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

Sofia K. Fanourakis[1,2], Janire Peña-Bahamonde[1], Pasan C. Bandara[1] and Debora F. Rodrigues[1,2*]

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.[9,16] 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]

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[1]Department of Civil and Environmental Engineering, University of Houston, Houston, TX 77204-4003, USA. [2]Department of Materials Science and Engineering, University of Houston, Houston, TX 77204-4003, USA. *email: dfrigirodrigues@uh.edu

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 could interfere with cardiac benefits of aspirin;[145] analgesics can cause negative developmental effects;[144] diclofenac can be bioaccumulated[146]
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.[147] Sulfonamides are found to be associated with birth defects[148]
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[149]
Anticonvulsant	Carbamazepine	Treat epileptic seizures	Could cause cancer[144,150] and negatively affect reproduction and development[144]
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[151]
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[152]
Antipsychotic	Loxapine Olanzapine Risperidone Chlorpromazine, 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.[14,153] They are up-taken from hospital effluent contaminated soil and bioaccumulate in plant tissues[15]
Antipyretic	Antipyrine, NSAIDs	Lower fever	Antipyrine is toxic to the mucosa and lungs and can cause organ damage[154]
Beta-blocker	Metoprolol, propranolol	Lower blood pressure	Can be toxic on organisms in aquatic environments and shows more toxicity to phytoplankton and zooplankton[155]
Fibrate	Gemfibrozil	Lower blood triglyceride levels	Developmental side effects and carcinogenic in rodents,[144] toxic to aquatic organisms[155]
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,[156] they persist in the environment and chlorination has been shown to cause mutagenicity and acute toxicity of iopromide[157]

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.[23,24,26] 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.[26,27] However, even these energy-intensive methods may not fully decontaminate water from CECs and may result in the generation of harmful byproducts.[28,29]

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[19,23,24,30] (Fig. 1). Direct potable water 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.[30–32] 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.[33,34] However, communities with limited natural recharge opportunities may be unable to accommodate long lag times between the discharge and reuse steps.[31] The possibility of artificial recharge systems resembling natural buffers has been raised as a method overcoming such limitations.[31,35]

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.[36] 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.[31,37,38] Therefore, application

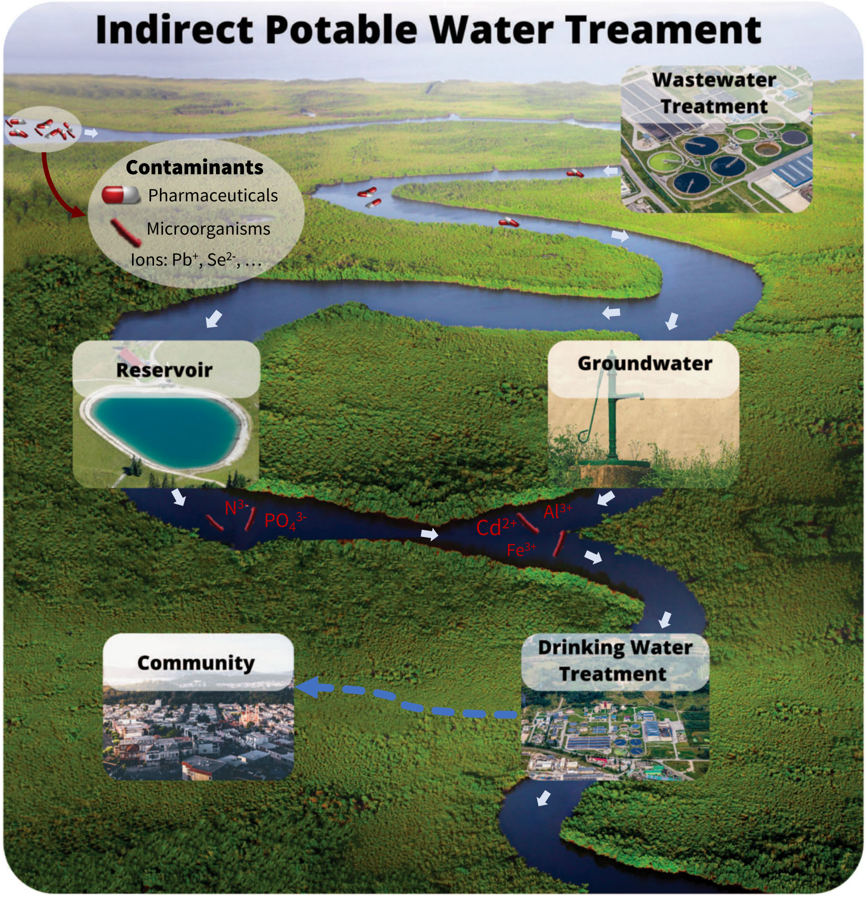

Fig. 1 **Representation of indirect potable water treatment for CECs.** Contaminants such as pharmaceuticals, microorganisms, and harmful ions can be present in water. To prepare contaminated water for potable use, it first goes through a wastewater treatment plant and is subsequently released in the environment (in lakes, reservoirs, and groundwater) where decontamination of water can occur through natural processes. To ensure all microorganisms and harmful contaminants do not reach the end user, the water undergoes a drinking water treatment before being released to the community.

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.[39–42] 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

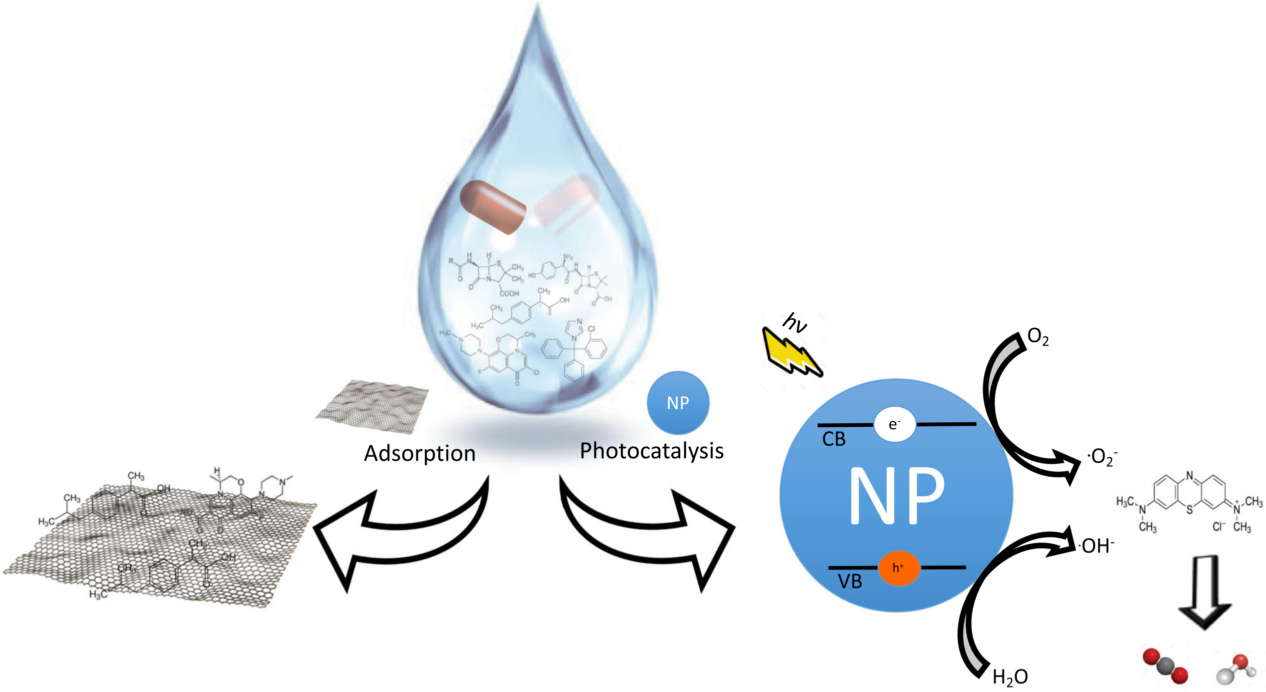

Fig. 2 Representation of adsorption and photocatalytic process.

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,[43] 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.[43] Additionally, as temperature is increased at pH 3, adsorption of ibuprofen has shown to increase.[43] 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.[44]

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.[45] Generally, in graphene-based nanomaterials, this process is dominated by non-electrostatic interactions such as π–π interactions between the aromatic rings,[46] hydrophobic interactions,[47,48] H-bonding interactions due to the presence of COOH, OH and NH_2 functional groups,[49] and electrostatic interactions.[50,51]

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.[52–55] 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.[56,57] The conjugated π region of graphene is capable of removing organic and inorganic contaminants by attracting aromatic pollutants.[58] 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[57–59] and graphene[52,60] have shown lower adsorption capacities for the majority of the reported EPCs compared to graphene oxide.[61,62] 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 Fe_3O_4,[53] MnO_2,[54] Fe/Cu[55] and the preparation of graphene hydrogels[56] 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[63] and activated graphene,[64] 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 m^2/g) than the magnetic chitosan grafted GO composite (388.3 m^2/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[65]

Table 2. Examples of adsorbents for the removal of EPCs.

EPC class	EPC	Adsorbent material	EPC concentration (ppm)	Removal (%)	Surface area (m^2/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
	Cephalexin	Graphene	0.25	81	570.2	10.9	62
		Graphene	6.7e-5	100	–	NA	160
		Graphene	0.2	100	49.4	NA	158
	Ciprofloxacin	Graphene oxide (GO)	20	74	–	379	161
		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
		Activated graphene	150	NA	512.6	194.6	64
	Norfloxacin	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
		TiO_2-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	163
		40%MnO_2/graphene	200	99.4	106	198	164
		Fe_3O_4@graphene	1	96.7	–	423	165
	Oxytetracycline	Fe_3O_4@graphene	1	96.7	–	336	165
Analgesic	Acetaminophen	Graphene	20	97.4	635.2	12.7	58
		Graphene	0.445	99	–	NA	160
		TiO_2@Graphene	–	96 (degradation)	131.0	–	166
		GO/β-Bi_2O_3/TiO_2/$Bi_2Ti_2O_7$ 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
		TiO_2-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	Diphenhydramine	Reduced graphene oxide–TiO_2 composites	1000	~100	148	NA	123
	Cetirizine	laccase-GO/alginate	40	98	–	–	69
Antidiabetic	Metformin	Graphene oxide	10	80	108.7	47.1	46

Table 2 (continued)

EPC class	EPC	Adsorbent material	EPC concentration (ppm)	Removal (%)	Surface area (m^2/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-Bi_2O_3/TiO_2/$Bi_2Ti_2O_7$ heterojuncted nanocomposite	20 µM	>99	–	NA	167
		TiO_2-reduced graphene oxide	5	54	–	–	114

(surface area of approximately 231.38 m^2/g) has an adsorption capacity of 235.6 mg/g of ciprofloxacin, while the magnetic chitosan grafted graphene oxide composite[66] (surface area of 388.3 m^2/g) has an adsorption capacity of 36.17 m^2/g.

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) GO and GO-based nanomaterial since the preparation and subsequent purification of such material 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, long washing process periods[69] and variation in the pH[46,70] 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.

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 EPC, advancements in graphene nanomaterial reusability have allowed increased utilization of a 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 cells[82–86] 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.

Advanced application of adsorbents

As previously mentioned, there are several advanced processes for water treatment applications. Membrane processes are one of such advanced processes, which have gained significant popularity in EPC removal due to their effectiveness and scalability. Membranes can be used as part of microfiltration, ultrafiltration, nanofiltration, or reverse osmosis systems removing pollutants from water by acting as a physical barrier against contaminants. While nanofiltration and reverse osmosis membranes are highly effective, they require more energy than microfiltration and ultrafiltration membranes. As such, different membrane technologies are continuously being investigated, such as ceramic membranes,[87,88] polymer membranes,[89,90] metal-organic frameworks,[67] or other advanced membranes.[91] While a vast variety of membranes exist, polyamide-based membranes are one of the most commonly used membranes for EPC removal.[92–97] Their properties, such as their porosity, fouling, stability, and hydrophilicity, can be altered by changing the polymerization conditions via the use of different monomers.[98] Furthermore, these properties can be altered via the use of membrane coatings such as AC and graphene-based material. For example, graphene and GO have been incorporated into different polymer membranes to alter their properties and make them more effective for water treatment. In particular, poly(*N*-vinylcarbazole) (PVK), polyamide, and polysulfone membranes modified with GO have shown antimicrobial inactivation and improvement of water flux across the membrane.[72,99–103]

The modification of ceramic membranes with graphene was able to remove different pharmaceutical compounds from 32 to 99%.[87] However, when the coating was with GO, the membrane was only able to remove approximately 50% of the EPC.[88] Furthermore, polymer membranes such as polyamide membranes[89] were able to remove 50 to 95% of the pharmaceutical compound studied.[97] The modification of polysulfone with graphene oxide showed efficiencies in removal higher than 90%. The inclusion of GO and AC in polymer ultrafiltration membranes has also shown to improve the retention of pharmaceutical compounds. The oxygen rich structure of GO has been shown to increase hydrophilicity, decrease pore size, as well as increase electrostatic repulsion, thereby, improving its removal mechanism of contaminants for water treatment.[88] In particular, GO coated membranes were shown to retain approximately 20% more of the pharmaceuticals (ibuprofen and sulfamethoxazole) than the uncoated ultrafiltration membrane.[88] Furthermore, 0.22 µm membranes coated with GO and AC have shown 98.9% removal of

Table 3. Examples of photocatalysts for the degradation of EPCs.

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/Sepiolite ZnO/Fe_3O_4-Sepiolite ZnO/SiO_2-Sepiolite	UV < 320 nm, 450 W/m^2	10	85 55 20	3.1 1.3 0.7	175
		Carbon doped TiO_2	440–490 nm, 5 W	15.1	94	5.0	127
		TiO_2/montmorillonite	UVA with ozonation, 8 W	5	50.1	–	176
	Acetaminophen (paracetamol specifically)	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_3PO_4/TiO_2 nanotube arrays	Simulated sunlight, 350 W	–	100	–	121
		g-C_3N_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, 40 W	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_3O_4-g-C_3N_4	Visible light, >420 nm, 300 W	10	20	4.7	116
	Ibuprofen (NSAID)	BiOCl nanosheets	UV, ~400 W	10	–	280	180
		g-$C_3N_4/TiO_2/Fe_3O_4$@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 Low pressure UV, 39W Visible, 40 W	5	81 41 18	9.0 3.3 1.3	114
		TiO_2 (in reactor with UV-LEDs)	UV < 382 nm, 40 W	213	100	24	182
		TiO_2 rutile nanorods	UV–Visible, 60 W	10	80	–	183
		ZnO/Sep ZnO/Fe_3O_4-Sep ZnO/SiO_2-Sep	UV < 320 nm, 450 W/m^2	10	100 95 80	6.4 4.6 2.8	175
		POM-γ-Fe_2O_3/$SrCO_3$	Solar light, N = 36° 18′ 41.6″, E = 59° 31′ 54.2″	10	–	–	184
	Naproxen (NSAID)	ZnO TiO_2 2ZnO–TiO_2	UV, 365 nm, 6 W	4.5	–	11.0 6.0 7.6	185
		TiO2	Solar light, 19° 19′ 42″ S and 146° 45′ 36″ E, sunny days between July and September	250	96	9.2	179
	Phenazopyridine	TiO_2-P25 nanoparticles in photoreactor	UV-C, 254 nm, up to 13 W	10	100	–	186
Analgesic, antipyretic	Antipyrine	ZnO/Sep ZnO/Fe_3O_4-Sep ZnO/SiO_2-Sep	UV < 320 nm, 450 W/m^2	10	70 50 50	2.2 1.2 1.3	175
Antibiotic	4-chlorophenol	ZrO2/Fe_3O_4 ZrO2/Fe_3O_4/Chitosan	Sunlight, 30 × 10^3 ± 100 lx	20	66 88.6	4.3 8.7	187

Table 3 (continued)

EPC Class	EPC	Material	Reaction Source	EPC Concentration (ppm)	Removal	Reaction rate, *k* ($x10^{-3}$/min)	Ref
	Cefixime	Nano N-TiO_2/graphene oxide/titan grid sheets	Visible, 7.45 W/m2	5	29 w/o ozone	9.9 w/ ozone	131
	Cefixime trihydrate	Nano α-Fe_2O_3/ZnO	UV–Vis, <365 nm (4 W), 480 nm (60 W)	10.1	99.1	–	188
	Ciprofloxacin	Mesoporous carbon (GMC)-TiO_2 nanocomposite	UV, 254 nm, 14 W	15	100	–	189
		TiO_2/montmorillonite	UVA with ozonation, 8 W	5	80.6	–	176
	Levofloxacin	Bi_2WO_6 nanocuboids	Visible, 400–520 nm, 150 W	10 15 20	80 69 60	8.5 – –	128
	Metronidazole	SnO_2-ZnO/clinoptilolite	Maximum at 435.8 nm, 35 W	2	–	13.0	190
		ZnO/NiO	Maximum at 435.8 nm, 35 W	2	–	16.6	191
		TiO_2/montmorillonite	UVA with ozonation, 8 W	25	64.6	–	176
	Oxytetracycline	Graphene/TiO_2/ZSM-5 composites	Visible light, 300 W	10	–	40	132
		Cobalt promoted TiO_2/GO	Solar/visible, 300W	10	>75	27.2	122
	Penicillin G (PENG)	Ti^{3+} self-doped TiO_2 (r-TiO_2) nano-catalyst	Full spectrum sunlight, 35 W	100	98.7	–	120
	Sulfadiazine	TiO_2 GAC-TiO_2	UV-C, 28 W	1	91.8 100	2092	192
		Zeolite coated with TiO_2 (TiO_2/ZEO)	UV, 265 nm, 20 W	10	93.3	21.2	193
	Sulfamethoxazole	TiO_2-rGO SOFs	High pressure UV, 160 W	5	–	12.6	79
		PVDF membrane with 25 ppm TiO_2	Low-pressure UV, 254 nm, 40 W	0.2–0.4	Too fast for analysis		46
	Sulfathiazole	$Lu_3Al_5O_{12}$:Ce Nanoparticles/ZnO nanostructures	UV–Vis, 350–800 nm, 1 kW	25.5	100	–	126
	Tetracycline	TiO_2 (P25)	UV, 254 nm, 9 W	10	–	21.9	194
		$AgInS_2$/$SnIn_4S_8$ heterojunction	Visible light, >420 nm, 300 W	10	77.2	–	129
		$FeNi_3$@SiO_2@TiO_2	UV, 254 nm, 18 W	10	100	25	195
		Ag/$AgIn_5S_8$	UV, 254 nm, 9 W	10	95.3	23	194
		$CuInS_2$/Bi_2WO_6 heterojunction	Visible light, >420 nm, 300 W	10	–	17.6	117
		MWCNT/TiO_2	UV, 240 nm, 12 W	10	100	64.2	115
	Trimethoprim	PVDF membrane with TiO_2	Low-pressure UV, 254 nm, 40 W	0.2–0.4	–	28	136
Penicillin antibiotic	Ampicillin	WO_3/ZrO_2 Ru/WO_3/ZrO_2	Solar light, 150 W	10	96 100	13 17.3	196
Synthetic antibiotic	Norfloxacin	Ag_3PO_4/$BiVO_4$ electrode	Visible, >420 nm, 300 W	5	100	26.3	125
Anticoagulant	Warfarin	PVDF membrane with TiO_2	Low-pressure UV, 254 nm, 40 W	0.2–0.4	–	34	136
Anticonvulsant	Carbamazepine	BiOCl microspheres	Visible, >420 nm, 350 W	2.5	70	93.5	134
		TiO_2-rGO SOFs	High pressure UV, 160 W	5	–	4.3	114
		C-TiO_2	Visible light, >400 nm, 150 W	0.050	100	34.8	119
		PVDF membrane with TiO_2	Low-pressure UV, 254 nm, 40 W	0.2–0.4	–	39	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
Antihistamine	Diphenhydramine	ZnO/Fe_2O_3/Zeolite TiO_2/Fe_2O_3/Zeolite	UV, 254 nm, 6 W	100	100 95	–	124
Antipsychotic	Loxapine	TiO_2, $SrTiO_3$	Solar spectrum, 280–800 nm, 750 W m2	10	99.8	–	197

Table 3 (continued)

EPC Class	EPC	Material	Reaction Source	EPC Concentration (ppm)	Removal	Reaction rate, k ($\times10^{-3}$/min)	Ref
Beta-blocker	Metoprolol	PVDF membrane with TiO_2	Low-pressure UV, 254 nm, 40 W	0.2–0.4	–	48	136
Fibrate	Gemfibrozil	PVDF membrane with TiO_2	Low-pressure UV, 254 nm, 40 W	0.2–0.4	–	43	136
X-ray contrast agent	Iopromide	PVDF membrane with TiO_2	Low-pressure UV, 254 nm, 40 W	0.2–0.4	Too fast for analysis		136
	Diatrizoic acid	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
N/A	Pharmaceutical wastewater	Octahedral $CdS/SnIn_4S_8$ nano-heterojunction	Visible, >420 nm, 300 W	35% mineralization efficiency			198
	Pharmaceutical wastewater (antibiotics, anti-inflammatory)	Fe-TiO_2	Solar light, 30.3398° N, 76.3869° E, October-November from 10 am to 4 pm, 788 W/m2 average intensity	83 COD removal			199
	Pharmaceutical wastewater	$CuInS_2/Bi_2WO_6$ heterojunction	Visible light, >420 nm, 300 W	53.7 COD removal			117
	Pharmaceutical wastewater	MWCNT/TiO_2	UV, 240 nm, 12 W	84.9 COD removal			115

tetracycline hydrochloride via vacuum filtration.[104] Since very little information about pharmaceutical removal is out there, assumptions about the behavior towards pharmaceutical removal are complicated, however, the inclusion of graphene and graphene oxide have been a probe to exhibit good antimicrobial and durability properties.[72,99,105]

Although incorporation of AC and graphene-based nanomaterial onto membranes has shown increased EPC removal, research exploring such membranes is vastly underexplored. Immobilization of adsorbents on membrane technologies could enable effective EPC removal. Furthermore, the lifetime and potential reusability of the material could be improved. In particular, evaluation of sorbent material reusability is necessary due to the continuously increasing demand for sustainable wastewater treatment systems. Therefore, coated membrane technologies should be further studied, and desorption and recyclability tests should also be taken into consideration for potential reusability.

Photocatalysis

Photocatalysts—semiconducting materials, typically metal oxides, such as titanium oxide and zinc oxide—rely on their ability to absorb light and generate reactive oxygen species (ROS), which are responsible for the degradation of pollutants.[106,107] Composites consisting of metal doped semiconductors, as well as adsorbent materials combined with semiconductor materials can be used for photocatalytic processes. Table 3 presents recent photocatalysts shown to degrade EPCs, some of which have been modified with graphene-based materials to increase the adsorptive and degradative properties of the composites.

As Fig. 2 depicts, once light hits the surface of the photocatalyst, if the light is equivalent to or greater than the material's bandgap, electrons in the material's valence band can be excited and can then jump to the conduction band creating an electron–hole pair. The generated electron–hole pair is responsible for the subsequent redox reactions that ultimately degrade pollutants. The method by which they degrade EPCs can be complex. Briefly, the electron is responsible for the reduction of dissolved oxygen to form the superoxide anion ($\bullet O_2^-$), and the hole is responsible for the oxidation of water forming hydrogen gas and the hydroxyl radical ($\bullet$OH). The superoxide anion and hydroxyl radical are oxidative agents, which are capable of degrading a variety of different compounds. Photodegradation can follow complex pathways depending on the contaminant structure, contaminant concentration, water chemistry, experimental conditions and nanomaterial loading. For example, sulfa drug (e.g. sulfachlopyridaxine, sulfapyridine, sulfisoxazole) degradation has been found to be dominated by hydroxyl radicals and holes created during photocatalysis.[108] Holes are thought to initiate the reaction by breaking the sulfur-nitrogen bond of the drug followed by hydroxyl radical incorporation in the sulfa drug structure, which ultimately dominates the breakdown of the drug.[108] In paracetamol photocatalytic degradation, the hydroxyl radical is also the predominant reactant causing the hydroxylation and breakdown of the aromatic rings.[29,45] The compounds formed due to the hydroxylation of paracetamol (ex. hydroquinone) are further oxidized producing unstable structures, which break down in aqueous solutions.[29] Furthermore, it has been found that when the concentration of the superoxide anion is greater than the hydroxyl radical, the superoxide anion is also capable of degrading paracetamol by acting as a Lewis acid.[29]

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.[109,110] Furthermore, recombination rate, charge carrier transfer rate, and charge carrier travel time can further limit the photocatalytic efficiency of the material.[111] To improve efficiency, material alterations, such as structural changes or doping can be performed.[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.[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.[28] Pharmaceuticals commonly have aromatic rings which, if not degraded, can form phenolic compounds that are known for their toxicity.[28] Additionally, they could form acids (as in the case of paracetamol degradation[29]) 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.[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.[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 use more feasible. For example, a number of the reported photocatalysts are capable of utilizing low power UV or visible light to degrade EPCs. Direct comparison of many of these photocatalysts is limited due to the complexity of the reactions, such as structural and chemical properties of the photocatalyst, type and amount of the EPC, light source parameters, stirring rate, among others, which can affect the results. For instance, when TiO_2-rGO loaded on optical fibers was used for degradation of different pharmaceuticals (ibuprofen, sulfamethoxazole, and carbamazepine) under the same concentrations (5 ppm) and same conditions (high pressure UV light of 140 W), the results were vastly different and with different reaction rates (8.98, 12.6, and 4.3×10^{-3}/min, respectively).[114] Furthermore, use of different light sources also yielded different results in the degradation of ibuprofen (160 W high pressure UV yielded a reaction rate of 8.89×10^{-3}/min, 39 W low-pressure UV yielded a reaction rate of 3.32×10^{-3}/min, and 40 W visible light yielded a reaction rate of 1.33×10^{-3}/min). With this in mind, we can safely say that the ability of a multiwall CNT with titanium dioxide photocatalyst to fully remove 10 ppm of tetracycline from water at a high reaction rate (64.2×10^{-3}/min) utilizing a 12 W UV lamp is notable.[115] Other materials tested on 10 ppm tetracycline either required more energy to fully degrade the EPC, or did not perform as well.

While photocatalysis effectiveness is increased when UV light is utilized, numerous materials have been shown to be capable of visible light photodegradation of pharmaceuticals.[109,114,116–134] Although power utilization of many visible light lamps is equivalent to that of low-pressure UV lamps, the lifetime of UV lamps is significantly lower. Furthermore, with the increased availability of LED lighting options, the power of using visible light photoreactors can be greatly reduced.

Regardless of the type of lighting used, inclusion of photocatalysts in water decontamination can decrease energy requirements. Conventional techniques for removal of organic chemicals such as EPCs may require the use of AOPs, which not only are energy-intensive processes but may be unable to fully remove EPCs. Use of photocatalysts, on the other hand, has been shown to remove non-biodegradable EPCs such as carbamazepine, iopromide, and norfloxacin.[114,119,125,134–136] However, as with any new technology additional research needs to be conducted examining their safety to humans and the environment before 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 reducing 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.[137,138] Recently, magnetic $FeNi_3/SiO_2/CuS$ has been synthesized for tetracycline removal,[139] while magnetic fluorinated mesoporous graphitic carbon nitride[140] and a magnetic TiO_2-GO-Fe_3O_4[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_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.[141] Furthermore, TiO_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.[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_2 in polyacrylonitrile membranes has been determined to be unsuitable for long-term use.[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 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 contaminants. 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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All authors contributed equally to the manuscript and have read and approved the final manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

Correspondence and requests for materials should be addressed to D.F.R.

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