Research progress and application exploration of techniques to remove emerging contaminants from water environment

Xiaohu Lin[1,2,3], Haifeng Fang[1,3], Shiyi Li[1,3], Shengjie Fu[1,3], Baohua Zhang[1], Wenming Zhou[1,3*], Jingcheng Xu[2*], Juwen Huang[2]

[1] PowerChina Huadong Engineering Corporation Limited, Hangzhou 311122, China;
[2] College of Environment Science and Engineering, Tongji University, Shanghai 200092, China
[3] Huadong Eco-environmental Engineering Research Institute of Zhejiang Province, Hangzhou 311122, China;

Abstract: Emerging contaminants in water have attracted more and more attention from scholars and the public. Various technologies have been gradually studied and applied to remove emerging contaminants in water, including adsorption technology based on carbon materials, membrane separation technology, advanced oxidation technology and constructed wetland. In this paper, the research progress of these technologies is reviewed, especially for photocatalysis, a promising technology, which is analyzed in detail. Immobilization is an important means for photocatalytic technology to be applied in engineering. In this paper, four existing immobilization methods of photocatalytic materials are analyzed, and the existing research is prospected. More in-depth research is urgently needed, and exploratory research aimed at application is encouraged. This study can provide some ideas and reference for the treatment of emerging contaminants in water.

1. Introduction

With the explosive growth of chemicals caused by industrial production and the rapid development of water environment analysis and detection technology, more and more contaminants have been frequently detected in water environment, from typical persistent organic pollutants (POPs) such as early organochlorine pesticides, polycyclic aromatic hydrocarbons and polychlorinated biphenyls, to emerging contaminants of concern in recent years, which include emerging POPs, pharmaceuticals and personal care products (PPCPs), endocrine disruptors (EDCs), disinfection by-products (DBPs), engineering nanomaterials, microplastics, etc. In recent years, these unconventional pollutants have been detected in sewage systems, surface water and even drinking water, and exist in the water environment at a low concentration, which is usually called micro-pollutants or emerging contaminants.

Some traditional water treatment technologies and innovative technologies have been proved to remove micro-pollutants efficiently in the water environment, including adsorption technology, membrane separation technology, advanced oxidation method, constructed wetland and some combined processes. In this paper, the research and application of these technologies in the removal of micro-pollutants are reviewed, and the research and application of photocatalytic technology are focused and discussed.

2. Current technologies for removing emerging contaminants in water

2.1. Adsorption

Adsorption is an effective technology for removing trace pollutants, which has the advantages of simple operation and convenient use. The commonly used adsorption materials include activated carbon, modified biochar, nano-adsorption materials, etc. Among them, activated carbon materials are carbon materials with early application and wide application range, mainly including granular activated carbon (GAC) and powder activated carbon (PAC). A large number of studies have shown that PAC has a strong removal effect on bisphenol A, diclofenac, caffeine, ibuprofen, estradiol and other micro pollutants[1, 2].

The development of nanomaterials has brought greater opportunities and prospects for the application of carbon materials in the removal of pollutants. Carbon nanomaterials have shown better potential in removing micro-pollutants due to their high specific surface area, sufficient reaction sites, and high surface free energy[3]. Shen et al.[4] prepared three-dimensional carbon nanomaterials by self-assembly of graphene nanosheets and carbon nanotubes and found that the adsorption capacity of emerging pollutants such as oxytetracycline could reach 1729 mg/g, the adsorption capacity of diethyl phthalate was 680 mg/g, and they also showed good

---

[*] zhou_wm@hdec.com (W.Z.), xujick@tongji.edu.cn (J.X.)

adsorption efficiency for the traditional pollutants such as methyl blue and Cd. Kumar et al.[5] synthesized g-C_3N_4/rGO composite nanomaterials, and their adsorption capacities for 17β-estradiol and ciprofloxacin were 144.4 mg/g and 1368 mg/g, respectively. Carbon materials have good adsorption performance due to their large specific surface area characteristics, and have many applications in pollutant removal. However, there are also some problems such as high cost of some materials, limited utilization rate, difficulty in recycling, easy to cause secondary pollution, and limited ability to remove emerging pollutants.

2.2. Membrane separation technology

At present, the commonly used membranes are mainly divided into microfiltration membrane MF, ultrafiltration membrane UF, nanofiltration membrane NF and reverse osmosis membrane RO. UF and MF can remove a certain amount of micropollutants, but the removal performance is relatively weak due to the large pore size of the membrane. In contrast, pressure-driven NF and RO can remove micropollutants in water more effectively[6]. Lopera et al.[7] detected emerging pollutants such as caffeine, caffeine and theophylline in the sewage of a Spanish sewage treatment plant. A reverse osmosis membrane device was installed at the outlet of the secondary sedimentation tank to carry out the test. After continuous operation for 72 h, it was found that these emerging pollutants could be completely removed and no membrane fouling was observed. Kim et al.[8] analyzed a large number of studies on the removal of emerging contaminants in water using membrane technology and found that the removal rate of emerging contaminants was RO≥FO>NF>UF. UF alone might not be able to effectively remove emerging pollutants in water, but it could be used as a pretreatment process for RO or FO. Studies have shown that RO has better performance in removing emerging pollutants than NF, and can achieve 100 % removal under optimal conditions. However, from the perspective of environmental assessment, NF is more environmentally friendly than RO since it consumes less energy.

Membrane separation technology, especially NF and RO, has the advantages of good treatment effect, simple operation and maintenance. However, membrane fouling, high energy consumption, high cost and limited scale are important factors restricting its wide application. In recent years, FO has been considered as a possible alternative technology[9], which uses osmotic gradient rather than pressure as a driving force and has advantages in reducing membrane fouling. Jang et al.[10] reported that the removal rate of 12 emerging contaminants by FO membrane was more than 80%, and the removal rate of sulfamethoxazole was 98.3%. Salamanca et al.[11] studied the removal effect of a hollow fiber FO membrane module on 24 emerging contaminants, and found that the removal efficiency of all pollutants was more than 93 %, and the removal rate of 19 emerging contaminants reached 99%. However, due to the short research and application history of FO technology, although the problem of membrane fouling has been reduced, other problems such as low membrane flux still need more research[11].

2.3. Advanced oxidation

Advanced oxidation processes have great potential in dealing with a variety of emerging contaminants or micro-pollutants. The core of the technology is in-situ generation of free radicals with high activity and low selectivity, including hydroxyl radical $\cdot OH$, superoxide radical $\cdot O_2^-$, which can completely mineralize the organic matter into CO_2, H_2O and inorganic ions or acid[12]. According to the method of producing free radicals, advanced oxidation methods can be divided into ozone oxidation, Fenton oxidation, photocatalytic oxidation, electrochemical oxidation, etc.

Almomani et al.[13] used ozone with a dose range of 0.82-2.55 mg O_3/ mg DOC to remove antibiotics, steroid hormones, lipid regulators, non-steroidal anti-inflammatory drugs and other pollutants, with the removal efficiency of most drugs studied reaching more than 99.9%. Luo et al.[14] studied the photodegradation of sulfamethoxazole (SMX) and ibuprofen under UV light (254 nm), and the removal rate constants of sulfamethoxazole were 0.91 min^{-1} and 0.36 min^{-1} at pH of 3 and 7.44, respectively. Loos et al.[15] studied the removal of four drugs including SMX and 17α-estradiol (EE2) by electrochemical methods, with72.9 % of SMX and 69.7% of EE2 removed within 180 min.

In recent years, many researchers have gradually carried out research on the combination of two or more advanced oxidation methods. Moreira et al.[16] combined TiO_2 photocatalysis with ozonation to remove amoxicillin and diclofenac, and found that these two pollutants were completely mineralized after 30 min and 120 min, respectively. Rivas et al.[17] combined TiO_2 with ozone to catalyze the oxidation of nine mixed drugs under UVB (313 nm) conditions and found that the highest removal rate of TOC could reach 95% within 120 min. Adityosulindro et al.[18] used Fenton coupling ultrasound (20 kHz) to enhance the degradation of ibuprofen (6.4 mM), and the degradation rate could reach 95% within 60 min.

The research and application of various advanced oxidation technologies show the great advantages and prospects of advanced oxidation technology in pollutant removal, but it is easy to oxidize organic matter in water to produce by-products. The removal of degradation products and toxicity assessment need further attention and research.

2.4. Constructed wetlands

As a low-cost and nature-based treatment technology, constructed wetlands are widely used in sewage treatment and ecological restoration. With the attention to micro-pollutants or emerging contaminants, more and more studies have focused on the application of constructed wetlands in the removal of micro-pollutants. Ramprasad et al.[19] constructed horizontal (HFCW) and vertical

(VFCW) subsurface flow constructed wetlands in experimental scale to remove three surfactants in domestic wastewater from student dormitories, sodium dodecyl sulfate, propylene glycol and trimethylamine, with the removal efficiencies of HFCW being 85 %, 90% and 95% respectively, and that of VFCW being 89%, 95% and 98% respectively, and the effluent of the two wetlands both met the reuse standard. Gorito et al.[20] analyzed the removal process of four drugs on the EU priority pollutant list by constructed wetlands, and the influence of design and operation parameters on the removal effect. Ilyas et al.[21] studied and analyzed the removal process of emerging contaminants such as drugs by four main types of constructed wetlands and found that the mechanisms for removing these pollutants by various types of constructed wetlands were different, including aerobic or anaerobic biodegradation, plant absorption, photodegradation, adsorption or dissolution. Even though constructed wetland is considered to be an eco-friendly and promising treatment technology, the research and application of constructed wetlands in the removal of emerging pollutants or micro-pollutants are still insufficient, and further research and practical exploration are needed. In particular, the removal selectivity of emerging contaminants, the influence of important parameters, the toxic effects of emerging pollutants on wetlands, and the removal mechanism of pollutants need to be further studied. The exploration of larger laboratory scale and engineering practice scale also needs to be carried out[22].

3. Research progress of photocatalytic materials used in catalytic degradation of micro-pollutants

As a kind of advanced oxidation technology, photocatalytic oxidation technology has the advantages of high efficiency and thoroughness, and is widely used in the research and application of micro-pollutant removal. During the photocatalytic reaction, the catalyst captures light energy to convert it into the energy required for the reaction, thereby generating a catalytic effect.

There are many common photocatalytic materials such TiO_2, ZnO and CdS. Semiconductor photocatalysts are the most widely studied and applied photocatalysts, and TiO_2 is a typical representative. The catalytic mechanism of the semiconductor material is that under the excitation of light, electrons transition from the valence band to the conduction band position, so that photogenerated holes are formed at the valence band, and photogenerated electrons are generated on the conduction band, thus forming photogenerated electron-hole pairs. Photogenerated holes have strong oxidation ability and photogenerated electrons have strong reduction ability. Both react with pollutants and promote the degradation and transformation of pollutants. Due to the advantages of stable properties, low toxicity, safety, low price and mature synthesis process, TiO_2 has been widely concerned and studied in many fields such as photocatalysis. However, because of the large band gap of titanium dioxide, it can exert its superior photocatalytic performance under ultraviolet light conditions. Meanwhile, the photogenerated electron hole pairs generated by TiO_2 are easy to recombine. Therefore, many studies are expected to modify TiO_2 to avoid defects and improve its photocatalytic performance. Common modification methods for TiO_2 mainly include metal ion doping modification, nitrogen, carbon and other non-metallic element doping modification, co-doping modification, noble metal deposition, composite semiconductor modification, etc.

Graphitic carbon nitride g-C_3N_4 has been widely studied and applied in photocatalytic degradation of micro-pollutants due to its advantages of easy synthesis, low cost, good stability, low toxicity and unique electronic structure [23, 24], g-C_3N_4 has a layered structure similar to graphene. C atoms and N atoms are combined into a directional conjugated ring structure through sp^2 hybridization, spreading outward and stacking to form carbon nitride.

In addition, many photocatalytic materials have attracted attention and research. Table 1 integrates the research and application exploration of photocatalytic materials in removing emerging contaminants in water in recent years.

Table 1. The research and application of photocatalytic materials in removing emerging contaminants.

Material	Pollutant	Light irradiation	Reaction rate constant k (min^{-1}) or removal efficiency	Reference
TiO_2	24 PPCPs	UV-LED	1~2min^{-1}	2021[25]
TiO_2-graphene core-shell structure	carbamazepine (CBZ)	100 W UV lamp, 500 W Xe lamp, 1000 W Xe lamp	0.004, 0.0015, 0.0029	2021[26]
TiO_2	bisphenol A (BPA), ibuprofen (IBP), flurbiprofen (FBP)	UV-A	0.0378, 0.0316, 0.0305	2018[27]
		Metal halide lamp (visible light)	0.0283, 0.0353, 0.0427	
ZnO	BPA, IBP, FBP	UV-A	0.0329, 0.0333, 0.0385	
		Metal halide lamp (visible light)	0.0257, 0.0311, 0.0296	
TiO_2/ZnO	BPA, IBP, FBP	UV-A	0.0406, 0.0400, 0.0301	
		Metal halide lamp (visible light)	0.0314, 0.0354, 0.0383	
RGO/TiO_2	BPA, IBP, FBP	UV-A	0.0562, 0.0585, 0.0725	
		Metal halide lamp (visible light)	0.0384, 0.0285, 0.0300	

RGO/TiO_2/ZnO	BPA, IBP, FBP	UV-A	0.0568, 0.0783, 0.0936	
		Metal halide lamp (visible light)	0.0529, 0.0390, 0.0329	
B-TiO_2	4-dichlorophenol, BPA, IBP, FBP	UV-A	0.0232~0.0692	2017[28]
		Metal halide lamp (visible light)	0.0109~0.0599	
CDs/TiO_2/g-C_3N_4	enrofloxacin	350 W Xe lamp	60 min 内去除 91.6%	2017[29]
CoP/N-g-C_3N_4	CBZ	300 W Xe lamp	0.291	2021[30]
CDs/g-C_3N_4/SnO_2	indomethacin	350 W Xe lamp	0.0081~0.0712	2021[31]
HCNS/CDs	naproxen	350 W Xe lamp	0.0188~0.1603	2020[32]
Ag/Fe,N-TiO_2/Fe_3O_4@SiO_2	IBP, benzophenone-3/BZP	300 W Xe lamp	0.015, 0.013	2019[33]
g-C_3N_4/TiO_2/Fe_3O_4@SiO_2	IBP、BZP	300 W Xe lamp	0.238, 0.056	
BiOBr/Fe_3O_4 @SiO_2	IBP、BZP	300 W Xe lamp	0.092, 0.048	
$BiOBr_{0.9}I_{0.1}$/Fe_3O_4@SiO_2	IBP、BZP	300 W Xe lamp	0.072, 0.040	
SnO_2@ZnS	Metoprolol, CBZ, acetaminophen, triclosan	high-pressure mercury lamp	0.0039~0.0064, 0.0018~0.0041, 0.0037~0.0107, 0.0019~0.0034	2020[34]
TACN/TiO_2/Fe_3O_4@SiO_2	IBP、BZP、CBZ	8 W fluorescent lamp	60 min: 99%, 98%, 100%	2020[35]
AgI/UiO-66	SMX	300 W Xe lamp (visible light)	0.32	2018[36]
MIL-101(Fe)/TiO_2	tetracycline	300 W Xe lamp (sunlight)	10 min: 92.76%	2019[37]

4. Study on immobilization application of photocatalytic materials

At present, most of the photocatalytic materials synthesized and used in many studies are in the form of powder. The application of powder photocatalytic materials in photodegradation can effectively contact with pollutants and maximize their photocatalytic performance. However, in practical engineering applications, the powdered photocatalyst is dispersed in water, which is difficult and costly to recover, and the photocatalytic performance of the recovered material will be affected due to loss and agglomeration. Therefore, the recycling of photocatalytic materials is one of the challenges in its engineering application. Immobilization is one of the solutions to solve this problem. By fixing the powder photocatalytic material on the carrier, the problem of recycling in material application can be effectively solved. The commonly used photocatalyst fixation methods mainly include inorganic carrier fixation, magnetic material fixation, polymer organic matter fixation and polymer carrier fixation.

4.1. Inorganic carrier fixation

The commonly used inorganic carriers are zeolite, activated carbon, glass, ceramics, etc. As a kind of aluminosilicate natural mineral, zeolite has many holes and channels in its structure, and has good performance in ion exchange, catalysis and adsorption. As a commonly used carbon material, activated carbon (AC) has the advantages of large specific surface area, strong adsorption capacity and many structural pores. As a fixed carrier of photocatalyst, it helps to adsorb pollutants around the photocatalyst and improve the reaction efficiency. Li et al.[38] adopted mesoporous biomass-based activated carbon as a carrier to load TiO_2, and found that the specific surface area of the prepared material reached 460.1 m^2/g, and had good photocatalytic degradation performance. Lu et al.[39] prepared activated carbon-graphite carbon nitride composites for photothermal assisted photocatalytic water treatment, and found that the light absorption and utilization capacity of the composites could reach 87.7 %, and 98 % of sulfamerazine could be degraded within 1 h under simulated sunlight irradiation. Liang et al.[40] synthesized SnO / activated carbon composite photocatalytic materials by a simple ultrasonic reaction method, and the amount of activated carbon added affects the visible light absorption capacity of SnO, with the best photocatalytic performance of removing 97.6% of methyl orange with 80 min achieved with SnO_3/3% AC.

As a fixed carrier, glass has the advantages of good light transmittance, low cost and controllable shape. Some researchers have fixed photocatalysts such as TiO_2 on glass beads to solve the problem of recycling of powder photocatalysts. Liu et al.[41] adopted the sol-gel method to prepare a supported V-N co-doped TiO_2 / glass bead photocatalytic composite material, which could degrade phenol by 100% under mercury lamp irradiation, and has good recovery performance and photocatalytic performance. Holze et al.[42] sprayed TiO_2 on glass beads and found that it had good photocatalytic activity and stability, which was related to the thickness of the sprayed TiO_2 layer.

4.2. Magnetic material fixation

Using magnetic materials as carriers, the components with photocatalytic activity are fixed on magnetic materials to prepare magnetic photocatalytic materials, which is helpful to reuse photocatalytic materials and reduce the cost of material recovery and reuse. Generally, the preparation methods of magnetic photocatalytic materials include hydrothermal synthesis, coprecipitation, sol-gel, ultrasonic chemical synthesis and so on. Choi et al.[43] prepared a recyclable Ag-Fe_3O_4@TiO_2 magnetic photocatalytic material, which could almost completely remove rhodamine B within 50 min under xenon lamp illumination, and the removal rate was still more than 80% after 5 reuse cycles. Cuauhtémoc-López et al.[44] synthesized Fe_2O_3-TiO_2 by chemical precipitation method, and prepared Rh/Fe_2O_3-TiO_2 composite magnetic nanomaterials by impregnating 1 wt% Rh with Fe_2O_3-TiO_2 by heat treatment at high temperature. It had high catalytic conversion performance, and the conversion rate was still close to 85 % after 6 cycles. Tao et al.[45] prepared magnetic $CoFe_2O_4$/g-C_3N_4 nanocomposites by ultrasonic hydrothermal method, which could degrade 75.1 % of ciprofloxacin in 120 minutes under light conditions with the photocatalytic degradation removal efficiency reaching 90% after 5 cycles, and could be rapidly separated and recovered under the action of external magnetic field.

4.3. Polymer organic fixation

As a natural copolymer, alginate is abundant in nature, which has the advantages of non-toxicity, good biocompatibility and good ion exchange capacity and has been widely used in various industries. Because its surface contains a large number of carboxyl groups and has strong adsorption properties, it has good application potential as a supporting material to fix photocatalysts such as TiO_2 and C_3N_4. The advantages of alginate gel in material fixation, shape size and porosity control make it a promising photocatalyst carrier. Tong et al.[46] synthesized SA-Ag/AgBr/TiO_2 photocatalyst using sodium alginate as the matrix, and the analysis by various characterization methods showed that the catalyst had stable structure and good photocatalytic activity. Rhodamine B in the solution could be completely degraded within 1 h of UV irradiation, and 54.1% of rhodamine B could be degraded within 2 h of visible light irradiation. Li et al.[47] synthesized calcium alginate gel-based RGO/C_3N_4 composite photocatalyst by external emulsification method and chemical reduction method, which could remove 81.8% of methylene blue by adsorption and photocatalysis.

4.4. Polymer carrier fixation

In recent years, many studies have been devoted to combining photocatalysts with polymers, or using polymers as supports to prepare membrane materials with photocatalytic properties and improve the application performance of photocatalytic materials. At present, the preparation methods of photocatalytic composite films mainly include mixing method, surface coating method and bottom-up synthesis method[48]. Among them, the mixing method includes phase conversion method, vacuum filtration and electrostatic rotation. The surface coating is generally realized by rotating coating, impregnation method, pure gel, etc. The bottom-up synthesis method includes chemical grafting, vapor deposition, layer-by-layer assembly method, etc.

In recent years, many scholars have tried to combine high-efficiency photocatalysts such as TiO_2 with polymers as adsorbents and photocatalysts for the removal of some organic pollutants. Cellulose-TiO_2 composites have been synthesized by sol-gel and polymerization methods[49]. Zhao et al.[50] prepared Ag_2O/TiO_2-deacetylated chitosan composite photocatalytic membrane, which had good adsorption and photocatalytic activity, and completely degraded ampicillin and methyl orange within 180 min and 30 min, respectively. The research group also reviewed the preparation of composite photocatalytic materials with biomaterial-TiO_2 as the main structure and their selective removal of trace environmental pollutants, and found that the core-shell structure of deacetylated chitosan, TiO_2/deacetylated chitosan/Ag, TiO_2-deacetylated chitosan/glass, cellulose-TiO_2 composite film and other composite materials had high adsorption performance and photocatalytic performance, with the removal efficiency of photocatalytic degradation of pollutants such as methyl orange and rhodamine B in dyes reaching 70-100% in most studies[49].

Polyethylene (PE), polytetrafluoroethylene (PTFE), polypropylene (PP), polyacrylonitrile (PAN), polyaniline (PANI), polydimethylsiloxane (PDMS), and other polymer have also attracted the attention of researchers, which are commonly used as photocatalyst carriers[51]. Subramaniam et al.[52] dispersed the hydrothermally synthesized titanium nanotube (TNT) into the PVDF solution, and prepared an asymmetric hollow fiber membrane by dry-wet phase conversion technology to remove the pigment in the palm oil factory wastewater treated by aerobic treatment under ultraviolet light with the optimal removal rate being 67.3%. Xu et al.[53] loaded the photocatalytic material $LiNbO_3$ stably on the surface of the PES film, and could remove 70 % of the dissolved organic matter under the UV light with the intensity of 0.92 mW cm^{-2}. Sun et al.[54] prepared PVDF/TiO_2 porous material by mixing TiO_2 and PVDF by solvent replacement method and found that 12 cm^2 of the composite membrane could degrade rhodamine B in dye wastewater under visible light and ultraviolet light, and the best removal efficiency could reach 94.8%. Milani et al.[55] fixed Ag-BiW(Mo)O_6 on PVDF membrane by hydrothermal synthesis to remove methylene blue in water, degrading 51% of the pollutant after 80 min of visible light irradiation. Li et al.[56] prepared bismuth tungstate/TiO_2/PAN electrospun nanofiber membrane by electrospinning, which could remove 95.2% of methylene blue under the illumination condition of 4.5 h and the removal rate could still reach 81.4% after repeated use for 6 times. Among various polymer-based photocatalyst immobilization methods, electrospinning technology, as a technology that can design the composition and microstructure of nanomaterials, has been gradually applied and developed in research, and has good research potential and application prospects.

5. Conclusions

With the continuous advancement of research and application, the treatment technologies of emerging contaminants have gradually increased and matured. Adsorption technology based on carbon materials, membrane separation technology, advanced oxidation method and constructed wetland have shown good performance in removing emerging contaminants in water, but they also have their own shortcomings and application limitations. Among them, photocatalytic technology, as a promising technology, shows the advantages of high efficiency and low secondary pollution in the removal of emerging contaminants. Immobilization is an important way for the application of photocatalytic technology. The existing immobilization methods have been explored in experiments and applications. However, in order to further promote the application of photocatalytic technology, it is urgent to carry out more in-depth research on several existing immobilization methods. In particular, it is recommended to carry out relevant small-scale and pilot-scale experimental research and application research on actual water bodies.

Acknowledgments

This research was funded by the scientific program from PowerChina Huadong Engineering Corporation Limited, grant number KY2021-HS-02-11 and KY2022-HS-02-20.

References

1. Grassi, M., et al., *Removal of Emerging Contaminants from Water and Wastewater by Adsorption Process*, in *Emerging Compounds Removal from Wastewater: Natural and Solar Based Treatments*, G. Lofrano, Editor. 2012, Springer Netherlands: Dordrecht. p. 15-37 (2012).
2. Rathi, B.S., P.S. Kumar, and P.-L. Show, *A review on effective removal of emerging contaminants from aquatic systems: Current trends and scope for further research.* Journal of Hazardous Materials, 409, 124413 (2021).
3. Zhao, L., et al., *Nanomaterials for treating emerging contaminants in water by adsorption and photocatalysis: Systematic review and bibliometric analysis.* Science of The Total Environment, 627, 1253-1263 (2018).
4. Shen, Y., et al., *Synergistic effects of 2D graphene oxide nanosheets and 1D carbon nanotubes in the constructed 3D carbon aerogel for high performance pollutant removal.* Chemical Engineering Journal, 314, 336-346 (2017).
5. Kumar, A., et al., *Solar-driven photodegradation of 17-β-estradiol and ciprofloxacin from waste water and CO2 conversion using sustainable coal-char/polymeric-g-C3N4/RGO metal-free nano-hybrids.* New Journal of Chemistry, 41(18), 10208-10224 (2017).
6. Watkinson, A.J., E.J. Murby, and S.D. Costanzo, *Removal of antibiotics in conventional and advanced wastewater treatment: Implications for environmental discharge and wastewater recycling.* Water Research, 41(18), 4164-4176 (2007).
7. Egea-Corbacho Lopera, A., S. Gutiérrez Ruiz, and J.M. Quiroga Alonso, *Removal of emerging contaminants from wastewater using reverse osmosis for its subsequent reuse: Pilot plant.* Journal of Water Process Engineering, 29, 100800 (2019).
8. Kim, S., et al., *Removal of contaminants of emerging concern by membranes in water and wastewater: A review.* Chemical Engineering Journal, 335, 896-914 (2018).
9. Blandin, G., et al., *Forward Osmosis as Concentration Process: Review of Opportunities and Challenges.* Membranes, 10(10), 284 (2020).
10. Jang, D., et al., *Relating solute properties of contaminants of emerging concern and their rejection by forward osmosis membrane.* Science of The Total Environment, 639, 673-678 (2018).
11. Salamanca, M., et al., *Study of the rejection of contaminants of emerging concern by a biomimetic aquaporin hollow fiber forward osmosis membrane.* Journal of Water Process Engineering, 40, 101914 (2021).
12. Dalrymple, O.K., D.H. Yeh, and M.A. Trotz, *Removing pharmaceuticals and endocrine-disrupting compounds from wastewater by photocatalysis.* Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology, 82(2), 121-134 (2007).
13. Almomani, F.A., et al., *Removal of emerging pharmaceuticals from wastewater by ozone-based advanced oxidation processes.* Environmental Progress & Sustainable Energy, 35(4), 982-995 (2016).
14. Luo, S., et al., *UV direct photolysis of sulfamethoxazole and ibuprofen: An experimental and modelling study.* Journal of Hazardous Materials, 343, 132-139 (2018).
15. Loos, G., et al., *Electrochemical oxidation of key pharmaceuticals using a boron doped diamond electrode.* Separation and Purification Technology, 195, 184-191 (2018).
16. Moreira, N.F.F., et al., *Fast mineralization and detoxification of amoxicillin and diclofenac by photocatalytic ozonation and application to an urban wastewater.* Water Research, 87, 87-96 (2015).
17. Rivas, F.J., F.J. Beltrán, and A. Encinas, *Removal of emergent contaminants: Integration of ozone and photocatalysis.* Journal of Environmental Management, 100, 10-15 (2012).
18. Adityosulindro, S., et al., *Sonolysis and sono-Fenton oxidation for removal of ibuprofen in (waste)water.* Ultrasonics Sonochemistry, 39, 889-896 (2017).
19. Ramprasad, C. and L. Philip, *Surfactants and personal care products removal in pilot scale horizontal and vertical flow constructed wetlands while treating greywater.* Chemical Engineering Journal, 284, 458-468 (2016).
20. Gorito, A.M., et al., *A review on the application of constructed wetlands for the removal of priority substances and contaminants of emerging concern*

listed in recently launched EU legislation. Environmental Pollution, 227, 428-443 (2017).

21. Ilyas, H. and E.D. van Hullebusch, *Performance comparison of different types of constructed wetlands for the removal of pharmaceuticals and their transformation products: a review.* Environmental Science and Pollution Research, 27(13), 14342-14364 (2020).
22. Li, Y., et al., *A review on removing pharmaceutical contaminants from wastewater by constructed wetlands: Design, performance and mechanism.* Science of The Total Environment, 468-469, 908-932 (2014).
23. He, D., et al., *A multifunctional platform by controlling of carbon nitride in the core-shell structure: From design to construction, and catalysis applications.* Applied Catalysis B: Environmental, 258, 117957 (2019).
24. Zhou, C., et al., *Visible-light-driven photocatalytic degradation of sulfamethazine by surface engineering of carbon nitride：Properties, degradation pathway and mechanisms.* Journal of Hazardous Materials, 380, 120815 (2019).
25. Fattahi, A., et al., *Effect of Background Water Matrices on Pharmaceutical and Personal Care Product Removal by UV-LED/TiO2.* Catalysts, 11(5), 576 (2021).
26. Fu, H. and K.A. Gray, *TiO2 (Core)/Crumpled Graphene Oxide (Shell) Nanocomposites Show Enhanced Photodegradation of Carbamazepine.* Nanomaterials, 11(8), 2087 (2021).
27. Bilgin Simsek, E., et al., *Graphene oxide based heterojunction TiO2–ZnO catalysts with outstanding photocatalytic performance for bisphenol-A, ibuprofen and flurbiprofen.* Journal of Industrial and Engineering Chemistry, 59, 115-126 (2018).
28. Bilgin Simsek, E., *Solvothermal synthesized boron doped TiO2 catalysts: Photocatalytic degradation of endocrine disrupting compounds and pharmaceuticals under visible light irradiation.* Applied Catalysis B: Environmental, 200, 309-322 (2017).
29. Su, Y., et al., *Decoration of TiO2/g-C3N4 Z-scheme by carbon dots as a novel photocatalyst with improved visible-light photocatalytic performance for the degradation of enrofloxacin.* RSC Advances, 7(54), 34096-34103 (2017).
30. Dong, C., et al., *N-doped graphitic C3N4 nanosheets decorated with CoP nanoparticles: A highly efficient activator in singlet oxygen dominated visible-light-driven peroxymonosulfate activation for degradation of pharmaceuticals and personal care products.* Journal of Hazardous Materials, 416, 125891 (2021).
31. Li, D., et al., *Synthesis of a carbon dots modified g-C3N4/SnO2 Z-scheme photocatalyst with superior photocatalytic activity for PPCPs degradation under visible light irradiation.* Journal of Hazardous Materials, 401, 123257 (2021).
32. Wu, Y., et al., *Highly active metal-free carbon dots/g-C3N4 hollow porous nanospheres for solar-light-driven PPCPs remediation: Mechanism insights, kinetics and effects of natural water matrices.* Water Research, 172, 115492 (2020).
33. Khan, M., et al., *Unravelling mechanistic reasons for differences in performance of different Ti- and Bi-based magnetic photocatalysts in photocatalytic degradation of PPCPs.* Science of The Total Environment, 686, 878-887 (2019).
34. Hojamberdiev, M., et al., *SnO2@ZnS photocatalyst with enhanced photocatalytic activity for the degradation of selected pharmaceuticals and personal care products in model wastewater.* Journal of Alloys and Compounds, 827, 154339 (2020).
35. Kumar, A., et al., *Visible–light–driven magnetically recyclable terephthalic acid functionalized g−C3N4/TiO2 heterojunction nanophotocatalyst for enhanced degradation of PPCPs.* Applied Catalysis B: Environmental, 270, 118898 (2020).
36. Wang, C., et al., *Effects of water environmental factors on the photocatalytic degradation of sulfamethoxazole by AgI/UiO-66 composite under visible light irradiation.* Journal of Alloys and Compounds, 748, 314-322 (2018).
37. He, L., et al., *A novel magnetic MIL-101(Fe)/TiO2 composite for photo degradation of tetracycline under solar light.* Journal of Hazardous Materials, 361, 85-94 (2019).
38. Li, Y., et al., Photocatalytic degradation kinetics of mesoporous bio-based activated carbon supported titanium dioxide. Acta Energiae Solaris Sinica, 41(7), 17-25 (2020).
39. Lu, S., et al., *Photothermal-assisted photocatalytic degradation with ultrahigh solar utilization: Towards practical application.* Chemical Engineering Journal, 2020. 379: p. 122382.
40. Liang, B., et al., *Efficient visible-light photocatalyst synthesized by modifying SnO with activated carbon.* Materials Research Express, 6(1), 015603 (2018).
41. Liu, G., et al., Preparation and photocatalytic properties of V-N co-doped TiOz/glass beadsphotocatalytic composite. Acta Materiae Compositae Sinica, 34(5), 1062-1068 (2017).
42. Holze, S., et al., *Influence of TiO2-Layer Thickness of Spray-Coated Glass Beads on Their Photocatalytic Performance.* Chemical Engineering & Technology, 40(6), 1084-1091 (2017).
43. Choi, K.-H., et al., *Recyclable Ag-coated Fe3O4@TiO2 for efficient photocatalytic oxidation of chlorophenol.* Surface and Coatings Technology, 320, 240-245 (2017).
44. Cuauhtémoc-López, I., et al., *Naphthalene hydrogenation using Rh/Fe2O3-TiO2 magnetic catalysts.* Catalysis Today, 360, 176-184 (2021).
45. Tao, C., et al., Photocatalytic degradation of ciprofloxacin by magnetic CoFe204/g-C3N4 nanocomposites. Acta Scientiarum Naturalium Universitatis Pekinensis, 57(3), 587-594 (2021).
46. Tong, Q., et al., High-efficient Synthesis and Photocatalytic Properties of Ag/AgBr/TiO2Monolithic Photocatalysts Using Sodium Alginate as Substrate. Journal of Inorganic Materials, 32(6), 637-642 (2017).

47. Li, Z., Preparation and properties of gel-based composite photocatalyst. China University of Geosciences Beijing (2018).
48. Li, N., et al., *Catalytic membrane-based oxidation-filtration systems for organic wastewater purification: A review.* Journal of Hazardous Materials, 414, 125478 (2021).
49. Zhao, Y., et al., *Fabrication of biomaterial/TiO2 composite photocatalysts for the selective removal of trace environmental pollutants.* Chinese Journal of Chemical Engineering, 27(6), 1416-1428 (2019).
50. Zhao, Y., et al., *Controlled synthesis and wastewater treatment of Ag2O/TiO2 modified chitosan-based photocatalytic film.* RSC Advances, 7(18), 11211-11221 (2017).
51. Wu, J., Preparation of polymer-based titanium dioxide composite fiber membrane and its adsorption and degradation of organic matter. China University of Geosciences Beijing (2020).
52. Subramaniam, M.N., et al., *AT-POME colour removal through photocatalytic submerged filtration using antifouling PVDF-TNT nanocomposite membrane.* Separation and Purification Technology, 191, 266-275 (2018).
53. Xu, H., et al., *Simultaneous removal of dissolved organic matter and nitrate from sewage treatment plant effluents using photocatalytic membranes.* Water Research, 143, 250-259 (2018).
54. Sun, X., et al., *Polyporous PVDF/TiO2 photocatalytic composites for photocatalyst fixation, recycle, and repair.* Journal of the American Ceramic Society, 104 (12), 6290-6298 (2021).
55. Mortazavi Milani, H., et al., *Ag-functionalized Bi2W(Mo)O6/PVDF membrane for photocatalytic water treatment.* Journal of Materials Science, 56(29), 16339-16350 (2021).
56. Li, H., et al., *Study on preparation and property of bismuth tungstate/TiO_2/PAN electrospun nanofibre membrane.* New Chemical Materials, 47(12), 235 (2019).