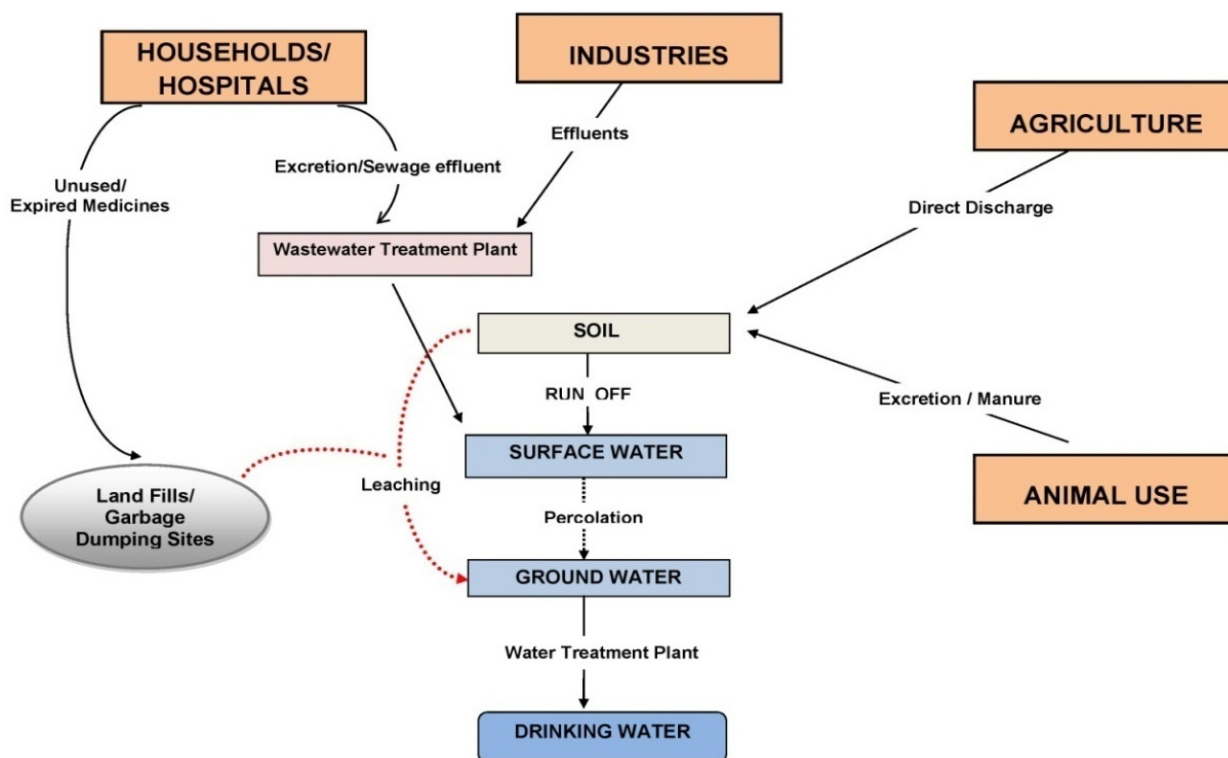


Fig. 1 Possible sources and pathways of PRs in the environment

use, agriculture/farming use and industrial manufacturing (Lee *et al.* 2017, Pavithra *et al.* 2017, Wu *et al.* 2012). Fig. 1 as shown below depicts above very well.

Hospitals are the major sources of PRs released in the environment. Only in few countries in the world, PRs are removed by wastewater treatment plants having adopted suitable technologies and in most of countries the residues are discharged in the aquatic environment. Due to this, there is continuous inflow of PRs in the environment leading to ubiquitous contamination. Pharmaceutical pollution has been found to cause acute and chronic effects in non-target organisms even at low concentrations. The effects include endocrine or hormonal system dysfunction, toxic effects on biomolecules, damage to DNA and RNA, oxidative stress, impaired neurotransmission and membrane lipid oxidation resulting in necrosis and cellular death (Antunes *et al.* 2013).

India figures among the top five manufacturers of medicines with drug exports growing 30% annually. Every third pill consumed in the world is produced in India and nearly 80% are consumed indigenously (Kallummal and Bugalya 2012). The amount of sewage generated in India far exceeds the treatment capacity; only 31% of the total sewage produced in 2008 (~38,254 million liters per day) was treated (Khan *et al.* 2016, Khan and Tian 2018, Subedi *et al.* 2015). In India (year 2017 data), various pharmaceutical residues like ciprofloxacin (11670 ng/l), erythromycin (9 ng/l), acetaminophen (690 ng/l), ibuprofen (980 ng/l), ampicilin (12.68 ng/l) etc have been detected in waste water treatment plant effluents, rivers, lakes and ground water (Balakrishna *et al.* 2017).

Presently, WHO drinking water quality guidelines don't list pharmaceuticals as pollutants (Al-Odaini *et al.* 2013).

Also, the evaluation of the presence, exposure and the subsequent effect of these residues on the health of general public are hindered by the lack of baseline data. The issue may turn worse due to lack of substantial research on the effect of these PRs on the human health. This may ultimately result in slow and irreversible accumulation of the toxic compounds in the living creatures mainly the humans. Besides, the problem is further alleviated by the inefficiency of conventional wastewater treatment plants in eliminating these residues completely. Since these residues are polar, non-volatile and non-biodegradable, the conventional treatment processes like sedimentation and biological treatment fail to remove them effectively and efficiently (Bagheri *et al.* 2016, Zhang *et al.* 2008).

Present day wastewater treatment methods like adsorption using activated carbon, air stripping and reverse osmosis have also been found to be ineffective in completely removing these residues (Blair 2016, Tong *et al.* 2012). These methods don't eliminate the PRs completely but simply transform them from one phase to another (Awfa *et al.* 2018). Other conventional water treatment methods such as sedimentation, adsorption, filtration and chemical oxidation are not able to remove these contaminants completely. They also generate toxic intermediates and secondary pollutants, besides being time consuming and costly. Effective alternative water treatment technologies are therefore required to improve treated effluent quality. Nanotechnology offers a novel technique that is not only effective and less expensive but also capable of simultaneous removal of multiple pollutants from wastewater. To improve the removal efficiencies of PRs, novel and efficient methods of wastewater treatment need to be devised. Nowadays advanced oxidation processes (AOP)

are being developed to prevent the persistent accumulation of these drugs in water bodies (Kanakaraju *et al.* 2014).

AOP involves use of ultraviolet (UV) radiation, combination of UV light with an oxidant like H<sub>2</sub>O<sub>2</sub> to generate hydroxyl (HO·) radicals and using hydrogen peroxide with Fe<sup>2+</sup> ions (photo-Fenton) to increase the production and efficiency of HO· radicals. These AOPs involve the generation of powerful reactive species (i.e., H<sub>2</sub>O<sub>2</sub>, OH·, O<sub>2</sub><sup>-</sup>, O<sub>3</sub>) that mineralize organic pollutants and various pathogens present in wastewater. Heterogeneous photocatalysis is an advanced oxidation process that employs semiconductor catalysts like titanium dioxide (TiO<sub>2</sub>), zinc oxide (ZnO), ferric oxide (Fe<sub>2</sub>O<sub>3</sub>), cadmium sulfide (CdS), gallium phosphide (GaP) and zinc sulfide (ZnS) to degrade various PRs into carbon dioxide and water.

The treatment of water laden PRs has become more important in present times due to COVID-19 pandemic. In this pandemic tons of medicines in the form of antibiotics, antipyretic etc are being used worldwide. There are more chances nowadays regarding the presence of PRs in the effluents and even water supplies. To get rid of these PRs the newer and versatile treatment technologies need to be adopted world over. By adopting nanotechnology based wastewater treatment technologies, general public at large won't be unintentionally consuming water laced with pharmaceutical residues and thus will be safe from various deformities and disorders.

## 2. Pharmaceutical residues in aquatic environment-World scenario

### 2.1 Marine water

Marine waters have been reported to contain many PRs with concentrations observed up to 2370 ng/l (Thomas and Hilton 2004, Roberts and Thomas 2006) as large dilution of marine water is expected to contain minute concentrations only. Some of the frequently used PRs that have been reported to occur in marine waters are: clofibrac acid (20-111 ng/l), diclofenac (8-195 ng/l), erythromycin (4-70 ng/l), ibuprofen (8-2370 ng/l), and paracetamol (upto 20 ng/l) (Thomas and Langford 2007). Arctic Ocean too has been found to contain PRs. One of the factors that contribute to the persistence of these residues in the aquatic environment is their half-life period. For example, ibuprofen and paracetamol have half-life period of 50 and 20 days respectively (Daniel *et al.* 2019).

### 2.2 Fresh water

Comparatively higher number of studies have been undertaken to study the presence of PRs in freshwater and accordingly a significant number of pharmaceutical medicines have been studied. Ibuprofen has been reported in many freshwater bodies in Switzerland (7.8 ng/l), Tyne river, UK (297 ng/l), Rhine river, Germany (41 ng/l). Another commonly used drug diclofenac also shows its presence in rivers like Elbe river, Germany (67 ng/l), Rhine river, Germany (35 ng/l) (Thomas and Langford 2007). In

addition to PRs, their metabolites have also been detected in freshwater bodies. For example, clofibrac acid has been detected in Germany freshwater bodies upto the concentration in the range of nanograms per litre (ng/l) where as its parent compound clofibrate was not detected.

### 2.3 Ground water

Presence of pharmaceutical residues in groundwater was reported since 1990. The sources of groundwater contamination can be direct discharge from industries, surface run-off from agricultural fields, leaching of contaminants from land fill sites and wastewater effluents from wastewater treatment plants (WWTPs), hospitals, homes etc. In a study conducted in Germany, PRs have been detected in groundwaters at concentrations upto micrograms per liter (µg/l). Most commonly used drugs that were reported include clofibrac acid (7.3 µg/l), diclofenac (µg/l), and ibuprofen (0.2 µg/l) (Thomas and Langford 2007).

### 2.4 Wastewater

Wastewater treatment plant effluents are another source of pharmaceutical residues in the aquatic environment. The measured concentration of PRs has been seen to increase further towards locations of point sources and discharge points. The amount of PRs is also governed by the factors like drug consuming profile of the population, physico-biochemical properties of the drugs and the methods of wastewater treatment used (Daughton and Ternes 1999). For example, aspirin is less likely to be detected in WWTP effluents due to its degradation into carbon dioxide and water (Richardson and Bowron 1985). Hydrophobic drugs and their metabolites due to their solubility are more likely to be detected in wastewater effluents.

The concentration of many PRs has been detected in ng/l range and even more. Clofibrac acid has been detected in WWTP effluents in Germany, Europe and Canada upto the concentration of 180 ng/l. Erythromycin concentration was found to be about 1.842 µg/l in a WWTP in UK. Similarly, diclofenac was detected in WWTP effluents in Germany (0.489 µg/l, UK (0.598 µg/l) and Europe (5.45 µg/l) (Thomas and Langford 2007).

Some metabolites of drugs like erythromycin and propranolol, can undergo deconjugation during treatment process in WWTPs. This causes discharge of parent drug in higher concentrations than the raw influent (Miao *et al.* 2002).

## 3. Pharmaceutical residues in water bodies - Indian scenario

### 3.1 Ground water

Relatively lesser studies in India have been carried out to detect the presence of PRs in groundwater. This might be due to analytical challenges associated with carrying out qualitative and quantitative studies with ground water. The presence of PRs in groundwater is attributed mainly to unscientific disposal of medicine containers after their

intended use or even before use into sewage, effluents and landfills fills. The contamination may increase during monsoons due to the high leaching and overflow of sewage effluents (Jones *et al.* 2002, Khan *et al.* 2020a, b).

Groundwater is mainly used for drinking and irrigation purposes in India (Balakrishna *et al.* 2017). Medicines like ciprofloxacin, norfloxacin, cetirizine have been found upto the concentration of 28 µg/l in the ground well water in Patancheru, Hyderabad. The WWTP near this area receives majority of its effluents from drug manufacturing industries established in the vicinity and the levels of PRs found in its wastewater are the highest ever reported in the world (Balakrishna *et al.* 2017). The levels of PRs in Indian groundwater far exceeds than developed countries like China. For example, the levels of ciprofloxacin in ground water in India was found to be 90 times higher than China and exceeded more than 40 times than levels in ground water in Spain (Cabeza *et al.* 2012). Municipal wastewater treatment plants treat less than 30 % of the generated sewage in India. So, mostly households use septic tank system or directly discharge the sewage into the ground water or surface water through sewer pipes causing PR contamination of both ground as well as surface water.

### 3.2 Rivers and lakes

Around eight studies have confirmed the presence of PRs in Indian rivers. The levels of medicines like ciprofloxacin, ketoprofen, gatifloxacin are higher in Indian water bodies when compared to the levels in China, while as erythromycin, diclofenac show their presence more in water bodies in China. This reflects the behavioral difference in drug consumption and health issues of the

two countries. The fact can be validated that around 64% of the population in India consumes medicines without a proper prescription (Mutiyaar and Mittal 2013), so India is likely to figure among the world's largest medicine markets. Patients in India are showing large inclination towards self medication, which will likely boost the over the counter (OTC) drugs market in the coming decade here (ICA 2020).

### 3.3 Wastewater treatment plants

The main source of PRs in the rivers and oceans are the outlets of wastewater treatment plants. The current WWTPs are not efficient enough to remove most of these PRs and these are also not degraded by microorganisms. Fick *et al.* (2009) reported higher levels of PRs (mg/l) in WWTPs that receive wastewater from pharma manufacturing industries while as PRs level in WWTPs processing domestic sewage was relatively lower (ng/l to µg/l). Ciprofloxacin levels in a WWTP in Okhla, Delhi showed higher levels than WWTPs of other countries. It was found to be nearly 2.5 and 5 times higher than that found in WWTPs of Australia (Al-Rifai *et al.* 2007) and Italy (Verlicchi *et al.* 2012) respectively.

Subedi *et al.* (2015) worked on five domestic sewage WWTPs in India and reported nearly 43 PRs and their metabolites. Amphetamine concentration was found to be 4.30-4.72 µg/l and is the highest ever reported concentration in wastewater.

## 4. Conventional methods of wastewater treatment

The conventional wastewater treatment methods like coagulation/flocculation, precipitation, evaporation,

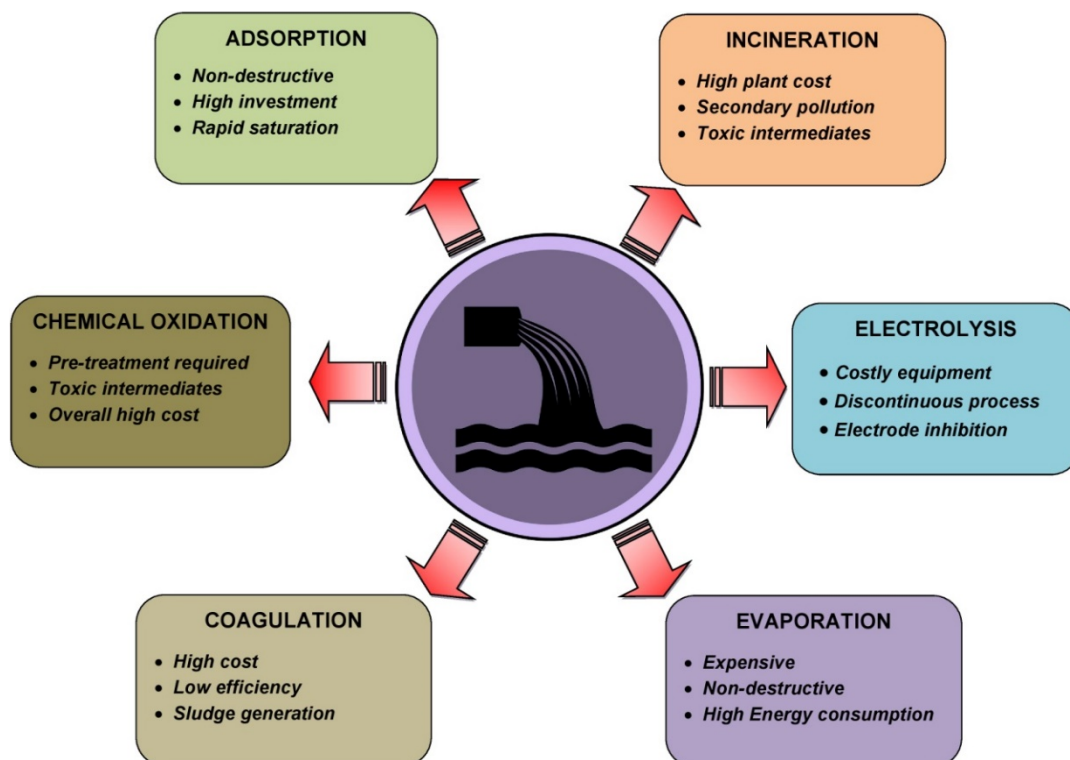


Fig. 2 Some conventional wastewater treatment methods and their drawbacks

Table 1 Shortcomings of various conventional wastewater treatment methods

| Method   | Disadvantages  |
|--|--|
| Adsorption/Filtration  | <ul style="list-style-type: none"> <li>• Nondestructive technique</li> <li>• High investment</li> <li>• Non-selective process</li> <li>• Rapid saturation of adsorbents</li> </ul>   |
| Incineration<br>(Catalytic/Thermal)  | <ul style="list-style-type: none"> <li>• High cost</li> <li>• Formation of secondary pollutants</li> <li>• Useful for concentrated effluents only</li> <li>• Air pollution</li> </ul>  |
| Electrolysis   | <ul style="list-style-type: none"> <li>• Costly equipment required</li> <li>• High maintenance cost</li> <li>• Discontinuous process</li> <li>• Inhibition of electrodes due to sludge deposition</li> </ul>   |
| Evaporation  | <ul style="list-style-type: none"> <li>• Expensive</li> <li>• High energy consumption</li> <li>• Requirement of other equipment to prevent air pollution</li> <li>• Non removal of volatile contaminants</li> </ul>  |
| Membrane filtration  | <ul style="list-style-type: none"> <li>• Higher energy requirement</li> <li>• High maintenance costs</li> <li>• Membrane fouling</li> <li>• Flow rate limitations</li> </ul>   |
| Chemical precipitation   | <ul style="list-style-type: none"> <li>• Ineffective in removal of metal ions</li> <li>• High sludge generation</li> <li>• Large amount of chemicals consumed</li> </ul>   |
| Coagulation/Flocculation   | <ul style="list-style-type: none"> <li>• High sludge generation</li> <li>• Low removal capacity</li> <li>• High cost</li> </ul>  |
| Biological methods<br>(Bioreactors, Microbial treatment,<br>Enzymatic degradation) | <ul style="list-style-type: none"> <li>• Slow method</li> <li>• Ineffective in removing non-biodegradable compounds</li> <li>• Optimum conditions required</li> <li>• Lower removal of dyes</li> </ul>   |
| Chemical Oxidation<br>(Ozone, H <sub>2</sub> O <sub>2</sub> etc.)                  | <ul style="list-style-type: none"> <li>• Pre-treatment required</li> <li>• Short half life of oxidants (ozone)</li> <li>• Formation of toxic intermediates</li> <li>• Sludge generation</li> <li>• Less efficiency in removal of some dyes</li> <li>• High cost</li> </ul> |

filtration and adsorption are used to remove colloidal solids, organic nutrients, metals etc from waste water effluents. However, these methods suffer from various disadvantages as shown in Fig. 2. Moreover, these methods are not able to degrade the pharmaceutical residues completely but only transform or remove them (Awfa *et al.* 2018, Blair 2016, Kanakaraju *et al.* 2014). Table 1 depicts some of the disadvantages of various conventional wastewater treatment methods (Crini and Lichtfouse 2019, Rathoure and Dhatwalia 2016, Robert and Malato 2002, Sharma and Sanghi 2012).

## 5. Role of nanotechnology in mitigation of pharmaceutical residues in water

Nano-materials are the structures with particle size of nanometers, typically one dimension having size less than 100 nm (Amin *et al.* 2014, Hejri *et al.* 2020, Hong 2019). Nanotechnology has contributed in the development of nanomaterials of varied forms like nanowires, tubes,

nanoparticles, nanofilms and nanocolloids (Lu and Astruc 2020). These nano-materials have proven to be effective and efficient in treatment of wastewater effluents, surface water, ground water and drinking water (Anjum *et al.* 2016, Herrera *et al.* 2017, Mauter and Elimelech 2008). Nanotechnology bestows an advanced wastewater treatment process that has added advantages of being eco-friendly and cost-effective. Nano-materials are also proving to be efficient tools for the simultaneous removal of multi-pollutants from wastewater (Khin *et al.* 2012, Lu and Astruc 2020, Mondal *et al.* 2015).

Nanomaterials are divided into three main groups: catalysts, adsorbents and membranes as depicted in Fig. 3. Nano-catalysts based on metal oxides/semiconductors (e.g., TiO<sub>2</sub>, ZnO, CuO, ZnS, CdS), fenton based (e.g., Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>) and electrocatalysts (e.g., Pt/Pd based carbon nanotubes) have been developed for treatment of wastewater (Daghrir *et al.* 2013, Das *et al.* 2016, Feng *et al.* 2003, Rajabi *et al.* 2018, Rocher *et al.* 2008, Safavi *et al.* 2017, Zeferino *et al.* 2019). These nano-catalysts have proven to be effective in degradation of organic pollutants

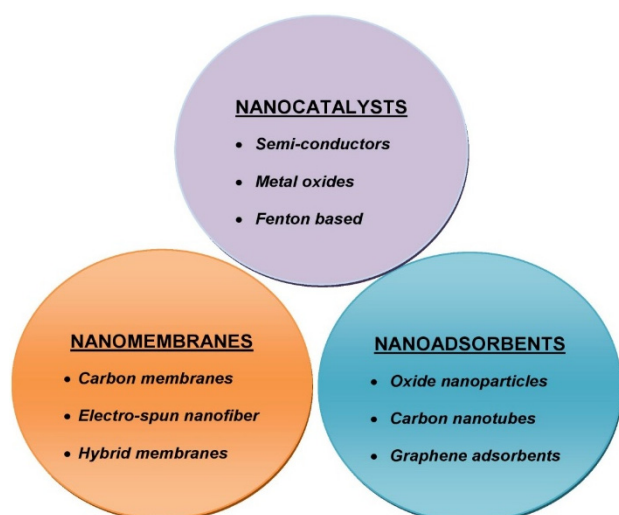


Fig. 3 Three main group of nanomaterials

in wastewater (Lin *et al.* 2015, Mathis *et al.* 2016).

Nano-adsorbents are made of elements composed of chemically active atoms, providing surface with high adsorption capacity like activated carbon, silica, oxides of metals and clay (Yu *et al.* 2016). The commonly used nano-adsorbents are oxide based nanoparticles (e.g., titanium/magnesium/manganese/zinc oxides), carbon nanotubes (multi-walled and magnetic) and graphene based (e.g., graphene oxide, graphene oxide-TiO<sub>2</sub> composite etc) (Jung *et al.* 2015, Qu *et al.* 2013, Walcarius and Mercier 2010). These nano-adsorbents have proven to be effective in removal of heavy metals and other organic contaminants from wastewater. The properties of these nano-adsorbents like surface area, adsorption, surface charge, mechanical strength, dispersion and hydrophobicity are effectively utilized for the treatment of wastewater (Smith and Rodrigues 2015, Yusoff *et al.* 2018).

Nano-membranes are used for treatment of wastewater using nano-filtration and have advantages over other membranes due to their small pore size, stability and increased efficiency (Ahmad *et al.* 2008, Cyna *et al.* 2002). Nano-membranes are developed from nano-metal/non-metal particles, carbon nano-tubes and nano-fibers. Nano-membranes are effectively used for the removal of dyes, heavy metals and disinfection of wastewater. Carbon based nano-membranes like carbon nanofibers,  $\beta$ -cyclodextrin carbon nanofibre composites, carbon nanotubes (single-walled and multi-walled), zeolite (e.g., sodalite) based nano-membranes, electrospun nanofiber membranes (polystyrene/polyurethanes/polyvinyl chloride/polycarbonate based) and hybrid membranes (e.g., polysulfone and zeolite coupled) are the most commonly used nano-membranes (Chen *et al.* 2011, Pant *et al.* 2014, Pedrosa *et al.* 2019, Sajadian *et al.* 2020, Wu *et al.* 2005).

### 5.1 Nano-photocatalysts a viable technology in the removal of pharmaceutical residues

Nano-catalysts are gaining more attention in wastewater treatment area because of their powerful oxidation potential

in degrading organic pollutants, work at mild conditions, effective even at low concentrations and anti-microbial properties. Nanoparticle based photocatalytic reactions involve interaction of light (UV/Visible) with the metal based nanoparticles for degradation of various pollutants like pharmaceutical residues, pesticides, herbicides and dyes (Girgis *et al.* 2015, Lin *et al.* 2014).

Nano-photocatalysts work on the principle of photoexcitation of electrons. The irradiation of photocatalyst with light, having energy higher or equal to the band gap energy of the catalyst, generates holes (h<sup>+</sup>) and excited electrons (e<sup>-</sup>). The holes (h<sup>+</sup>) react with water molecules and form hydroxyl radicals ( $\cdot$ OH). The  $\cdot$ OH radicals are highly reactive and powerful oxidizing agents, causing degradation of organic pollutants like PRs into carbon dioxide and water (Anjum *et al.* 2017, Lee *et al.* 2017, Vinu and Madras 2011).

TiO<sub>2</sub> semiconductor is a widely used photocatalyst owing to its ability to initiate a series of oxidation and reduction reactions on its surface. It has three polymorph crystals, anatase, rutile and brookite. Anatase form has been reported to exhibit highest photocatalytic activity among all the three polymorphs and therefore preferred in photocatalysis process. The photoexcited and photogenerated electrons in anatase form of TiO<sub>2</sub> are also reported to show longest lifetime and fastest migration rate respectively (Awfa *et al.* 2018, Shah and Rather 2020).

The presence of a lone electron in the outer orbital of TiO<sub>2</sub> is responsible for its photocatalytic activity. When a light energy (h $\nu$ ) having intensity greater than or equal to the bandgap energy (the energy difference between the valence band and the conduction band) of TiO<sub>2</sub> (3.2 eV for anatase), the lone electron gets excited from the valence band (VB) to the empty conduction band (CB) within femto (10<sup>-15</sup>) seconds (Chong *et al.* 2010, Foo and Hameed 2010). The wavelength of such energy usually corresponds to  $\lambda < 400$  nm and leads to generation of an electron-hole pair (e<sup>-</sup> and h<sup>+</sup>), leaving behind an unfilled empty valence band. The electrons and holes participate in a series of oxidation-reduction reactions on the photo-activated surface of the reactive species such as hydroxyl radical ( $\cdot$ OH) and superoxide radical anion ( $\cdot$ O<sub>2</sub><sup>-</sup>) as shown in Fig. 4. The key reactions and the mechanism involved in the photocatalysis are summarized in the Table 2 (Awfa *et al.* 2018, Chong *et al.* 2010, Dong *et al.* 2015).

As shown in Eqs. (1)-(3), the surface trapped VB electrons (e<sup>-</sup><sub>TR</sub>) and CB holes (h<sup>+</sup><sub>TR</sub>) are generated after the photonic excitation of the catalyst. It has been reported that their recombination occurs much more slowly than in the bulk (Dong *et al.* 2015, Chong *et al.* 2010). The presence of electron scavenger species is vital for slowing down the recombination and successful photooxidation of organic compounds. Eq. (4) shows the recombination of photoexcited electron with the valence band hole in the absence of electron scavengers. The recombination occurs in nanoseconds and is accompanied by dissipation of heat.

Mostly photocatalytic degradation of emerging contaminants and other organic compounds is carried out in the presence of photocatalyst, oxygen and water. Surface adsorbed hydroxyl radicals ( $\cdot$ OH<sub>ads</sub>) are formed when the

Table 2 Key oxidative-reductive reactions that occur at the photo-activated surface of the catalyst

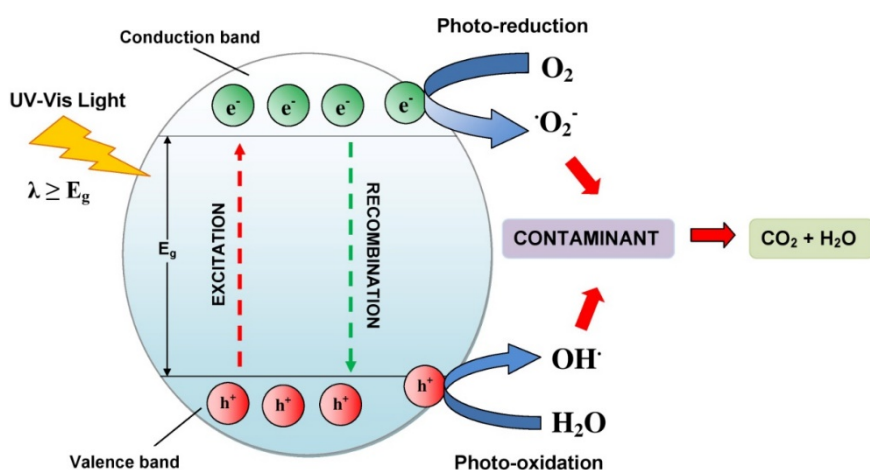
|                                       | Reactions   | Eq. no. |
|---------------------------------------|---|---------|
| Photoexcitation                       | $\text{TiO}_2 + h\nu \rightarrow e^- + h^+$   | 1       |
| Charge-carrier trapping of $e^-$      | $e^-_{\text{CB}} \rightarrow e^-_{\text{TR}}$   | 2       |
| Charge-carrier trapping of $h^+$      | $h^+_{\text{VB}} \rightarrow h^+_{\text{TR}}$   | 3       |
| Electron-hole recombination           | $e^-_{\text{TR}} + h^+_{\text{VB}}(h^+_{\text{TR}}) \rightarrow e^-_{\text{CB}} + \text{heat}$  | 4       |
| Oxidation of hydroxyls                | $(\text{OH}^-)_{\text{ads}} + h^+ \rightarrow \cdot\text{OH}_{\text{ads}}$  | 5       |
| Photoexcited $e^-$ scavenging         | $(\text{O}_2)_{\text{ads}} + e^- \rightarrow \text{O}_2^-$  | 6       |
| Protonation of superoxides            | $\text{O}_2^- + \text{OH} \cdot \rightarrow \text{HOO} \cdot$   | 7       |
| Co-scavenging of $e^-$                | $\text{HOO} \cdot + e^- \rightarrow \text{HO}_2^-$  | 8       |
| Formation of $\text{H}_2\text{O}_2$   | $\text{HOO}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}_2$  | 9       |
| Photodegradation by $\text{OH} \cdot$ | $\text{R} - \text{H} + \text{OH} \cdot \rightarrow \text{R}' + \text{H}_2\text{O}$  | 10      |
| Direct photoholes                     | $\text{R} + h^+ \rightarrow \text{R}^+ \rightarrow \text{Intermediate(s)}/\text{Final Degradation Products}$  | 11      |
| Over all reaction                     | $\text{Organic contaminants} \xrightarrow{\text{TiO}_2/h\nu} \text{Intermediate(s)} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Inorganic ions}$ | 12      |

positive holes react with the surface  $\text{OH}^-$  groups on the  $\text{TiO}_2$  surface as shown in Eq. (5). The presence of oxygen results in the formation of superoxide radicals ( $\text{O}_2^-$ ) and prevents electron-hole pair recombination (Eq. (6)). Further protonation of  $\text{O}_2^-$  forms hydroperoxyl radical ( $\text{HO}_2 \cdot$ ) that can react further to form  $\text{H}_2\text{O}_2$  (Eqs. (7)-(9)). The degradation of emerging contaminants/organic pollutants (R) is carried out by the photogenerated holes and hydroxyl radicals (Eqs. (10) and (11)). The  $\text{HO}_2 \cdot$  radical formed in the photocatalysis process is also reported to act as a scavenger and along with other radical species can prolong the recombination time of  $h^+_{\text{TR}}$ . Also, the presence of water and dissolved oxygen is important for the photocatalysis process. The photodegradation of liquid phase organic contaminants is hindered in the absence of water molecules as highly reactive hydroxyl radicals ( $\text{OH} \cdot$ ) are not generated (Chong *et al.* 2010, Shah and Rather 2019).

Many studies have been conducted to understand the degradation mechanism of various emerging contaminants over  $\text{TiO}_2$  surface. During heterogeneous photocatalysis, liquid phase organic contaminants are broken down to their

corresponding intermediates. As shown in Eq. (12), these intermediates are further mineralized to carbon dioxide, water and inorganic ions (from heteroatoms) (Awfa *et al.* 2018, Chong *et al.* 2010, Dong *et al.* 2015, Herrmann 1999, Reddy *et al.* 2017, Yang *et al.* 2008). Fig. 3 shows the mechanism of formation of electron hole pair in  $\text{TiO}_2$  nano-photocatalyst (Shah and Rather 2020).

Nano-catalysts have proven to be better tools for the degradation of PRs from wastewater, groundwater, surface water and drinking water. These nano-catalysts provide better advantage than the conventional wastewater treatment methods like degradation of recalcitrant PRs, less treatment time, low catalyst dosage, function at natural pH of wastewater and ability to completely degrade the contaminants into carbon dioxide and water (Hering *et al.* 2013). Most widely used photocatalysts are  $\text{TiO}_2$  and  $\text{ZnO}$  due to their high reactivity and chemical stability. But these nano-materials have wide band gap, 3.2 eV in case of  $\text{TiO}_2$ , which makes them effective in UV radiations only. The photocatalysts are modified to decrease their band gap and make them effective in visible region also (Anjum *et al.*

Fig. 4 Mechanism of electron-hole pair formation in  $\text{TiO}_2$  (Shah and Rather 2020)

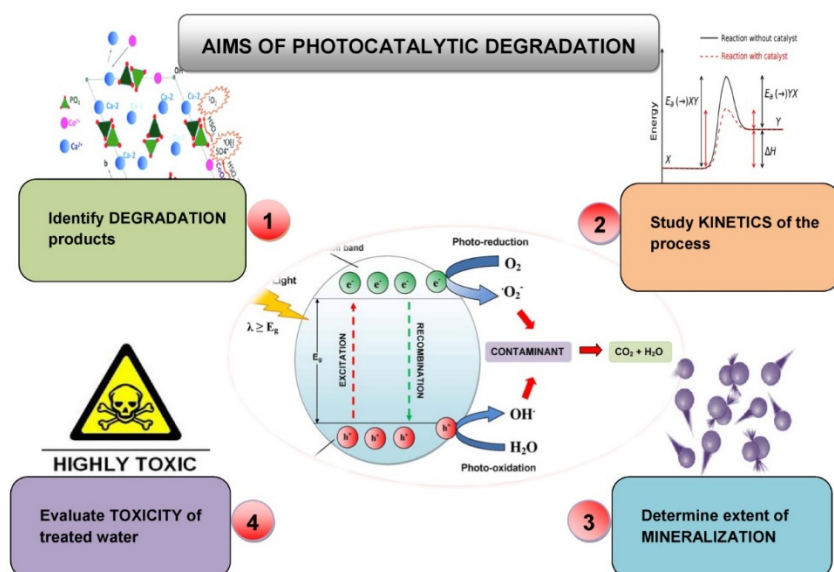


Fig. 5 General objectives of photocatalytic degradation of pharmaceutical residues

Table 3 Heterogenous TiO<sub>2</sub> photocatalytic degradation of some selected pharmaceutical residues

| Pharmaceutical compound   | Irradiation source                          | Experimental findings  | Reference                            |
|---------------------------|---|--|--------------------------------------|
| Moxifloxacin              | UVA lamp (365 nm)                           | TiO <sub>2</sub> catalyst dose of 5 g/l, temperature of 298 K and air sparging rate of 60 ml/min resulted in maximum degradation   | Van Doorslaer <i>et al.</i> (2012)   |
| Chlorhexidine             | UVA lamp (10 W)                             | 68.2% of chlorhexidine degraded by 200 mg/L of TiO <sub>2</sub> within 60 minutes at optimum pH of 10.5  | Das <i>et al.</i> (2014)             |
| Carbamazepine             | UVA lamp (3 × 8W; 365 nm)                   | 99% degradation of carbamazepine was achieved in 1.5 hours at catalyst loading of 1.5 g/l.   | Carabin <i>et al.</i> (2015)         |
| Carbamazepine             | Solar simulator (1000W Xe lamp)             | The degradation rate after 2 hours and in presence of the catalyst was 0.015 min <sup>-1</sup> while as it was compared to only 0.0005 min <sup>-1</sup> using light alone. Also, the degradation rate was higher in the presence of NOM like humic acid.  | Drosos <i>et al.</i> (2015)          |
| Naproxen (and diclofenac) | Medium pressure Hg lamp (200-600 nm)        | TiO <sub>2</sub> photocatalytic degradation rate of naproxen in the river water samples was found to be 0.21 min <sup>-1</sup> (catalyst alone), 0.10 min <sup>-1</sup> (addition of phosphate ions) and 0.11 min <sup>-1</sup> (addition of phosphate and chloride anions)                                      | Kanakaraju <i>et al.</i> (2015)      |
| Methamphetamine           | UV lamp (9W; 365 nm)                        | The degradation rates of 100 µg/l methamphetamine were found to be 0.12 min <sup>-1</sup> and 2.34 min <sup>-1</sup> for catalyst dosage of 0.01 and 0.1 g/l.  | Kuo <i>et al.</i> (2015)             |
| Metoprolol                | Solar box (Xe lamp; 1 kW)                   | Highest TOC removal of 45.6% was obtained at a catalyst dose of 0.4 g/l with degradation rate constant of 0.12 min <sup>-1</sup> compared to 0.0061 min <sup>-1</sup> for catalyst concentration of 0.05 g/l.  | Romero <i>et al.</i> (2015)          |
| Dicloxacillin             | Black lamp (30-150 W; 365 nm)               | Study of effects of TiO <sub>2</sub> concentration and power on the degradation of dicloxacillin was conducted. Highest degradation (800 ppm) was obtained for catalyst dose of 2 g/l and 150 W applied power.   | Villegas-Guzman <i>et al.</i> (2015) |
| Ibuprofen                 | Medium pressure Hg lamp (125 W)             | TiO <sub>2</sub> degradation of ibuprofen was studied using UV light and solar irradiation. compared to solar UV irradiation. Under UV light (Hg lamp), 92% degradation and 78% TOC removal was obtained.  | Candido <i>et al.</i> (2016)         |
| Aspirin and Paracetamol   | UVA lamp (315-400 nm; 75 W/m <sup>2</sup> ) | The photocatalytic performance of TiO <sub>2</sub> P25 and TiO <sub>2</sub> K1077 was compared. The catalyst dose of 0.1 g/L TiO <sub>2</sub> P25 resulted in better degradation and mineralization of mixture of aspirin and paracetamol (12.5 mg/l each) compared to similar amount of TiO <sub>2</sub> K1077. | Bianchi <i>et al.</i> (2017)         |

Table 3 Continued

| Pharmaceutical compound                        | Irradiation source  | Experimental findings   | Reference                         |
|--|---|---|-----------------------------------|
| Methotrexate                                   | UVA lamp (8W; 352 nm)   | The effect of $\text{HCO}_3^-$ ions (400 mg/L) on the degradation of methotrexate (100 mg/l) was studied using $\text{TiO}_2$ photocatalyst. The half-life of methotrexate was found to reduce from 13.8 min. to 1.8 min on addition of $\text{HCO}_3^-$ ions in the photocatalytic reaction mixture.   | Lai <i>et al.</i> (2017)          |
| Venlafaxine                                    | UVA lamp (9W/78; 340-400 nm)  | Complete degradation of venlafaxine (2.5 mg/l) was achieved in 20 mi at a catalyst dose of 0.4 g/l.   | Lambropoulou <i>et al.</i> (2017) |
| Ibuprofen                                      | UV-LED (4 × 10 W; 382 nm)   | Complete degradation of ibuprofen (60 mg/l) was achieved in 30 min using 4 LEDs (100 W).  | Jallouli <i>et al.</i> (2018)     |
| Naproxene                                      | UV light source (6W, 365 nm)  | Comparison of photocatalytic efficiency of ZnO, $\text{TiO}_2$ and their mixture was studied. The degradation rate constants of $0.011 \text{ min}^{-1}$ , $0.006 \text{ min}^{-1}$ and $0.00764 \text{ min}^{-1}$ were obtained for ZnO, $\text{TiO}_2$ and $2\text{ZnO-TiO}_2$ nanocrystals.  | Strbac <i>et al.</i> (2018)       |
| Carboplatin                                    | UV-A (9 W, 366 nm), visible irradiation source (9 W, 440 nm)                                | The best degradation and mineralization of carboplatin was achieved using $\text{TiO}_2$ P25/UV-A system. The phytotoxicity of 20 mg/l aqueous solution of carboplatin is reduced within 60 min.  | Kitsiou <i>et al.</i> (2018)      |
| Diclofenac                                     | Visible light source (400 W Metal Halide Lamp)  | Visible light driven photocatalytic degradation was carried using $\text{TiO}_2\text{-WO}_3$ catalysts. TW10 (molar ratio 10:1) was found to be the most effective catalyst in the elimination of diclofenac, with 92% mineralization. Catalyst efficiency was 80% even after four consecutive reaction cycles.   | Mugunthan <i>et al.</i> (2018)    |
| Carbamazepine and sulfamethoxazole             | Solar simulator (MS-35AAA, Ushio Lighting Edge Technologies, Japan) $1000 \text{ W m}^{-2}$ | Under solar irradiation, <2% of carbamazepine and 20-50% of sulfamethoxazole was degraded. NOM reduced the photodegradation rate of $\text{TiO}_2$ for carbamazepine and sulfamethoxazole from $4.2 \times 10^{-2}$ and $4.7 \times 10^{-2} \text{ min}^{-1}$ to $6 \times 10^{-3}$ and $5 \times 10^{-3} \text{ min}^{-1}$   | Awfa <i>et al.</i> (2019)         |
| Metoprolol                                     | 4 × 15 W UV-A lamps 365 nm  | Metoprolol (100 ppm) is completely degraded in 150 min at optimum conditions of pH=9.6 and $\text{TiO}_2$ dose of 0.5 g. 80% of mineralization occurs after six hours of reaction.  | Leyva <i>et al.</i> (2019)        |
| Propranolol and atenolol                       | 4 × 8W low pressure mercury vapour lamps ( $\lambda_{\text{max}}$ 254 nm)                   | Four commercial $\text{TiO}_2$ samples; Aeroxide P25, Hombikat UV 100, Kronoclean 7000 and Merck $\text{TiO}_2$ were used for photocatalytic degradation. Aeroxide $\text{TiO}_2$ P25 showed highest degradation efficiency for both the pollutants. For propranolol, the optimum conditions are Aeroxide $\text{TiO}_2$ P25 (0.03g/l), Substrate Concentration $5 \times 10^{-5} \text{ M}$ , neutral pH. For atenolol, optimum conditions are: Aeroxide $\text{TiO}_2$ P25 (0.03g/l), Substrate Concentration $2 \times 10^{-4} \text{ M}$ , 9.1 pH for initial reaction solution. Addition of $\text{H}_2\text{O}_2$ had no significant effect on increasing degradation rate for both the pollutants. | Ponkshe and Thakur (2019)         |
| Sulfamethazine                                 | Natural solar light   | The complete degradation of sulfamethazine was achieved in 135 min at optimum conditions of pH=7, single-walled carbon nanotubes content of 10%, Cu content of 4%, sulfamethazine concentration of 30 mg/l and catalyst dosage of 0.9 g/l   | Payan <i>et al.</i> (2019)        |
| Ibuprofen, naproxen and cetirizine             | 125W Xenon lamp, $\lambda > 420 \text{ nm}$   | Using visible light, complete photodegradation of ibuprofen, naproxen and Cetirizine was achieved at 210, 50 and 90 min respectively. The photodegradation efficiency was highest at acidic pH (pH=2–4) and low efficiencies (60–70%) were observed at alkaline pH.   | Uheida <i>et al.</i> (2019)       |
| Ibuprofen and naproxen                         | 350 W Xenon lamp (380-900 nm)   | Nitrogen and sulfur doped $\text{TiO}_2$ was coated on polycarbonate. At optimized condition, 83% and 100% degradation of ibuprofen and naproxen was achieved in 120 min irradiation time.  | Eslami <i>et al.</i> (2020)       |
| Diclofenac, carbamazepine and sulfamethoxazole | Xenon lamp System (300 W), 290–800 nm   | After 4 hours, degradation of 100% diclofenac, 50% sulfamethoxazole and 70% carbamazepine with rate of degradation of 0.715, 0.185 and 0.327 mg/l.min respectively.   | Daou <i>et al.</i> (2020)         |

Table 3 Continued

| Pharmaceutical compound | Irradiation source           | Experimental findings   | Reference                   |
|-------------------------|------------------------------|---|-----------------------------|
| Sulfamethoxazole        | UVA lamp, 300-400 nm.        | The photodegradation of sulfamethoxazole depends on the amount of TiO <sub>2</sub> in the nanocomposite. After 120 minutes of UV-A irradiation, degradation rates were 26.3, 51.3 and 76.3% for TiO <sub>2</sub> doses of 1, 5 and 10% respectively | Mourid <i>et al.</i> (2020) |
| Diclofenac              | 5 × 250 W lamps (420–720 nm) | The best photocatalytic degradation removal efficiency (53.65%) under visible irradiation was obtained at the catalyst dose of 1.5 g/l, Nguyen <i>et al.</i> (2020a) with TOC removal of 25.94%   |                             |
| Sulfamethoxazole        | UVA lamp, 300-400 nm.        | The photodegradation of sulfamethoxazole depends on the amount of TiO <sub>2</sub> in the nanocomposite. After 120 minutes of UV-A irradiation, degradation rates were 26.3, 51.3 and 76.3% for TiO <sub>2</sub> doses of 1, 5 and 10% respectively | Mourid <i>et al.</i> (2020) |

2016). Various methods used for catalyst modification are adding metal impurities, dye sensitization, forming nanocomposites using semiconductors, which lower the band gap energy, creating a narrow band gap which makes the photocatalysts sensitive to visible light also (Lee *et al.* 2017).

TiO<sub>2</sub> has been doped with metals like Pt, Au, Ag and Pd, showing excellent photocatalytic activities compared to unmodified TiO<sub>2</sub>. ZnO, ZnS, ZnSe, CuO, CdS, are other nano-catalysts that have been doped with dopants like Co, Ni, Al, Cu, Eu, Mn, Fe, Cr, Mg, Ga to form nanocomposites having higher photocatalytic degradation activities (Chandrakar *et al.* 2015, Jamal *et al.* 2012, Letti *et al.* 2017).

Photocatalysts have not only proven to be effective tools for treatment of wastewater but also have shown to act as anti-microbial agents. TiO<sub>2</sub> and Ag doped TiO<sub>2</sub> have shown efficient anti-microbial activity against pathogens like *E. coli* (Akhavan 2009, Liu *et al.* 2008, Sur 2014).

### 5.2 TiO<sub>2</sub> based heterogeneous photocatalytic degradation of pharmaceutical residues

The main focus of the TiO<sub>2</sub> photocatalytic degradation of pharmaceutical residues as shown in the Fig. 5 is to study the kinetics of the reaction involved, optimization of the factors and determine the extent of mineralization and degradation. It also involves the identification of the degradation products obtained during the process and evaluation of the toxicity of the reaction mixture to ensure that the treated water is not harmful to the aquatic ecosystem. Photocatalytic degradation of various pharmaceuticals like analgesics, antipyretics, antibiotics, anesthetics,  $\beta$  blockers and lipid regulators has been studied extensively. This is due to their high consumption worldwide and subsequent detection in aquatic environment.

TiO<sub>2</sub> photocatalytic degradation has proven to be a successful process for the efficient removal of PRs from wastewater. Mostly those medicines have been selected for the degradation studies that are consumed in large quantities worldwide and thus have high chances of showing presence in the aquatic environment. These medicines include paracetamol (acetaminophen), diclofenac, amoxicillin, naproxen, aspirin, ibuprofen, metoprolol, cetirizine etc. and

are summarized in Table 3.

TiO<sub>2</sub> photocatalytic degradation studies involve the optimization of various parameters like initial concentration of the medicine, catalyst dosage, pH, nature of the catalyst (doped/undoped), light source and effect of organic matter. In addition to these parameters, effect of factors like stirring speed, temperature of the reaction mixture, type of gas (and rate) used for sparging of the solution and design of the photoreactor vessel on the photocatalytic degradation have also been studied (Bianchi *et al.* 2017, Jallouli *et al.* 2018, Kanakaraju *et al.* 2015, Villegas-Guzman *et al.* 2015).

The effect of TiO<sub>2</sub> dosage, initial concentration of the substrate, stirring rate, temperature of the reaction mixture and rate of sparging of gases (oxygen, nitrogen) on the degradation of moxifloxacin were studied by Van Doorslaer *et al.* (2012). The study concluded that TiO<sub>2</sub> catalyst dose of 5 g/l, temperature of 298 K and air sparging rate of 60 ml/min resulted in maximum degradation. The effect of pH on the photocatalytic degradation rate was studied by Das *et al.* (2014) for chlorhexidine. pH of 10.5 was found to be optimum for the degradation (68.2% removal within 60 min). For degradation of metoprolol (100 ppm), complete degradation was achieved in 150 min at optimum pH of 9.6 (Leyva *et al.* 2019). They also observed the pH of the reaction mixture with time and found that the solution became acidic (pH = 5.7) after one hour of photocatalytic process. The pH increased slowly in the later stages of the photocatalytic oxidation process due to the release of amines. The photodegradation efficiency of ibuprofen, naproxen and cetirizine was found to be highest at acidic pH (pH = 2-4) and lower degradation rate (upto 70%) was observed at alkaline pH (Uheida *et al.* 2019). Neutral pH (pH = 7) was reported to be the optimum pH for degradation of sulfamethazine under natural sunlight (Payan *et al.* 2019). A unique study on the effects of TiO<sub>2</sub> concentration and applied power on the degradation of dicloxacillin was conducted by Villegas-Guzman *et al.* (2015). They reported that the highest degradation (800 ppm) was obtained for catalyst dose of 2 g/l and 150 W applied power.

The photocatalytic performance is governed by the physical material properties of the photocatalyst such as morphology, surface area, size, surface charge, phase composition and band gap. Variations in the photocatalytic

Table 4 Comparison of properties of commonly used commercial TiO<sub>2</sub> photocatalysts

| Photocatalyst type            | BET surface area (m <sup>2</sup> g <sup>-1</sup> ) | Particle size (nm) | Crystal form                | Photocatalytic efficiency | References   |
|-------------------------------|--|--------------------|-----------------------------|---------------------------|--|
| Aeroxide TiO <sub>2</sub> P25 | 50   | 21                 | 75% Anatase<br>25% Rutile   | 96%                       | Kanakaraju <i>et al.</i> (2018);<br>Ponkshe and Thakur (2019);<br>Carabin <i>et al.</i> (2015) |
| Hombikat UV 100               | 250  | 5                  | Anatase                     | 73%                       | Kanakaraju <i>et al.</i> (2018);<br>Ponkshe and Thakur (2019);<br>Carabin <i>et al.</i> (2015) |
| Kronoclean 7000               | 225  | 15                 | Anatase                     | 41%                       | Ponkshe and Thakur (2019)  |
| Merck TiO <sub>2</sub>        | 20   | 27                 | Anatase                     | 80%                       | Ponkshe and Thakur (2019)  |
| Ti (IV) oxide Aldrich         | 190-290  | 15                 | Anatase                     | 89%                       | Kanakaraju <i>et al.</i> (2018)  |
| Evonik-Degussa P90            | 90   | 13-23              | 90 % Anatase<br>10 % Rutile | 69%                       | Carabin <i>et al.</i> (2015)   |
| PC500                         | 336  | 9                  | Anatase                     | 50%                       | Carabin <i>et al.</i> (2015)   |
| ST01                          | 312  | 9                  | Anatase                     | 39%                       | Carabin <i>et al.</i> (2015)   |
| Evonik P25                    | 52   | 26                 | 80 % Anatase<br>20 % Rutile | 60%                       | Bianchi <i>et al.</i> (2017)   |
| Micro-sized K1077             | 11   | 130                | Anatase                     | 88%                       | Bianchi <i>et al.</i> (2017)   |

efficiency can be explained on the basis of the differences in these material properties. The properties of the commonly used commercial TiO<sub>2</sub> photocatalyst are shown in the Table 4. The photocatalytic degradation of carbamazepine using five different TiO<sub>2</sub> photocatalysts was carried out by Carabin *et al.* (2015). TiO<sub>2</sub> P90 was found to be the most efficient photocatalyst with 69% removal efficiency. Similar study was conducted by Bianchi *et al.* (2017) to compare the photocatalytic performance of TiO<sub>2</sub> P25 and TiO<sub>2</sub> K1077 on the degradation of aspirin and paracetamol. The catalyst dose of 0.1 g/l TiO<sub>2</sub> P25 resulted in better degradation and mineralization of mixture of aspirin and paracetamol (12.5 mg/l each) compared to similar amount of micro-sized TiO<sub>2</sub> K1077. Ponkshe and Thakur (2019) compared photocatalytic efficiency of four commercial TiO<sub>2</sub> samples; Aeroxide TiO<sub>2</sub> P25, Hombikat UV 100, Kronoclean 7000 and Merck TiO<sub>2</sub>. It was reported that Aeroxide TiO<sub>2</sub> P25 showed highest degradation efficiency for propranolol as well as atenolol.

The water quality parameters play an important role in photocatalytic degradation of PRs but limited studies have been conducted on real wastewater effluents, water from lakes, rivers, ponds and drinking/tap water. The presence of radical scavenging agents like carbonate ions (HCO<sub>3</sub><sup>-</sup>) have been reported to affect the degradation rate of pharmaceuticals. The half-life of methotrexate was found to reduce from 13.8 min. to 1.8 min on addition of HCO<sub>3</sub><sup>-</sup> in the photocatalytic reaction mixture (Lai *et al.* 2017). The effect of water matrix and anions on the TiO<sub>2</sub> photocatalytic degradation rate of diclofenac was studied by Kanakaraju *et al.* (2015). The diclofenac degradation decreased due to the addition of phosphate and chloride ions.

Natural organic matter (NOM) such as humic acid, tannic acid and fulvic acid act as light absorbing agents or cause quenching of photo-excited species and decrease the photodegradation efficiency. They also act as promoters of photodegradation by increasing the contact time of PRs on

the catalyst surface. The degradation rate of carbamazepine was found to be higher in the presence of NOM like humic acid (Drosos *et al.* 2015). However, at higher concentration, NOM decreased the adsorption of PRs on the catalyst surface and hence reduced the degradation rate. NOM induced decrease in the photocatalytic degradation rate of carbamazepine and sulfamethoxazole was also observed by Awfa *et al.* (2019).

Photocatalytic degradation experiments are usually performed using laboratory-scale photoreactors with artificial UV/Visible light sources. The operating conditions can be easily controlled in these reactors as compared to pilot scale reactors that operate using sunlight as light source. However, pilot scale reactor studies and results are more reliable and realistic for practical scale operations.

Another aim of the TiO<sub>2</sub> based photocatalytic treatment process is to enhance the biodegradability of PRs present in the wastewater. The extent of mineralization is expressed in terms of chemical oxygen demand (COD) or as removal of dissolved organic carbon (DOC) and total organic carbon (TOC). However, the complete degradation of medicines or other organic pollutants does not imply complete mineralization. For example, 92% of ibuprofen was reported to undergo degradation using TiO<sub>2</sub> photocatalyst and UV light irradiation but the TOC removal was found to be only 78% (Candido *et al.* 2016). Likewise, the highest TOC removal of only 45% was obtained during the TiO<sub>2</sub> photocatalytic degradation of metoprolol although degradation efficiency was calculated to be much higher (Romero *et al.* 2015). In some cases, this difference in the degradation and mineralization rate has been attributed to the formation of stable intermediates. These intermediates and transformed by-products may turn to be more toxic than the parent pharmaceuticals, thus making the toxicity evaluation studies necessary (Calza *et al.* 2006).

Degradation studies by Lai *et al.* (2017) indicated the higher toxicity of the TiO<sub>2</sub> treated methotrexate solution in

the presence of  $\text{HCO}_3^-$  ions, thereby making it necessary to ensure that no toxic intermediates and end-products are generated during the degradation process. Only few studies have identified the intermediates and end-products formed during the degradation process as it involves complex sample preparation procedure and analysis techniques. Degradation intermediates and end-products are identified by techniques like liquid chromatography mass spectrometry (LC-MS), gas chromatography mass spectrometry (GC-MS) and high performance liquid chromatography mass spectrometry (HPLC-MS) (Jallouli *et al.* 2018, Kanakaraju *et al.* 2016, Kuo *et al.* 2015, Lambropoulou *et al.* 2017).

One of the draw-back of using  $\text{TiO}_2$  photocatalyst is the recovery of the catalyst after the photocatalysis process is over. This problem has been overcome by immobilizing  $\text{TiO}_2$  nanoparticles on suitable materials like glass, activated carbon, polycarbonate and cellulose (Daneshvar *et al.* 2005, Eslami *et al.* 2020, Huang *et al.* 2006, Jallouli *et al.* 2017). The degradation of sulfamethoxazole was carried out using  $\text{TiO}_2$  impregnated on layered double hydroxide which was synthesized using co-precipitation method (Mourid *et al.* 2020). It was observed that the degradation rate increases with increase in the amount of  $\text{TiO}_2$  in the nanocomposite and after 120 minutes of irradiation, the degradation rate was 76.3% for 10%  $\text{TiO}_2$  dose. Photocatalytic degradation of platinum based anti-cancer drug carboplatin was studied under UV-A light and using  $\text{TiO}_2$  nanoparticles (Kitsiou *et al.* 2018). The study also examined the deposition and recovery of the platinum on the surface of the photocatalyst.

Degradation of diclofenac, carbamazepine and sulfamethoxazole pharmaceuticals was carried out by Daou *et al.* (2020) using nanocomposite of activated carbon (AC) obtained from nutshells of *Argania spinosa* tree and  $\text{TiO}_2$ . The 9%  $\text{TiO}_2$ -AC composite (0.1 g/l) was found to degrade 40, 48.9 and 54% of diclofenac, carbamazepine and sulfamethoxazole respectively in 4 hours of irradiation using Xe lamp. Another study on the photocatalytic degradation of diclofenac was carried out using N-doped  $\text{TiO}_2$  (Nguyen *et al.* 2020b). The study also investigated the effect of  $\text{H}_2\text{O}_2$  on the photodegradation and to understand the kinetics, degradation pathway and possible mechanism. Nitrogen and sulphur doped  $\text{TiO}_2$  and supported on polycarbonate, was studied for the degradation of ibuprofen and naproxen using visible light (Eslami *et al.* 2020). The doped catalyst resulted in the degradation of 83 and 100 % of ibuprofen and naproxen respectively in 2 hours of irradiation. Similarly, Tungsten doped  $\text{TiO}_2$  nanocomposite ( $\text{TiO}_2$ - $\text{WO}_3$ ) was used for removal of diclofenac and the catalyst efficiency was reported to be 80% even after four cycles of catalyst reuse (Mugunthan *et al.* 2018). A comparative study of efficiency of  $\text{TiO}_2$  and ZnO nanoparticles in the removal of acetaminophen under simulated solar light showed that the ZnO photocatalyst proved to be a better catalyst, with a degradation of 83% compared to 47% only for  $\text{TiO}_2$  (Zyoud *et al.* 2020). In another comparative study of photocatalytic degradation of naproxene using  $\text{TiO}_2$  and ZnO nanocomposites, it was concluded that 2:1 molar ratio of ZnO and  $\text{TiO}_2$  showed higher efficiency than the  $\text{TiO}_2$  (Strbac *et al.* 2018).

However, more studies need to be conducted to identify the toxic potential of degradation intermediates and end-products, especially when a solution containing more than one pharmaceutical is used. This can help in giving insights about the type and nature of interactions occurring between different PRs in water, specifically the real wastewater as currently there is limited data available related to the efficiency of this technique in simultaneous removal of multiple pharmaceuticals from the mixture. Also, the effect of other co-pollutants like ions, dyes, organic matter and heavy metals too needs to be investigated and knowledge gap addressed.

## 6. Conclusions

The presence of pharmaceutical residues in marine water, surface water, ground water and drinking water clearly pose a huge environmental challenge, especially when the effects on human health are unknown and the impact on aquatic flora and fauna is still not clearly understood. Current wastewater treatment methods like adsorption using activated carbon, air stripping and reverse osmosis have been found to be ineffective in removing these pharmaceutical residues. Presence of PRs in water bodies is nowadays a serious threat to the health of humans, animals and aquatic life. There is an urgent need in first place to detect the presence of all the PRs existing in our water supplies. Their undue presence and subsequent unintentional assimilation by humans, animals and aquatic organisms may lead to life threatening diseases like hormonal disruptions, sterility, impaired neurotransmission, resistance to antibiotics etc. Simultaneously, we need to revisit our present day drinking water treatment technologies world over, where often focus on the treatment of PRs is lacking especially in third world countries like India.  $\text{TiO}_2$  photocatalysis is an efficient advanced oxidation process for treatment and removal of various emerging contaminants from wastewater. Numerous studies have demonstrated the effective performance of this method through reaction-kinetics studies as well as role of parameters like catalyst dose, concentration of pollutants/PRs, pH, temperature, nature of water matrix and presence of other ions. However, limited studies have been conducted that investigate the formation and identification of intermediates/by-products during photocatalytic degradation process along with the possible degradation mechanism. Thus, there is scope for future research in this area.

There is also a huge potential for exploring the use of hybrid advanced oxidation processes like photocatalytic ozonation, sonophotocatalysis, photocatalytic-fenton oxidation etc for degradation as well as enhanced mineralization of pharmaceuticals. In spite of these encouraging findings, lack of consistency in rate of degradation and mineralization, complex intermediates and by-product formation, underscore the complexity of the interaction of the pharmaceutical residues towards  $\text{TiO}_2$  photocatalysis. Thus, there is scope for further studies on optimization of reaction kinetics parameters and studying

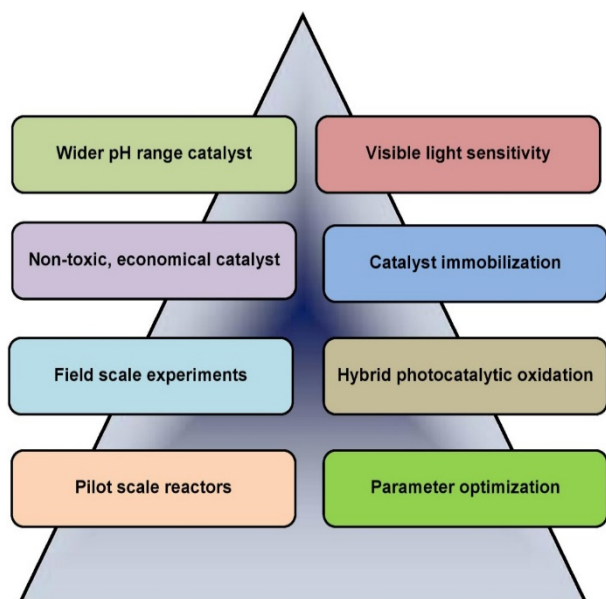


Fig. 6 Some of the constraints that need to be addressed in photocatalytic degradation of pharmaceutical residues

interaction between drugs and water matrix.

The use of TiO<sub>2</sub> photocatalysis as an advanced oxidation process for the treatment of wastewater containing pharmaceuticals has several other impediments (as shown in Fig. 6) that range from catalyst preparation to parameter optimization including reactor design. The constraints that need to be addressed include:

- catalyst improvisation to make it functional under visible region of solar radiation
- separation of catalyst by using various immobilization methods
- optimize the pH sensitivity range of the catalyst to minimize the use of oxidants
- effective designing of reactor that can utilize solar radiation also
- development of low cost, easy and eco-friendly methods of synthesizing catalyst
- investigate the effects of inorganic ions, impurities and NOM on the photocatalytic process
- performing field-scale experimental studies to study efficiency in real wastewater treatment plants
- enhance recovery and separation of catalyst by introducing magnetic properties. This will reduce the operation cost as the catalyst can be reused multiple times after magnetic separation.
- toxicity of photocatalyst and intermediates/by-products formed during degradation studies needs to be investigated. Toxic intermediates or by-products can decrease the rate of the reaction and also cause secondary pollution.

The photocatalytic degradation of emerging contaminants like pharmaceuticals using TiO<sub>2</sub> based nanocatalysts has received great attention during few decades. Present study is aimed at reviewing and

emphasizing the presence of many of such PRs in our day to day water supplies. We also focus on bringing forth the manifestation of nanotechnology as an advanced oxidation process (TiO<sub>2</sub> based photocatalysis) to treat these emerging contaminants. This study is also of immense importance due to ongoing COVID-19 pandemic, when tons of medicines are being used world over for treating it and subsequent likelihood of high PR concentrations in environment due to this pandemic.

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