Nano-based adsorbent and photocatalyst use for pharmaceutical contaminant removal during indirect potable water reuse

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Increasing human activity, including commercial and noncommercial use of pharmaceuticals, personal care products, and agricultural products, has introduced new contaminants that can be challenging to remove with currently available technologies. Pharmaceuticals, in particular, can be especially challenging to remove from the water supply and can pose great harm to people and local ecosystems. Their highly stable nature makes their degradation with conventional water treatment techniques difficult, and studies have shown that even advanced treatment of water is unable to remove some compounds. As such, decontamination of water from pharmaceuticals requires the development of advanced technologies capable of being used in indirect and direct potable water reuse. In this review, we discuss pharmaceutical removal in indirect potable water treatment and how recent advancements in adsorption and photocatalysis technologies can be used for the decontamination of pharmaceutical-based emerging contaminants. For instance, new materials that incorporate graphene-based nanomaterials have been developed and shown to have increased adsorptive capabilities toward pharmaceuticals when compared with unmodified graphene. In addition, adsorbents have been incorporated in membrane technologies, and photocatalysts have been combined with magnetic material and coated on optical fibers improving their usability in water treatment. Advancements in photocatalytic material research have enabled the development of highly effective materials capable of degradation of a variety of pharmaceutical compounds and the development of visible-light photocatalysts. To understand how adsorbents and photocatalysts can be utilized in water treatment, we address the benefits and limitations associated with these technologies and their potential applicability in indirect potable water reuse plants.

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INTRODUCTION

Potable water can be considered the most important human need. However, human activities have introduced dangerous contaminants in water systems requiring a multibarrier treatment approach to purify water for potable use. From the Ganges River Basin in India to the surface water in Milan, contaminants such as pharmaceuticals and personal care products have been detected.1–9 These contaminants are difficult to remove and can cause harm not only to humans but to wildlife and local ecosystems as well. Pharmaceuticals, personal care products, persistent organic pollutants, methanesulfonic acids, artificial sweeteners, transformation products, and engineered nanomaterials have all been identified as current contaminants of emerging concern (CECs).10–13 In this review, we focus on emerging pharmaceutical contaminants (EPCs) because of their potential adverse effects to humans and the ecosystem (Table 1). For instance, EPCs such as antibiotics can give rise to antibiotic resistant bacteria, which can cause irreparable harm to humans and the ecosystem.

Although detection of alarming concentrations of EPCs in wastewater streams has been a major concern for years, the true fate of some EPCs continues to be understudied. With the currently available information, it can be clearly seen that EPCs bioaccumulate in animal and plant tissues and often persist in the environment.14,15 For example, antibiotic presence in water and related ecosystems is already leading to an increase in antibiotic resistant bacteria.16 More alarming is the amount of these contaminants ending up in effluent streams as a result of their continuous usage in the treatment of various diseases. As such, the existence of EPCs in water sources is a globally important issue requiring increased attention on how non-target organisms are affected and how EPCs can be removed from potable water.

Due to the multiple concerns surrounding the decline of freshwater resources and increasing water demand, water reclamation and reuse projects are widely popularizing all around the world.17–19 With CEC detection in freshwater sources and revelations about CEC harm on human health and safety, potable water treatment facilities require careful design of additional steps to ensure water is safe for consumption.20–22 Conventionally, harmful contaminants are removed from wastewater with a multiple barrier approach.20,22,23 Primary and secondary treatment techniques are well established and capable in removing dissolved organic matter as well as larger particles (suspended particles and biodegradable solids are removed via physical and biological means, respectively).19,24 In the case of CECs, many stable and non-biodegradable compounds can survive these steps requiring further treatment.23,25

The next treatment step is determined by different water reuse downstream approaches, which can be categorized as unplanned, direct, and indirect. The unplanned potable reuse water cycle is the simplest, where treated water is released to a natural water system after the primary and secondary treatment steps.19,23,24
processes. However, even these energy-intensive methods are often removed with advanced contaminants that are not removed by primary and secondary operations in a water treatment plant is important as system downstream. The ef

Both direct and indirect potable reuse plants contain a tertiary (advanced) treatment step before being released from the plant. This step can include one or more of the following processes: membrane filtration, carbon adsorption, ion exchange, chlorination, and advanced oxidation processes (AOPs), such as ozone and UV radiation. Selection of the appropriate combination of tertiary operations in a water treatment plant is important as contaminants that are not removed by primary and secondary processes, such as CECs, are often removed with advanced processes. However, even these energy-intensive methods may not fully decontaminate water from CECs and may result in the generation of harmful byproducts.

While direct potable reuse water plants feed treated water from the tertiary step to the distribution system located before a drinking water treatment plant, indirect potable reuse plants purposely release it to a natural water source such as a surface water reservoir, river, sea, or groundwater aquifer (Fig. 1). Direct potable reuse is a common practice in areas with few source waters and high demands. Indirect potable reuse plant operation is plausible only when there is an adequate natural system downstream. The effluent from the treatment plant is expected to be held in the environmental buffer for a specified retention time where the water can be treated by natural processes such as direct photolysis, adsorption, filtration through natural media, and natural microbiota. Certain CECs can travel through the water subsurface for up to 60 days, therefore, a longer time in the buffer may reduce CEC concentrations in the source water making it cleaner for the subsequent drinking water treatment step. However, communities with limited natural recharge opportunities may be unable to accommodate long lag times between the discharge and reuse steps. The possibility of artificial recharge systems resembling natural buffers has been raised as a method overcoming such limitations.

It is important to note that uncertainties related to removal and potential hazards of unremoved contaminants can account for a considerably larger proportion of the associated risk of maintaining the plant. In terms of cost, indirect potable water treatment can cost more than the direct potable treatment mainly due to the environmental buffer used along with the indirect potable reuse plant. Although, the cost of water treatment after the environmental buffer is less for the indirect potable reuse plants as they receive much cleaner source water making it easier to treat. Furthermore, inclusion of reverse osmosis or other advanced treatment techniques increases treatment plant cost, however, currently, these techniques are the most successful in removing most pharmaceutical contaminants. Therefore, application

Table 1. EPCs, examples, and their effects.

| EPC class       | EPC examples                                      | EPC function                                      | Harmful effects                                                                 |
|-----------------|---------------------------------------------------|---------------------------------------------------|---------------------------------------------------------------------------------|
| Analgesic       | Acetaminophen, phenazopyridine, non-steroidal anti-inflammatory drugs (NSAID) such as diclofenac, ibuprofen, naproxen | Pain relief, NSAID also reduce inflammation       | Ibuprofen can interfere with cardiac benefits of aspirin; analogues can cause negative developmental effects; diclofenac can be bioaccumulated |
| Antibiotics     | Tetracycline, ciprofloxacin, ofloxacin, sulfonamides (ex. sulfadiazine), amoxicillin, cefixime, metronidazole, trimethoprim | Kill or inhibit bacterial growth                   | Antibiotics have been shown to create antibiotic resistant bacteria (tetracycline resistant enterococci, antibiotic resistant Escherichia coli) and can negatively affect plant growth. Sulfonamides are found to be associated with birth defects |
| Anticoagulant   | Warfarin                                           | Disrupt blood clotting factor synthesis or function to avert formation of blood clots | Warfarin, after prolonged exposure, could lead to severe bleeding due to its prolonged inhibition of vitamin K |
| Anticonvulsant  | Carbamazepine                                      | Treat epileptic seizures                          | Could cause cancer and negatively affect reproduction and development |
| Antidiabetic    | Metformin, insulin, pramlintide, acarbose, chlorpropamide | Lower glucose levels in the blood                | Antidiabetics, such as metformin, can act as an endocrine disruptor, and is not easily degradable and is highly mobile in the environment |
| Antihistamine   | Diphenhydramine                                    | Block histamine action to treat allergic reactions | Diphenhydramine has been shown to cause acute and chronic toxicity to a variety of aquatic organisms |
| Antipsychotic   | Loxapine, Olanzapine, Risperidone, Clozapine       | Treat psychosis and other emotional or mental health conditions | Olanzapine, risperidone, chlorpromazine, clozapine are shown to be persistent, bioaccumulative, and toxic to human health and the ecosystem. They are up-taken from hospital effluent contaminated soil and bioaccumulate in plant tissues |
| Antipyretic     | Antipyrine, NSAIDs                                 | Lower fever                                       | Antipyrine is toxic to the mucosa and lungs and can cause organ damage |
| Beta-blocker    | Metoprolol, propranolol                            | Lower blood pressure                              | Can be toxic on organisms in aquatic environments and shows more toxicity to phytoplankton and zoo plankton |
| Fibrate         | Gemfibrozil                                        | Lower blood triglyceride levels                   | Developmental side effects and carcinogenic in rodents; toxic to aquatic organisms |
| X-ray contrast agent | Iopromide, diatrizoic acid                         | Enhance visibility of internal organs or structures for diagnostic X-rays | While x-ray contrast agents are generally non-toxic they persist in the environment and chlorination has been shown to cause mutagenicity and acute toxicity of iopromide |

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of low-cost EPC removal techniques can have a clear effect on reducing water purification costs, and development of such techniques can potentially guarantee the complete removal of EPCs.

In this review, we focus on the advancements in nanotechnologies using adsorption or photocatalysis to decontaminate water from pharmaceutical contaminants. Adsorption and photocatalysis are the two most widely studied water purification methods due to their effectiveness and potential scalability. Due to the popularity of such material in research, literature presenting carbon-based adsorbents and/or photocatalysts for the removal of pharmaceuticals have been published in recent years. In this review, we compile additional recent studies on graphene-based adsorbents and a wide range of photocatalysts without limiting the material presented to TiO$_2$-based photocatalysts. In addition, we present recent advancements on modifications that have been made on adsorbents and photocatalysts to increase their applicability in water treatment. For instance, we present studies incorporating adsorbents on membranes and studies on magnetic photocatalysts and photocatalysts immobilized on optical fibers. Furthermore, we focus on discussing the limitations of the material as well as the limitations of available research in determining whether these materials can be utilized in water treatment facilities to reduce EPCs released in the environment, which has not been previously discussed in other review articles.

**TECHNOLOGICAL ADVANCEMENTS**

Utilization of nanomaterials such as graphene and metal-based nanoparticles in water treatment has shown promise due to their superior adsorptive and photocatalytic properties enabling removal and breakdown of harmful EPCs. Figure 2 shows a pictorial representation of the adsorptive and photocatalytic removal of contaminants.

In this section, we present some of the recent investigations on pharmaceutical removal from water using nanomaterials such as carbon-based nanomaterials and photocatalysts. We focus on understanding these technologies and their applicability in indirect potable water treatment processes. Additionally, we address the benefits and limitations of the nanomaterials and speculate about potential new research strategies.

Advancements in adsorption using nanomaterials

Adsorption processes utilizing carbon-based nanomaterials are considered effective in removing organic and inorganic matter from water. Adsorption is defined as a surface phenomenon where organic and inorganic matter attaches to an adsorbent's surface by adhesion arising from physical-chemical forces mainly caused by van der Waals and electrostatic interactions.

An effective adsorbent must present a number of different properties such as being inert, biocompatible, resistant to mechanical forces, and needs to exhibit a high adsorption capacity to guarantee waste removal. These features are
important as they can determine the utility of the material. Adsorption processes depend on a number of factors including: temperature, pH, concentration of pollutants, contact time, particle size, and the physical and chemical nature of the adsorbate and adsorbent. For example, pH can influence adsorption capacity by altering the surface groups present on the adsorbent and the pollutant charge, and an increase in temperature can improve adsorption capacity in endothermic reactions. In ibuprofen adsorption on activated carbon (AC), adsorption is more favorable at pH 3 than at pH 7. Additionally, as temperature is increased at pH 3, adsorption of ibuprofen has shown to increase. Depending on the adsorbent utilized, increasing contact time with the pollutant can increase the adsorbed amount since the time required for the adsorbent to become saturated varies depending on the surface and solution chemistry. Thus, a material can be a good adsorbent in a certain system and not in other systems.

The number of aromatic rings and the chemical structure of EPCs make the adsorption process suitable for their removal from water. EPCs with more aromatic rings show faster adsorption rates. Generally, in graphene-based nanomaterials, this process is dominated by non-electrostatic interactions such as π–π interactions between the aromatic rings, hydrophobic interactions, H-bonding interactions due to the presence of COOH, OH and NH₂ functional groups, and electrostatic interactions.

Nanotechnology, while unexplored in industrial scale adsorption processes, creates a great opportunity to guarantee effectiveness of water treatment processes for EPC removal. AC is the current industrially used adsorbent. However, there are different adsorbents suitable for EPC removal that can replace AC including materials such as graphene, carbon nanotubes (CNTs), clay minerals, siliceous adsorbents, and polymeric materials. Graphene and graphene-based nanomaterials are being considered above all as good candidates for water treatment applications due to their unique structures and properties. They demonstrate appreciably fast adsorption kinetics due to their large surface area to volume ratio and other physiochemical properties, such as the π–π electron donor acceptor and electrostatic interaction with contaminants. The conjugated π region of graphene is capable of removing organic and inorganic contaminants by attracting aromatic pollutants. Graphene has been employed for several applications and is receiving increasingly more attention in water treatment. Different attempts have been made to modify graphene’s surface to increase its adsorption capacity and reusability (see Table 2).

Reduced graphene oxide and graphene have shown lower adsorption capacities for the majority of the reported EPCs compared to graphene oxide. This can be attributed to the increased hydrophobicity and decreased number of oxygen functional groups on the surface, which would hinder adsorption of EPCs present in water. The modification of graphene oxide with Fe₃O₄, MnO₂, Fe/Cu and the preparation of graphene hydrogels exhibit low surface area, however, show larger adsorption capacities compared to the unmodified graphene. These modifications can alter the hydrophobicity of the composites and introduce different functional groups on its surface that promote more EPC removal. It is worth to note that while these material properties seem to enhance the adsorption capacity, the surface area can also play a role in the adsorption process. Increasing the surface area can effectively increase the number of sites EPCs can adsorb to, thus, increasing the adsorption capacity of the material. Comparing the adsorption capacity of magnetic chitosan grafted GO composite and activated graphene, we can see that activated carbon has a higher adsorption capacity towards ciprofloxacin (194.6 mg/g) than the magnetic chitosan grafted GO composite material (36.17 mg/g). This could be due to the differences in surface area. Activated graphene has a larger surface area (512.65 m²/g) than the magnetic chitosan grafted GO composite (388.3 m²/g), which can allow for increased adsorption of ciprofloxacin. While surface area can play an important role, comparison of material based on the resulting adsorption capacity can be more informative since it can be a better indicator as to the performance of the material. For instance, several materials with large surface area have lower adsorption capacities than materials with smaller surface areas. For example, graphene hydrogel.
Table 2. Examples of adsorbents for the removal of EPCs.

| EPC class | EPC       | Adsorbent material                        | EPC concentration (ppm) | Removal (%) | Surface area (m²/g) | Adsorption capacity (mg/g) | Ref   |
|-----------|-----------|-------------------------------------------|-------------------------|-------------|---------------------|-----------------------------|-------|
| Antibiotic| Amoxicillin| Graphene                                   | 0.2                     | 100         | 49.4                | NA                          | 158   |
|           |           | Magnetic graphene nanoplatelets (M-GNPs)   | 10                      | 40–90       | 543.2               | 14.1                        | 159   |
| Cephalaxin|           | Graphene                                   | 0.25                    | 81          | 570.2               | 10.9                        | 62    |
|           |           | Graphene                                   | 6.7e-5                  | 100         | –                   | NA                          | 160   |
| Ciprofloxacin|         | Graphene hydrogel                          | 50                      | NA          | –231.4              | 235.6                       | 65    |
|           |           | Non-covalent functionalized graphene oxide | 10                      | 96.2        | 237.4               | NA                          | 66    |
|           |           | Fibers of 6% graphene oxide/calcium alginate| 9.8                     | 78.9        | –                   | 39.1                        | 162   |
|           |           | Reduced graphene oxide/magnetite composites (rGO-M) | 5                      | NA          | –                   | 10.9                        | 59    |
|           |           | Magnetic chitosan grafted graphene oxide composite | 200                  | ~95%        | 388.3               | 36.2                        | 63    |
| Norfloxacin|           | Activated graphene                         | 150                     | NA          | 512.6               | 194.6                       | 64    |
|           |           | Reduced graphene oxide/magnetite composites (rGO-M) | 5                      | NA          | –                   | 11.1                        | 59    |
| Ofloxacin |           | Graphene                                   | 0.2                     | 100         | 49.4                | NA                          | 158   |
| Sulfadiazine|          | Graphene                                   | 0.2                     | 100         | 49.4                | NA                          | 158   |
| Sulfamethazine|         | Graphene                                   | 0.2                     | 100         | 49.4                | NA                          | 158   |
| Sulfamethoxazole|     | Graphene                                   | 0.1                     | 34          | 570.2               | 6.2                         | 62    |
|           |           | Graphene                                   | 0.2                     | 100         | 49.4                | –                           | 158   |
|           |           | Graphene                                   | 0.125                   | 98          | –                   | NA                          | 160   |
|           |           | TiO₂-reduced graphene oxide                | 5                       | 92          | –                   | –                           | 114   |
|           |           | Graphene oxide                            | 40                      | 98          | –                   | 240                         | 161   |
| Tetracycline|           | Graphene                                   | 0.2                     | 100         | 49.4                | NA                          | 158   |
|           |           | Graphene oxide                            | 266                     | NA          | –                   | 370                         | 50    |
|           |           | Fe/Cu/graphene                            | 100                     | 100         | 108.6               | 201.9                       | 165   |
|           |           | 40%MnO₂/graphene                          | 200                     | 99.4        | 106                 | 198                         | 164   |
|           |           | Fe₃O₄@graphene                            | 1                       | 96.7        | –                   | 423                         | 165   |
| Oxytetracycline|       | Fe₃O₄@graphene                            | 1                       | 96.7        | –                   | 336                         | 165   |
| Analgesic | Acetaminophen | Graphene                                  | 20                      | 97.4        | 635.2               | 12.7                        | 58    |
|           |           | Graphene                                   | 0.445                   | 99          | –                   | NA                          | 160   |
|           |           | TiO₂@Graphene                              | –                       | 96 (degradation) | 131.0       | –                           | 168   |
|           |           | GO/β-Bi₂O₃/TiO₂/Bi₂Ti₂O₇ heterojuncted nanocomposite | 20 µM     | >99         | –                   | NA                          | 167   |
| Aspirin   |           | Graphene                                   | 20                      | 81          | –                   | 17.0                        | 58    |
| Diclofenac|           | Graphene                                   | 10                      | 97          | 890                 | NA                          | 168   |
|           |           | Graphene oxide                            | 70                      | NA          | –                   | 653.9                       | 169   |
|           |           | Three-dimensional reduced graphene oxide (rGO)-based hydrogels | 100                  | >80         | –                   | 56.2                        | 60    |
|           | Sodium diclofenac drug|                       | rGO                     | 20–200      | –                   | 98                          | 59.7  | 61    |
| Ibuprofen |           | Graphene                                   | 10                      | 95.5        | 890                 | NA                          | 168   |
|           |           | Metal-organic Frameworks                  | 2–35                    | NA          | 990–3030            | 114–185                     | 170   |
|           |           | TiO₂-reduced graphene oxide               | 5                       | 81          | –                   | –                           | 114   |
|           |           | Three-dimensional reduced graphene oxide (rGO)-based hydrogels | 100                  | >70         | –                   | 12.6                        | 60    |
| Naproxen  |           | Metal-organic Frameworks                  | 2–35                    | NA          | 990–3030            | 114–185                     | 170   |
|           |           | Three-dimensional reduced graphene oxide (rGO)-based hydrogels | 100                  | >65         | –                   | 39.5                        | 60    |
| Salicylic acid|          | Functionalized graphene                  | 50                      | 55          | 68.7                | NA                          | 171   |
| Antihistamine|         | Reduced graphene oxide–TiO₂ composites   | 1000                    | ~100        | 148                 | NA                          | 123   |
| Diphenhydramine|       | Iaccase-GO/alginate                       | 40                      | 98          | –                   | –                           | 69    |
| Cetirizine|           | Iaccase-GO/alginate                       | 40                      | 98          | –                   | –                           | 69    |
| Antidiabetic|         | Metformin                                 | 10                      | 80          | 108.7               | 47.1                        | 46    |
As we can see in Table 2, the adsorption process by nanomaterials is a fast and effective method for EPC removal from aquatic environments. Most examples showed more than 50% removal of different EPCs, and several demonstrated removal efficiencies of more than 99%. However, adsorption processes have the disadvantage that the EPC attaches to the adsorbent limiting material reusability and creating a potential new environmental contaminant after disposal. While the interaction between the EPC and the adsorbent is not permanent, an extra step in the removal process must be included to separate the two. Some investigations propose the use of organic solvents or changes in the pH of the media to remove the organic molecule from the adsorbent.46,67

Currently, high cost and reusability are the two main problems associated with graphene oxide and graphene-based nanomaterials. Therefore, the subsequent purification of such materials are exhausting and time-consuming processes. While production of reusable nanomaterial can reduce the overall cost, the strong electrostatic interactions of the material might influence the adsorption/desorption equilibrium and also influence its reusability making this nanomaterial inefficient for reuse.68 For example, methods such as washing of the material such as washing with water and acetate buffer after each removal step need to be performed to remove the CEC. Thus, making large-scale production, high cost, and reusability some of the unresolved problems associated with GO and GO-based nanomaterials, which can hinder their use in environmental pollution management.66,67

However, keeping in mind the rapid growth and development in science and technology, material reusability problems are expected to be solved in the near future, which is an important factor for the potential application of GO and GO-based nanomaterials on a commercial scale. Although only a few studies investigate graphene-based adsorbent reusability for EPCs, advancements in graphene nanomaterial reusability have allowed increased utilization of single batch of material reducing the need for additional material purchases. For instance, GO has demonstrated high removal of metformin even after undergoing five sorption/desorption cycles in which sodium hydroxide and Milli-Q water were used to desorb metformin from the GO. The GO had a 31.60 mg/g absorption capacity after five cycles.46 Furthermore, a laccase-GO/alginate composite was used to remove cetirizine from solution where the material was washed with distilled water and acetate buffer after each removal experiment to recycle the adsorbent, and demonstrated a 23% reduction from the original 98% in cetirizine removal after four cycles.69 Adsorbents can also be modified with catalysts or photocatalysts to increase their removal capacity. Modification of graphene with catalysts, for instance, can make the sorption process easier and faster since CEC degradation will occur.71

Ultimately, as with any material, the lifetime of graphene-based material is finite, as such, its disposal will be required. Used graphene-based material can undergo similar disposal procedures to the currently utilized adsorbents in water treatment plants, which tend to forgo regeneration procedures in the United States. While the biocompatibility of graphene and graphene-based nanomaterials in terms of their antibacterial properties,72–79 antifungal properties,80,81 and cytotoxicity on human cells82–86 has been demonstrated for biomedical and environmental applications, only a few human cell lines have been studied. Hence, additional research is necessary before determining the health and environmental impacts of graphene.

**Table 2 (continued)**

| EPC class   | EPC          | Adsorbent material                                      | EPC concentration (ppm) | Removal (%) | Surface area (m²/g) | Adsorption capacity (mg/g) | Ref |
|-------------|--------------|---------------------------------------------------------|-------------------------|-------------|---------------------|---------------------------|-----|
| Anticonvulsant | Carbamazepine | Graphene                                                | 10                      | 97.0        | 890                 | NA                        | 168 |
|             |              | Graphene-P25 (Gr-P25) nanocomposites                   | 0.168                   | 100         | 45.0--48.1         | –                         | 172 |
|             |              | (GO)/β-Bi2O3/TiO2/Bi2Ti2O7 heterojunctioned nanocomposite | 20 µM                  | >99         | –                   | NA                        | 162 |
|             |              | TiO2-reduced graphene oxide                            | 5                       | 54          | –                   | –                         | 114 |

(surface area of approximately 231.38 m²/g) has an adsorption capacity of 235.6 mg/g of ciprofloxacin, while the magnetic chitosan grafted graphene oxide composite66 (surface area of 388.3 m²/g) has an adsorption capacity of 36.17 m²/g.
| EPC Class | EPC | Material | Reaction Source | EPC Concentration (ppm) | Removal | Reaction rate, $k$ (x10^{−3}/min) | Ref |
|-----------|-----|----------|----------------|------------------------|---------|----------------------------------|-----|
| Analgesic | Acetaminophen | BaTiO$_3$/TiO$_2$ composite | UV-Visible, 200–800 nm, 500 W | 10 | 82.8 | 9.2 | 173 |
| | | WO$_3$/TiO$_2$/SiO$_2$ composite | UV-Visible, 200–800 nm, 500 W | 10 | 88 | 11.7 | 174 |
| | | Graphene/titanium dioxide nanotubes | UV, 14 W | 5 | – | 24.8 | 166 |
| | | ZnO/Seepiolite | UV < 320 nm, 450 W/m$^2$ | 10 | 85 | 3.1 | 175 |
| | | ZnO/Fe$_3$O$_4$/Seepiolite | UV < 320 nm, 450 W/m$^2$ | 55 | 1.3 | – | 175 |
| | | ZnO/SiO$_2$/Seepiolite | UV < 320 nm, 450 W/m$^2$ | 20 | 0.7 | – | 175 |
| | | Carbon doped TiO$_2$ | 440–490 nm, 5 W | 15.1 | 94 | 5.0 | 177 |
| | | TiO$_2$/montmorillonite | UVA with ozonation, 8 W | 5 | 50.1 | – | 176 |
| Analgesin (paracetamol specifically) | Acetaminophen | Magnetic ZnFe-CLDH/RGO composites | Solar light (>300nm), 500 W | 5 | 95 | 7.4 | 177 |
| | | TiO$_2$, TiO$_2$/cellulosic fiber | 200–280 nm, 11 W | 40.1 | – | 10.2 | 178 |
| Diclofenac (NSAID) | | Ag$_2$PO$_4$/TiO$_2$ nanotube arrays | Simulated sunlight, 350 W | – | 100 | – | 121 |
| | | g-C$_3$N$_4$/BiVO$_4$ photoanode | Visible light, >420 nm | 10 | 30.1 | 3.2 | 118 |
| | | C-TiO$_2$ | Visible light, >400 nm, 150 W | 0.05 | 100 | 33.4 | 119 |
| | | PVDF membrane with TiO$_2$ | Low-pressure UV, 254 nm, 40W | 0.2–0.4 | Too fast for analysis | – | 136 |
| | | C doped TiO$_2$ coated on zeolites | Solar, 300–400 nm (65 W/m$^2$), 400–570 nm (1,844 W/m$^2$) | 0.1 | >95 | – | 135 |
| | | TiO$_2$ | Solar light, 19° 19′ 42″ S and 146° 45′ 36″ E, sunny days between July and September | 250 | 100 | 9.5 | 179 |
| Diclofenac sodium (NSAID) | | Co$_3$O$_4$-g-C$_3$N$_4$ | Visible light, >420 nm, 300 W | 10 | 20 | 4.7 | 116 |
| Ibuprofen (NSAID) | | BiOCl nanosheets | UV, 400 W | 10 | – | 280 | 180 |
| | | g-C$_3$N$_4$/TiO$_2$/Fe$_2$O$_3$@SiO$_2$ heterojunction | Visible light, 64 W | 2 | 98 | – | 130 |
| | | Zn-Fe mixed metal oxides | Solar light, >300 nm, 500 W | 250–1000 | 95.7 | 15.8 | 181 |
| | | TiO$_2$–2.7% rGO SOFs | High pressure UV, 160 W | 5 | 81 | 9.0 | 114 |
| | | TiO$_2$ (in reactor with UV-LEDs) | Low pressure UV, 39W | 41 | 41 | 3.3 | 114 |
| | | TiO$_2$ rutile nanorods | Visible, 40 W | 18 | 1.3 | – | 114 |
| | | ZnO/Seepiolite | UV < 320 nm, 450 W/m$^2$ | 10 | 80 | – | 114 |
| | | ZnO/Fe$_3$O$_4$ Seepiolite | UV < 320 nm, 450 W/m$^2$ | 10 | 100 | 6.4 | 175 |
| | | ZnO/SiO$_2$/Seepiolite | UV < 320 nm, 450 W/m$^2$ | 95 | 4.6 | – | 175 |
| Naproxen (NSAID) | | POM-γ-Fe$_2$O$_3$/SrCO$_3$ | Solar light, N = 36° 18′ 41.6", E = 59° 31′ 54.2" | 10 | – | – | 184 |
| | | ZnO | UV, 365 nm, 6 W | 4.5 | – | 11.0 | 185 |
| | | TiO$_2$ | – | 4.0 | – | 6.0 | 185 |
| | | ZnO–TiO$_2$ | – | 0.7 | – | 7.6 | 185 |
| Phenazopyridine | | TiO$_2$ | Solar light, 19° 19′ 42″ S and 146° 45′ 36″ E, sunny days between July and September | 250 | 96 | 9.2 | 179 |
| Analgesic, antipyretic | Antipyrine | TiO$_2$-P25 nanoparticles in photoreactor | UV-C, 254 nm, up to 13 W | 10 | 100 | – | 186 |
| | | Antipyrine | UV < 320 nm, 450 W/m$^2$ | 10 | 70 | 2.2 | 175 |
| | | Antipyrine | UV < 320 nm, 450 W/m$^2$ | 50 | 1.2 | – | 175 |
| | | Antipyrine | UV < 320 nm, 450 W/m$^2$ | 50 | 1.3 | – | 175 |
| Antibiotic | 4-chlorophenol | ZnO2/Fe$_2$O$_3$ | Sunlight, 30 × 10$^3$ ± 100 lx | 20 | 66 | 4.3 | 187 |

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| EPC Class          | EPC          | Material                                      | Reaction Source                      | EPC Concentration (ppm) | Removal | Reaction rate, $k$ \( \times 10^{-3} \text{/min} \) | Ref |
|-------------------|-------------|-----------------------------------------------|--------------------------------------|-------------------------|---------|---------------------------------------------|-----|
| Cefixime          |             | Nano N-TiO2/graphene oxide/titan grid sheets | Visible, 7.45 W/m²                   | 5                      | 29 w/o ozone | 9.9 w/ ozone                               | 131 |
| Cefixime trihydrate |            | Nano α-Fe2O3/ZnO | UV–Vis, <365 nm (4 W), 480 nm (60 W)     | 10.1                    | 99.1     | –                                             | 168 |
| Ciprofloxacin     |             | Mesoporous carbon (GMCS-I-TiO2) nanocomposite | UV, 254 nm, 14 W                    | 15                     | 100      | –                                             | 169 |
| TiO2/montmorillonite |          | UVA with ozonation, 8 W                        | 5                              | 80.6                    | –        | 176                                           |
| Levofoxacin       |             | Bi2WO6 nanocuboids                              | Visible, 400–520 nm, 150 W         | 10                     | 80       | 8.5                                           | 128 |
|                   |             |                                               |                                      | 15                     | 69        | –                                             |     |
|                   |             |                                               |                                      | 20                     | 60        | –                                             |     |
| Metronidazole     |             | SnO2·ZnO/clinoptilite                           | Maximum at 435.8 nm, 35 W           | 2                      | –        | 13.0                                          | 190 |
|                   |             | ZnO/NIO                                        | Maximum at 435.8 nm, 35 W           | 2                      | –        | 16.6                                          | 191 |
|                   |             | TiO2/montmorillonite                            | UVA with ozonation, 8 W             | 25                     | 64.6     | –                                             | 176 |
| Oxytetracycline   |             | Graphene/TiO2/ZSM-5 composites                 | Visible light, 300 W                | 10                     | –        | 40                                            | 132 |
|                   |             | Cobalt promoted TiO2/GO                        | Solar/visible, 300 W                | 10                     | >75      | 27.2                                          |     |
|                   |             | T1⁺⁻ self-doped TiO2 (r-TiO2) nano-catalyst    | Full spectrum sunlight, 35 W        | 100                    | 98.7     | –                                             |     |
| Sulfadiazine      |             | TiO2                                          | UV-C, 28 W                          | 1                      | 91.8     | 2092                                          | 192 |
|                   |             | GAC-TiO2                                       |                                       | 10                     | 93.3      | 21.2                                          |     |
|                   |             | Zeolite coated with TiO2 (TiO2/ZEO)            | UV, 265 nm, 20 W                    | 10                     | 93.3      | 21.2                                          |     |
| Sulfamethoxazole  |             | TiO2–rGO SOFs                                  | High pressure UV, 160 W             | 5                      | –        | 12.6                                          | 79  |
|                   |             | PVDF membrane with 25 ppm TiO2                 | Low-pressure UV, 254 nm, 40 W       | 0.2–0.4                | Too fast for analysis                        |     |
| Sulfathiazole     |             | Lu2Al5O12:Ce Nanoparticles/ZnO nanostuctures   | UV–Vis, 350–800 nm, 1 kW            | 25.5                   | 100      | –                                             |     |
| Tetracycline      |             | TiO2 (P25)                                     | UV, 254 nm, 9 W                     | 10                     | –        | 21.9                                          | 194 |
|                   |             | AgInS2/SnIn5S8 heterojunction                  | Visible light, >420 nm, 300 W       | 10                     | 77.2     | –                                             |     |
|                   |             | FeNi4@SiO2@TiO2                                 | UV, 254 nm, 18 W                    | 10                     | 100      | 25                                            | 129 |
|                   |             | Ag/AgIn5S8                                     | UV, 254 nm, 9 W                     | 10                     | 95.3     | 23                                            |     |
|                   |             | CuInS2/Bi2WO6 heterojunction                   | Visible light, >420 nm, 300 W       | 10                     | –        | 17.6                                          | 117 |
|                   |             | MWNT/TiO2                                       | UV, 240 nm, 12 W                    | 10                     | 100      | 64.2                                          | 115 |
| Trimethoprim      |             | PVDF membrane with TiO2                        | Low-pressure UV, 254 nm, 40 W       | 0.2–0.4                | –        | 28                                            | 136 |
| Penicillin antibiotic |         | Ampicillin                                     | Solar light, 150 W                  | 10                     | 96       | 13                                            | 196 |
|                   |             | WO3/ZnO                                        |                                       | 10                     | 100      | 17.3                                          |     |
| Synthetic antibiotic |           | Norfloxacin                                    | Visible, >420 nm, 300 W             | 5                      | 100      | 26.3                                          | 125 |
|                   |             | AgPO4/BIVO4 electrode                           |                                       | 5                      | 100      | 26.3                                          |     |
| Anticoagulant     |             | Warfarin                                       | Low-pressure UV, 254 nm, 40 W       | 0.2–0.4                | –        | 34                                            | 136 |
| Anticonvulsant    |             | Carbamazepine                                   | Low-pressure UV, 254 nm, 40 W       | 0.2–0.4                | –        | 39                                            |     |
|                   |             | BiOCl microspheres                             | Visible, >420 nm, 350 W             | 2.5                    | 70       | 93.5                                          | 134 |
|                   |             | TiO2–rGO SOFs                                  | High pressure UV, 160 W             | 5                      | –        | 4.3                                           |     |
|                   |             | C–TiO2                                         | Visible light, >400 nm, 150 W       | 0.050                  | 100      | 34.8                                          | 119 |
|                   |             | PVDF membrane with TiO2                       | Low-pressure UV, 254 nm, 40 W       | 0.2–0.4                | –        | 39                                            |     |
|                   |             | C doped TiO2 coated on zeolites                | Solar, 300–400 nm (65 W/m²), 400–570 nm (1,844 W/m²) | 0.1 | >95 | – | 135 |
| Antihistamine     |             | Diphenhydramine                                | UV, 254 nm, 6 W                     | 100                    | 100      | –                                             | 124 |
| Antipsychotic     |             | Loxapine                                       | TiO2, SrTiO3                       | 10                     | 99.8     | –                                             | 197 |
Table 3 (continued)

| Material | EPC Class | EPC | Reaction Source | Reaction rate, k (x10^7 min^-1) | Reaction rate, k | Ref |
|----------|-----------|-----|-----------------|-----------------------------|-----------------|-----|
| Beta-blocker Metoprolol | PVDF membrane with TiO2 | Low-pressure UV, 254 nm, 40 W | 0.2 | Too fast for analysis | N/A | 136 |
| X-ray contrast agent Iopromide | PVDF membrane with TiO2 | Low-pressure UV, 254 nm, 40 W | 0.2 | Too fast for analysis | N/A | 137 |
| Diatrizoic acid | C doped TiO2 coated on zeolites | Solar, 300-400 nm (65 W/m²), 400-570 nm | 0.1 | 35% mineralization efficiency | N/A | 135 |
| Pharmaceutical wastewater | Octahedral CdS/SnIn4S8 nanoheterojunction | Visible, >420 nm, 300 W | 35% COD removal | COD removal | N/A | 198 |
| Pharmaceutical wastewater | Fe-TiO2 | Solar light, 30.3398° N, 76.3869° E, October-November from 10 am to 4 pm, 788 W/m² | 35% COD removal | COD removal | N/A | 199 |
| Pharmaceutical wastewater | CuInS2/Bi2WO6 heterojunction | Visible light, >420 nm, 300 W | 53.7 COD removal | COD removal | N/A | 117 |
| Pharmaceutical wastewater | MWCNT/TiO2 | UV, 240 nm, 12 W | 84.9 COD removal | COD removal | N/A | 115 |

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Recent advancements in photocatalysts have effectively enabled the degradation of numerous EPCs as shown in Table 3. However, photocatalysts present several limitations that need to be overcome to increase their effectiveness. Inherently, they require energy to overcome the bandgap energy required for electron excitation. However, they may require additional energy...
due to insubstantial light penetration and absorption, which effectively increase cost requirements due to the increased power needed for UV lamps.\textsuperscript{109,110} Furthermore, recombination rate, charge carrier transfer rate, and charge carrier travel time can further limit the photocatalytic efficiency of the material.\textsuperscript{111} To improve efficiency, material alterations, such as structural changes or doping can be performed.\textsuperscript{109} These methods can make the bandgap smaller and may also decrease recombination rates. In addition to bandgap engineering, use of plasmonic material can further lower energy requirements.\textsuperscript{109,110}

Another limitation of photocatalytic material is their potential impact to the environment. The possible transformation products are of great concern especially if released in the environment. In some cases, as in the case of diclofenac degradation, the degradation can result in harmful constituents such as phenol derivatives.\textsuperscript{28} Pharmaceuticals commonly have aromatic rings which, if not degraded, can form phenolic compounds that are known for their toxicity.\textsuperscript{29} Additionally, they could form acids (as in the case of paracetamol degradation)\textsuperscript{26}) which could alter environmental conditions causing harm to local organisms. Another concern with photocatalyst release in the environment arises due to their instability in water. The ions released during their dissolution in water can have harmful effects to the environment.\textsuperscript{112} Thus, the photocatalysts’ degradation mechanisms as they pertain to EPCs and photocatalyst stability in water need to be understood prior to their use in water treatment facilities. Additionally, generating composites and using stabilizing agents, whether natural or chemical in nature, can improve photocatalyst stability and efficiency.\textsuperscript{113} Furthermore, by improving their stability their harmful effects in the environment can be reduced.

Despite their limitations, photocatalysts offer great possibilities in commercial applications. For example, titanium dioxide, a UV activated photocatalyst, has been introduced in commercially available water purification products and could be potentially applied to the AOPs to help degrade a variety of contaminants. With advancements in photocatalytic materials, photocatalysts are becoming increasingly more cost effective and their large-scale utilization. While they are highly suitable for use in indirect potable water treatment, without a full examination of their properties and environmental impact, measures should be taken to ensure they are not released in the environment.

**Advanced applications of photocatalysts**

In an effort to increase usability of photocatalysts, a variety of materials have been developed, namely magnetic nanocomposites and optical fiber coated materials. Magnetic composites can make the removal of the photocatalysts from water easier and more effective reusing the chance that they may unintentionally end up in the environment. Furthermore, their degradative properties have been shown to increase with the introduction of magnetic materials in the composite.\textsuperscript{137,138} Recently, magnetic FeNi\textsubscript{5}/SiO\textsubscript{2}/CuS has been synthesized for tetracycline removal,\textsuperscript{139} while magnetic fluorinated mesoporous graphitic carbon nitride\textsuperscript{140} and a magnetic TiO\textsubscript{2}-GO-Fe\textsubscript{3}O\textsubscript{4}\textsuperscript{137} have been synthesized for amoxicillin removal.

In addition to magnetic material, photocatalytic materials loaded on optical fibers have been developed. Immobilization of photocatalysts on optical fibers can allow light to better reach the nanoparticles as less light is absorbed by other particles present in the solution. Furthermore, the nanoparticles do not require specialized methods for recovery. TiO\textsubscript{2} has been successfully coated on optical fibers, which has resulted in the development of a compact, easy-to-use reactor utilizing light-emitting diodes for photocatalytic water treatment.\textsuperscript{141} Furthermore, TiO\textsubscript{2}-rGO composites have also been used to coat optical fibers and have been shown to be capable of degrading pharmaceutical compounds such as sulfamethoxazole and ibuprofen.\textsuperscript{142}

Use of magnetic materials in photocatalyst composites and coating photocatalysts on optical fibers can be promising in potable water treatment. However, without modification of the existing potable water treatment plant equipment or processes, their use may not be as feasible. Inclusion of photocatalysts in membrane technologies, similar to the introduction of graphene-based material in membranes, can greatly improve the functionality of the membranes and can be easily introduced in water treatment plants. While photocatalysts can reduce fouling and degrade contaminants, they can also degrade membrane materials reducing the lifetime of the membranes. For instance, use of TiO\textsubscript{2} in polyacrylonitrile membranes has been determined to be unsuitable for long-term use.\textsuperscript{143} Thus, additional research is needed to explore potential use of photocatalysts in membrane technologies.

**CONCLUSIONS AND PERSPECTIVES**

This review presents recent studies related to pharmaceutical removal with nanoparticles involving two different processes, adsorption and photocatalysis. We presented studies where nanomaterial demonstrated superior adsorptive or photocatalytic properties in the removal of EPCs. We also included photocatalysts modified with graphene in order to combine both properties, adsorption and degradation of organic molecules. These studies

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quantify EPC removal in simple solutions or in wastewater. However, most of these studies do not examine material use in actual water treatment systems. To fill the gap between fundamental research and practical applications there needs to be a focus on the potential practical applications of the different EPC removal techniques in indirect potable reuse water systems. While EPC removal efficiencies are important, it is important to investigate at what concentration these EPCs pose a threat to humans, animals, and the ecosystem regardless of the fact that many recent research articles demonstrate high EPC removal efficiencies. Little is known about nanoparticle stability in solution, and the effects of ingestion of the particles or their solutes is largely unknown. Furthermore, the production of toxic byproducts from EPC degradation should be of concern since disinfection byproducts account for a different class of regulated contamin-

ants. Intermediate degradation products can exhibit increased solubility as compared to that of the original contaminant, and higher toxicity values. Thus, it is important to thoroughly evaluate nanoparticle toxicity (toxic amount and maximum exposure time) and the risks associated with the employment of nanoparticles in water treatment.

Currently, AOPs are the best strategy to remove EPCs from water. However, associated costs are a major concern in communities with limited financial support. Scaling techniques to match industrial levels will be required. As seen in recent studies, inclusion of different nanomaterials in membranes or on optical fibers and use of magnetic photocatalysts result in significant EPC removal. Use of such technologies can help meet safe drinking water demands while reducing EPCs entering the environment. However, when used in indirect potable water cycles, these techniques need to break down a great variety of EPCs.

To guarantee water safety, the indirect potable reuse process requires understanding environmental and health standards. As such, the employment of recent technologies needs thorough risk assessments and health and safety evaluations performed to mitigate potential risks of the technology itself. While no legislation pertaining to EPC maximum allowable concentrations in water has been established, legislations regulating drinking water processes tend to be very strict to ensure human health and environmental safety. For instance, in an ongoing effort to maintain the safety of drinking water and lessen the effect of EPCs, the European Union has added additional requirements for pharmaceuticals whereby more extensive environmental risk assessments need to be conducted for each pharmaceutical’s use to be allowed.144 Furthermore, pharmaceutical contaminants in the environment are to be potentially monitored more extensively in order to be able to better evaluate their risk and environmental effects. Still, maximum EPC removal may be necessary, and the employment of nanotechnology in water treatment can be critical when it comes to human health and EPC persistence in environmental systems.

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COMPETING INTERESTS
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