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Persulfate-based advanced oxidation processes: The new hope brought by nanocatalyst immobilization

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1 **Abstract:**

2 Persulfate-based advanced oxidation processes (persulfate-AOPs) offer great promise for
3 environmental remediation, with heterogeneous catalysts providing the backbone of
4 many wastewater purification technologies. Unlike conventional nanocatalyst
5 heterogeneous systems, the immobilized-catalyst system can bypass the separation
6 problem to reduce scour and prevent aggregation by anchoring nanoparticles onto porous
7 or large-particle carriers. This review presents the state-of-the-art of knowledge
8 concerning immobilization methodologies and reactors, reaction mechanisms, and
9 activation performance. Immobilization techniques onto supports are summarized and
10 discussed, including membrane-based reaction systems (immersion mode, and filtration
11 mode), electrocatalytic auxiliary systems, and alternative supports (metallic glasses,
12 aerogels, hydrogels, and specific materials). Key scientific problems and important
13 prospects for the further development of immobilized catalysts are outlined.

14 **Keywords:** advanced oxidation process; nanocatalyst immobilization; persulfate;
15 wastewater treatment

Full Text	Abbreviation
Persulfate-based advanced oxidation processes	persulfate-AOPs
Advanced oxidation processes	AOPs
Reactive oxygen species	ROS
Peroxymonosulfate	PMS
Peroxydisulfate	PDS
Reduced graphene oxide	rGO
Polyvinylidene fluoride	PVDF
Polyacrylonitrile	PAN
Scanning electron microscope	SEM
S, N-doped carbon and iron nanoparticles	NSC-Fe
Layered double hydroxides	LDH
Nanofibers	NFs
Metal-organic frameworks	MOFs
Cellulose nanofibers	CNFs
Electrospun nanofibers	ENFs
Zero-valent iron	ZVI
Metallic Cu-doped C/SiO ₂ nanofibers	CINMs
Ag-La _{0.8} Ca _{0.2} Fe _{0.94} O _{3-δ}	Ag-LCF
Zeolitic imidazolate framework	ZIF
Calotropis gigantea fiber	CGF
Carbon nanotubes	CNTs
N-doped microtubule composites/PVDF	CFP
Biomimetic polydopamine	PDA
Polypropylene	PP
Total dissolved solids	TDS
Poly tetrafluoroethylene	PTFE
Metallic glass(es)	MGs/MG
Ultraviolet-visible light	UV-Vis
Three-dimensional	3D
Co-doped carbon aerogels	CoCA
Selective laser melting	SLM
Isotropic CoFe ₂ O ₄ @graphene hybrid aerogel	CFO@GA-I
Anisotropic CoFe ₂ O ₄ @graphene hybrid aerogel	CFO@GA-A
Graphene hybrid aerogel	GA
Polyacrylic acid	PAA
Graphene oxide	GO
Chemically bonded Co ₃ O ₄ nanoflowers sponge	SP-50
Double-network hydrogel templated FeS/graphene	DMG
Polyvinyl alcohol	PVA

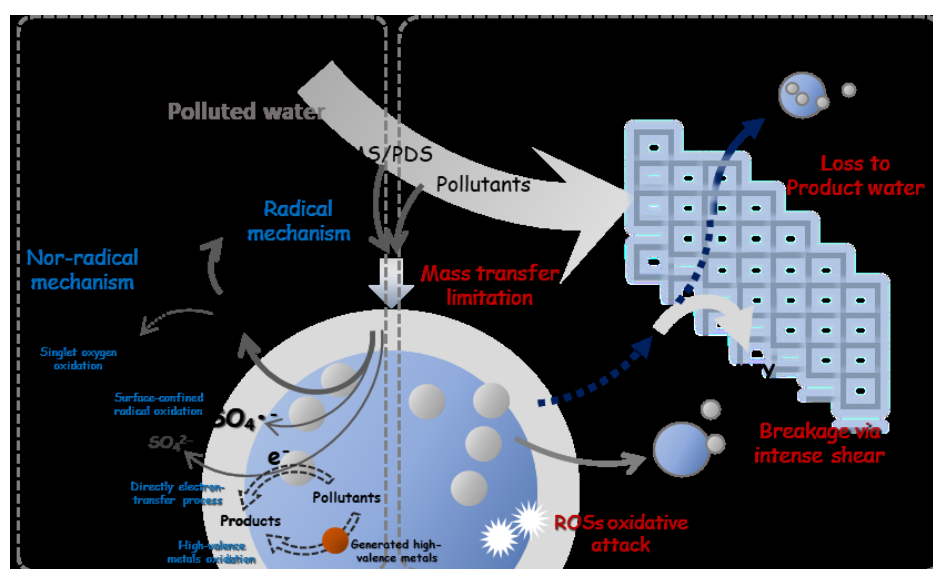
TiO ₂ nanotubes	TNTs
CoFe ₂ O ₄ on quartz sand support	CoFe ₂ O ₄ -QS
<i>In situ</i> chemical oxidation	ISCO
Capacitive deionization	CDI
Multiwalled carbon nanotube	MWCNT
Activated carbon fiber	ACF
Electro PDS	E-PDS
Electro PMS	E-PMS
Carbon fiber paper	CFP
Carbon fiber	CF
Flow-through cathode	FTC
Flow-by cathode	FBC
Asymmetric quasi capacitive deionization	AQCDI
Covalent organic frameworks	COFs
Natural organic matter	NOM
Polyethersulfone	PESF
1-methyl-2-pyrrolidinone	NMP
CoFe alloy and CoFe ₂ O ₄ encapsulated in N-doped microtubes	CoFe-NMTs
Carbon black nano-spheres	CBNS

18 **1. Introduction**

19 The importance of water safety for economic development and public and
20 environmental health cannot be overstated. Yet, despite rising levels of contamination
21 and salinity of inland freshwater [1], more than 650 million people currently lack access
22 to safe water [2]. Common natural pollutants, including pathogenic microorganisms,
23 earth-derived heavy metals, cyanobacterial toxins, and metal-like substances (e.g.,
24 arsenic), can be removed through traditional water treatment methods (i.e., filtration
25 and precipitation) [2]. However, the application of these basic technologies is limited
26 by throughput requirements. Furthermore, priority pollutants and emergent
27 contaminants have been found in natural streams, drinking water sources, and even
28 sewage treatment plant effluents, thus posing a threat to human and ecosystem health.
29 This is exacerbated by the proliferation and discharge of multidrug-resistant bacteria in
30 certain sewage treatment plants, leading to health risks and reduced productivity [3-5].
31 The foregoing highlight the need for technological innovation and resilience to improve
32 inefficient water treatment infrastructure.

33 Advanced oxidation processes (AOPs) provide a powerful means of degrading and
34 even mineralizing refractory organic pollutants through the induction of reactive
35 oxygen species (ROS), thus avoiding the need for further treatment of contaminant-
36 laden sorbents or membrane concentrate streams [6]. In general, hydroxyl radicals ($\bullet\text{OH}$)
37 [7, 8], sulfate radicals ($\text{SO}_4^{\bullet-}$) [9, 10], chlorine radicals ($\text{Cl}\bullet$ and $\text{Cl}_2^{\bullet-}$) [11, 12], and
38 radicals that enable direct electron transfer possess [13] can achieve rapid

39 decomposition of various organic pollutants and pathogenic bacteria. Owing to their
 40 lack of pH dependency and selective oxidation, persulfate-based advanced oxidation
 41 processes (persulfate-AOPs) have begun to receive more research attention than
 42 standard Fenton systems. Nanomaterials have provided an immense impetus as
 43 heterogeneous catalysts for peroxymonosulfate (PMS, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) and
 44 peroxydisulfate (PDS, $\text{Na}_2\text{S}_2\text{O}_8$ or $\text{K}_2\text{S}_2\text{O}_8$) activation. The key mechanism behind the
 45 persulfate heterogeneous activation reaction is the direct transfer of electrons from
 46 catalysts to persulfate ions (labeled as “Radical mechanism” in **Fig. 1**). Researchers
 47 have recently proven the existence of a non-radical oxide pathway (marked as “Non-
 48 radical mechanism” in **Fig. 1**), involving a direct electron transfer process, reaction with
 49 surface-activated complex (or surface-confined radical), direct oxidation of high-
 50 valence metals, and the participation of singlet oxygen in the catalytic oxidation of
 51 organic contaminants [14-16].



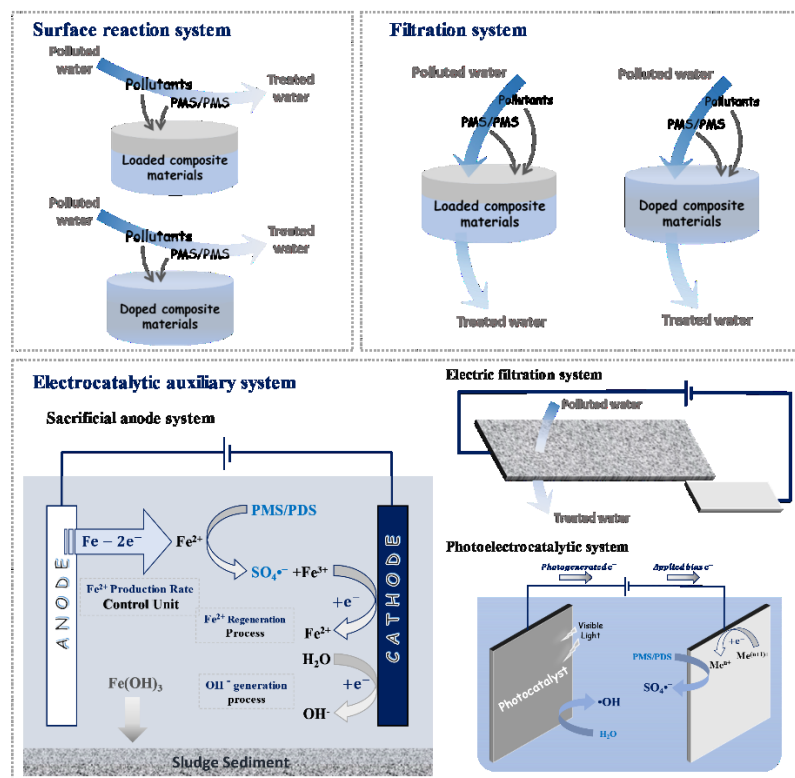
52
 53 **Fig. 1.** Heterogeneous activation mechanism of persulfates, and challenges to nanocatalysts in persulfate-
 54 based-AOPs.

55 However, nanocatalyst loss to product water, mass transfer limitations, ROS

56 oxidative attack, and breakage under intense shear are almost inevitable in a
57 nanoparticle catalytic system [17, 18]. Although nanotechnology cannot solve all water
58 treatment problems, nanomaterials might enable the development of next-generation
59 engineered water purification systems, which are compact and simple to deploy [2, 19].
60 Immobilization has recently been reported to help minimize leaching, inducing an
61 obvious degradation effect and reducing the cost associated with separation of
62 nanocatalysts, thus leading to more effective application of nanoparticle-based AOPs
63 for water remediation [20-22]. The future development of persulfate-AOPs depends on
64 the optimization and immobilization of nanocatalysts in addition to reactor design. For
65 instance, reduced graphene oxide doped with nitrogen/polyvinylidene fluoride matrix
66 (rGO-N-PVDF) composite membrane was prepared and used in a specific filtration
67 system with compact structure, convenient operation, and easy recovery in water
68 treatment [23]. Conversion of pharmaceuticals in the range 54%–91% was then
69 obtained even after 24 h of operation in full continuous mode, thus demonstrating the
70 activation performance of rGO-N-PVDF for PDS conversion. However, the pollutant
71 removal efficiency decreased in preliminary experiments using surface water compared
72 to those using ultrapure water. Therefore, this research field presents both opportunities
73 and challenges, requiring more comprehensive scientific research in the future.

74 Simultaneous specific reaction systems and reactors have recently been
75 established, mainly based on a surface reaction system formed from composite material
76 and a synergistic filtration system, as shown in **Fig. 2**. These can be directly
77 supplemented with light and heat sources to achieve more efficient, faster wastewater

78 treatment [16, 24, 25]. Nevertheless, specially designed reactors are required in
 79 electrocatalytic auxiliary systems (examples shown in **Fig. 2**). This review describes
 80 the current state of knowledge of persulfate activation methods, different
 81 immobilization methodologies and reactors, reaction mechanisms, and activation
 82 performance. Challenges and future prospects are discussed, including the lack of a
 83 universal optimization principle for catalyst preparation and reactor design, and the use
 84 of blank standardized experimental methods in various complex water matrices which
 85 ignore cost and life-cycle effects. The overall goal is to gain insight into design
 86 approaches for next-generation multifunctional treatment systems that reduce water
 87 pollution and energy consumption.

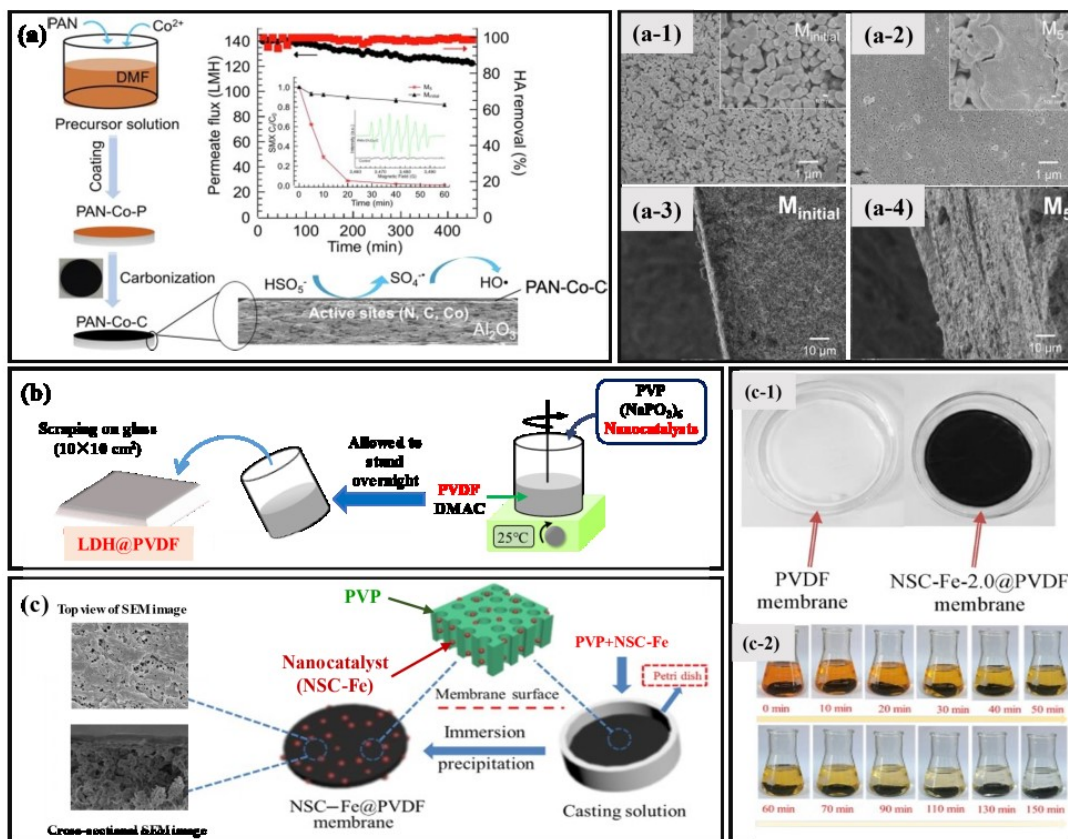


88
 89 **Fig. 2.** Construction strategy for persulfate activation systems based on immobilized nanocatalysts.

90 **2. Membrane-based reaction systems**

91 *2.1 Immersion mode reaction systems*

92 The working pH in a PMS activation system is harsh; thus, the standards for
93 catalyst stability and raw membrane material are higher compared to other systems.
94 Moreover, maintenance of catalytic performance relies on the redox reaction (i.e., metal
95 valence state transformation), whereas very strong nanoparticle-support interactions
96 between the support and nanoparticles usually make it difficult to reduce nanoparticles.
97 Based on their superior characteristics in terms of long life-span, thermal stability, and
98 excellent tolerance to pH, ceramic membranes have attracted much attention in recent
99 years, as summarized in **Table 1**. For example, the composite membrane covered with
100 polyacrylonitrile (PAN)-Co-C and a Co/C layer shown in **Figs. 3(a-1)–(a-4)** has a
101 porous surface and cross-section [26]. The catalysis performance of such membranes
102 has been ascribed to abundant active functional sites (C, N, and Co), thus importing an
103 intrinsic antifouling effect in the membrane filtration process. The formation of a
104 chemical bond between the C/Co layer and Al₂O₃ results in more robust functionalized
105 membranes with stable catalytic performance. However, these ceramic membranes are
106 extremely brittle, which means that they can easily break and disperse during
107 application. Moreover, the fragments are difficult either to collect or to recover.



108

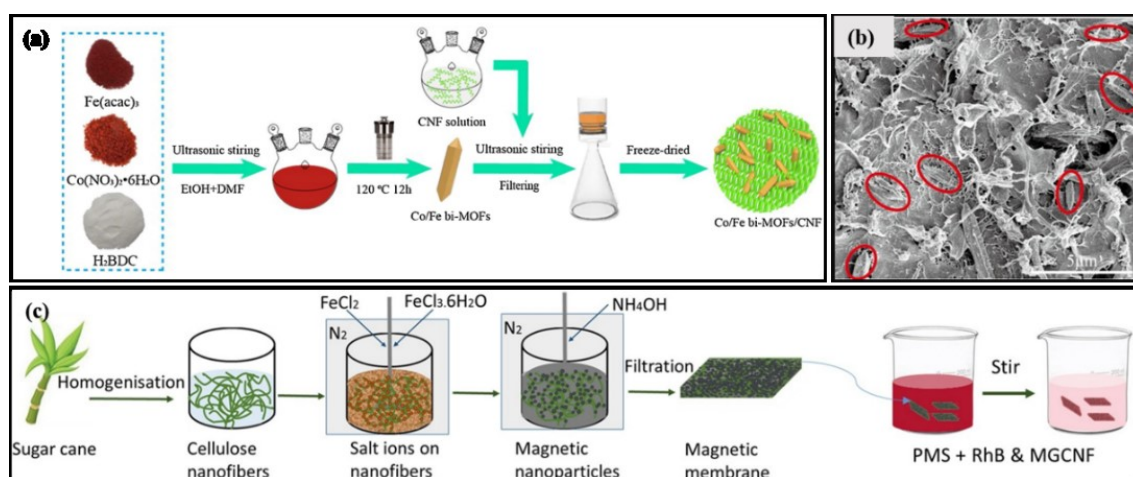
109 **Fig. 3.** Typical composite membrane prepared via ceramic and polymeric substances, and then used in
 110 immersion mode reaction systems: (a) synthetic procedure for PAN-Co ceramic membrane, with SEM
 111 surface images of (a-1) initial Al_2O_3 membrane, and (a-2) functionalized PAN-Co-C membrane, and
 112 SEM cross-section images of (a-3) initial Al_2O_3 membrane, and (a-4) functionalized PAN-Co-C
 113 membrane (reprinted with permission from [26], copyright 2019 Elsevier); (b) synthetic procedure for
 114 LDH@PVDF membrane (reprinted with permission from [27], copyright 2020 Elsevier); and (c)
 115 synthetic procedure for NSC-Fe@PVDF membranes, with (c-1) digital photograph of NSC-Fe@PVDF
 116 membrane and (c-2) color changes of Orange II in NSC-Fe@PVDF/PMS system (reprinted with
 117 permission from [28], copyright 2017 Elsevier).

118 Generally, polymeric substances are easy to synthesize and manufacture; thus,
 119 they play an important part in nanocatalyst immobilization. In particular, composite
 120 membranes fabricated via polymeric substances show great suppleness, which means
 121 that they can be collected and washed using a simple treatment process (see **Table 1**)
 122 to achieve recycling of catalytic materials. Polyvinylidene fluoride (PVDF) is a

123 promising membrane substrate that features: (i) great physical and chemical stability,
124 allowing it to be applied under a wide range of conditions; (ii) excellent flexibility,
125 enabling it to be processed into different shapes; and (iii) cost-effectiveness and eco-
126 friendliness. As shown in **Figs. 3(b) and (c)**, hybrid catalytic PVDF membranes are
127 readily fabricated by the phase inversion technique. For instance, the functionalized,
128 pure, white PVDF membrane appears black after being doped by iron nanoparticles
129 embedded in S, N-cooped carbon (**Fig. 3(c-1)**), demonstrating a uniform distribution of
130 nanocatalysts [28]. The synergistic effect between S, N-doped carbon, and iron
131 nanoparticles (NSC-Fe) improves the catalytic ability of NSC-Fe@PVDF; thus,
132 substantial decolorization of orange II occurs with low metal leaching (**Fig. 3(c-2)**).
133 **Table 1** lists data that confirm the great activation performance and durability of layered
134 double hydroxides (LDH)@PVDF and the CuO@CuS/PVDF membrane.

135 During the heterogeneous catalytic reaction, the degradation effect of target
136 pollutants correlates positively with the interaction between PMS and catalyst.
137 Therefore, catalyst with high specific surface area and porosity is required, in order to
138 promote interaction with PMS [29]. Nanofibers (NFs) are widely considered to be a
139 promising support for nanoparticle immobilization because of their high surface area.
140 Generally, nanocatalysts immobilize uniformly and tightly on the surface of NFs when
141 exposed to reactants, such as oxidizing agents, contaminants, and coexisting ions or
142 organic matter [27, 30]. With their large continuous surface area and high flexibility,
143 NFs can form random arrays and macroscopic mats, which are beneficial for catalyst
144 separation, recovery, and reuse [31]. **Fig. 4(a)** illustrates vacuum filtration, an efficient

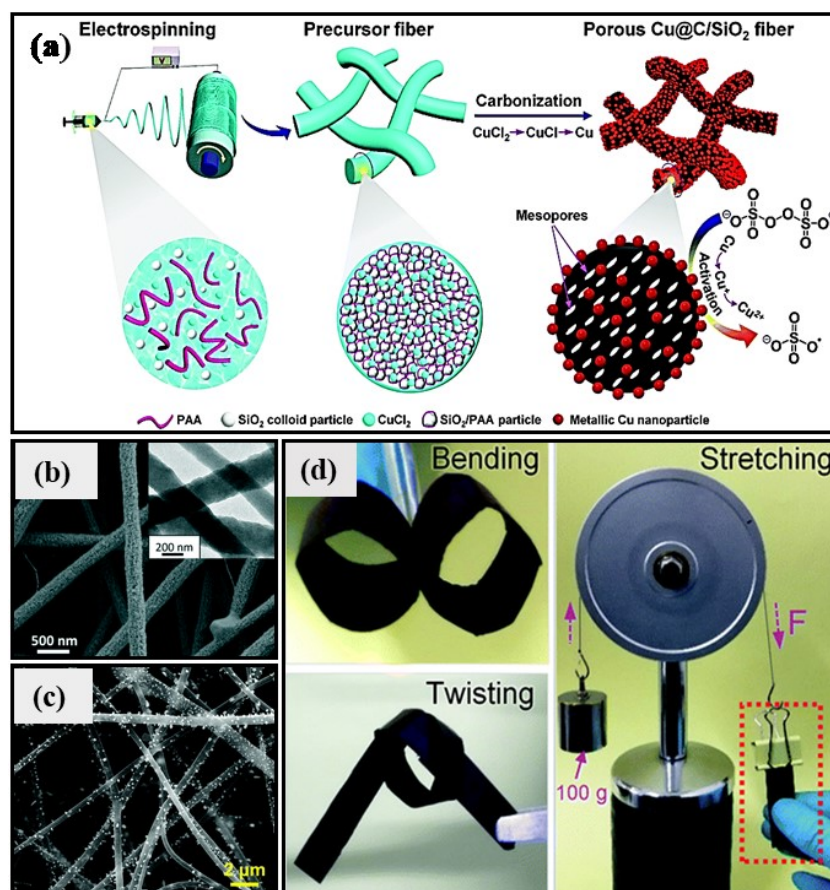
145 method for loading Co/Fe metal–organic framework (MOF) nanocatalysts onto
 146 cellulose nanofiber (CNF) membranes [32]. Due to the two redox cycles of Co (II-III-
 147 II) and Fe (II-III-II) in Co/Fe MOFs nanoparticles, $\text{SO}_4^{\bullet-}$ is continually induced through
 148 PMS activation to degrade pollutants. CNFs simultaneously solve the problem of
 149 nanocatalyst agglomeration (**Fig. 4(b)**) and functionalized membranes can be easily
 150 collected from the solution. As shown in **Fig. 4(c)**, CNFs have also been used as a
 151 template to prepare magnetic nanocatalysts with uniform size distribution via filtration
 152 [33]. Given their high concentration of magnetic Fe_3O_4 nanoparticles, the flexible
 153 magnetic membranes exhibited superparamagnetic properties and persulfate of high
 154 activation performance, thereby facilitating convenient recovery of the composite
 155 membrane (in **Table 1**) avoiding loss of nanoparticles. Even so, further information is
 156 required on the mineralization efficiency of pollutants, metal leaching concentration,
 157 and catalytic stability.



158
 159 **Fig. 4.** Typical composite membrane prepared from nanofibers through filtration, and used in immersion
 160 mode reaction systems: (a) synthetic procedure, (b) SEM image of Co/Fe bi- MOFs/CNFs membrane
 161 (reprinted with permission from [32], copyright 2020 Elsevier); and (c) schematic representation of
 162 magnetic nanocellulose membrane preparation and PMS activation process (reprinted with permission

163 from [33], copyright 2020 Elsevier).

164 Thus far, owing to the absolute discontinuity of nanoparticles, the mechanical
165 properties of the foregoing composite membrane prepared by vacuum filtration are
166 much lower than those of existing advanced fiber-reinforced composites [34, 35].
167 Electrospinning is a technique that produces continuous NFs by jetting polymer
168 solutions in high electric fields, thus providing excellent control over NF dimensions
169 and orientation, as illustrated in **Fig. 5(a)** [36]. Compared with nanofibers synthesized
170 using other methods, electrospun nanofibers (ENFs) provide overwhelming benefits,
171 including: (i) potential for controllable synthesis; (ii) large specific surface area, high
172 aspect ratio, and oriented charge transfer pathways; (iii) excellent compositional and
173 structural stability; and (iv) cost control of mass production, especially for
174 multicomponent composite fibers, suitable for industrial application [37]. A previous
175 study synthesized composite α -Fe@carbon ENFs by co-electrospinning and pyrolysis
176 self-reduction [38]. In **Fig. 5(a)**, small particles of average diameter ... nm could be
177 observed on the surface of the fiber, demonstrating that iron species were distributed
178 uniformly and welded firmly in the fibrous scaffolds. Based on active zero-valent iron
179 (ZVI), the ENFs exhibited excellent PMS activation activity, high stability, and easy
180 magnetic separation during the contaminant removal process. However, the flexible
181 ENF membranes (nonporous or microporous, < 2 nm) were unable to provide sufficient
182 active sites for pollutant adsorption and ROS transportation, thus limiting further
183 improvement in catalytic capability [39, 40].



184

185 **Fig. 5.** Typical composite membrane prepared from electrospun nanofibers, and used in immersion mode
 186 reaction systems: (a) synthetic procedure for metallic Cu-doped C/SiO₂ nanofibers (CINMs) by sol-gel
 187 electrospinning method; (b) SEM image of α -Fe@carbon ENFs (reprinted with permission from [38],
 188 Copyright 2017 RSC); (c) SEM image of CINMs; and (d) optical photograph showing that the CINMs
 189 could be folded into a paper crane without any fracturing (reprinted with permission from [39], copyright
 190 2019 RSC).

191 A recent study of inorganic membranous catalysts that have extraordinary
 192 flexibility and large mesopores by Shan et al. [39] has provided convincing evidence
 193 for the improvement of their catalytic oxidation activity in persulfate-AOPs. Shan et al.
 194 successfully fabricated Cu@C/SiO₂ nanofiber membranes (CINMs) through
 195 electrospinning and *in situ* carbonization (**Figs. 5(c)** and **(d)**). As indicated in **Fig. 5(c)**,
 196 the synthesized nanoparticles were able to break through the ground and become firmly
 197 fixed on the NFs surface, indicating the structural stability of the resultant membranes

198 and the validity of the electrospinning method. Furthermore, the as-obtained CINMs,
199 which have large mesopores and are very flexible, can withstand large bending and
200 torsional deformations with no detectable fractures (see **Fig. 5(d)**). This synthetic
201 strategy therefore overcomes the obstacles of brittleness and the poor mechanical
202 properties of crystalline inorganic NF membranes, and can be further extended to other
203 metal-embedded inorganic membranes.

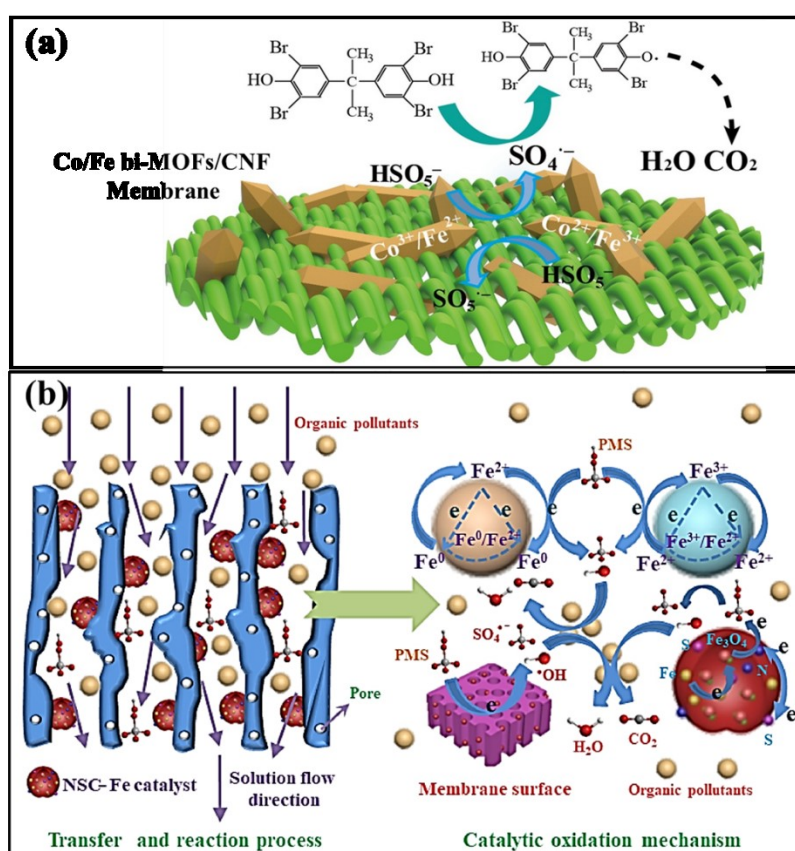
204 The integrated effect of randomly arranged NFs, sufficient hydroxyl groups, and
205 rough surfaces of nanostructures endows synthesized CINMs with superhydrophilicity,
206 a property conducive to water purification. Furthermore, as indicated in **Table 1**, novel
207 Co–Al₂O₃ and Pt–Al₂O₃ NFs membranes prepared using electrospinning have
208 demonstrated great flexibility and excellent PMS activation capability [41, 42]. Given
209 its flexible membrane form, the shape of Pt/Al₂O₃ can be adjusted for use in different
210 membrane reactors [42]. As for the reaction mechanism, PMS can be easily adsorbed
211 on the surface of Pt/Al₂O₃ fiber through its oxygen atom, due to the positive charge of
212 Pt/Al₂O₃ during the reaction process. Meanwhile, electron-rich organic molecules with
213 aromatic rings in the structure may also be adsorbed on the fiber and contribute
214 electrons to PMS through Pt as a medium, thereby leading to further destruction of
215 organic pollutants and gradual decomposition of PMS.

216 Ma et al. [43] processed Ag-La_{0.8}Ca_{0.2}Fe_{0.94}O_{3-δ} (Ag-LCF) into hollow fiber
217 membranes by means of a phase-inversion and sintering method. They examined the
218 reaction of the Ag-LCF hollow fiber membrane, whereby a methylene blue and
219 persulfate solution was pumped into the fiber lumen at a prescribed flow rate. SEM

220 images revealed pinhole defects and exposed particles that appeared on the inner
221 surface with increasing grain size (see inset). The membrane wall, especially the dense
222 membrane core, was kept intact to prevent wastewater from leaking from the cavity
223 into the shell side. However, further measurements are still needed, including the
224 mineralization efficiency of pollutants, metal leaching concentration, reusability, and
225 active sites of Ag-LCF.

226 From the above collection of mixed systems based on catalytic membranes, a
227 possible reaction mechanism has been identified, as depicted in **Fig. 6** [28, 32]. First,
228 pollutant and persulfate ions (i.e., HSO_5^- and $\text{S}_2\text{O}_8^{2-}$) adsorb on active sites on the
229 membrane surface. Next, surface adsorbed persulfate is activated by catalytic sites to
230 induce ROS, and then interacts with adsorbed organic molecules and/or bacteria
231 through an *in situ* reaction, after which the preoccupied sites are released. These
232 released free sites accelerate the transfer of aqueous reactant, thereby initiating a new
233 adsorption-oxidation cycle. The foregoing cycle repeats itself until most or all of the
234 target pollutants are removed. The nano-size effect of metal particles and the relatively
235 low diffusion resistance of organic matter on the surface of catalytic membranes are
236 conducive to full contact between organic matter and active sites, which is beneficial
237 to the catalytic performance of the membrane [28]. For carbon-based and carbon-doped
238 catalytic membranes, the work function of metal nanoparticles embedded in carbon is
239 lower than that of a carbon surface due to facile electron transfer from the metallic
240 active sites to the carbon atom [44]. At the same time, the carbon shell forms a reservoir
241 that effectively delays the process of iron dissolution (in the solution). Hence, such

242 composite membranes intrinsically display enhanced stability and excellent catalytic
 243 performance. However, organic molecules and persulfate ions experience difficulty in
 244 entering the catalytic membrane pores in batch mode (**Table 1**), which prevents full
 245 utilization of the possible active sites in the membrane pore walls (see **Fig. 2**). An
 246 alternative approach is to assemble the composite membranes in the filtration reactor,
 247 enabling the internal active sites to be properly exploited.



248
 249 **Fig. 6.** Schematic illustration of reaction mechanism for organic removal by (a) Co/Fe bi-MOFs/cellulose
 250 NFs membrane/PMS system (reprinted with permission from [32], copyright 2020 Elsevier), and (b)
 251 NSC-Fe@PVDF/PMS system (reprinted with permission from [28], copyright 2017 Elsevier).

252 2.2 Filtration mode reaction systems

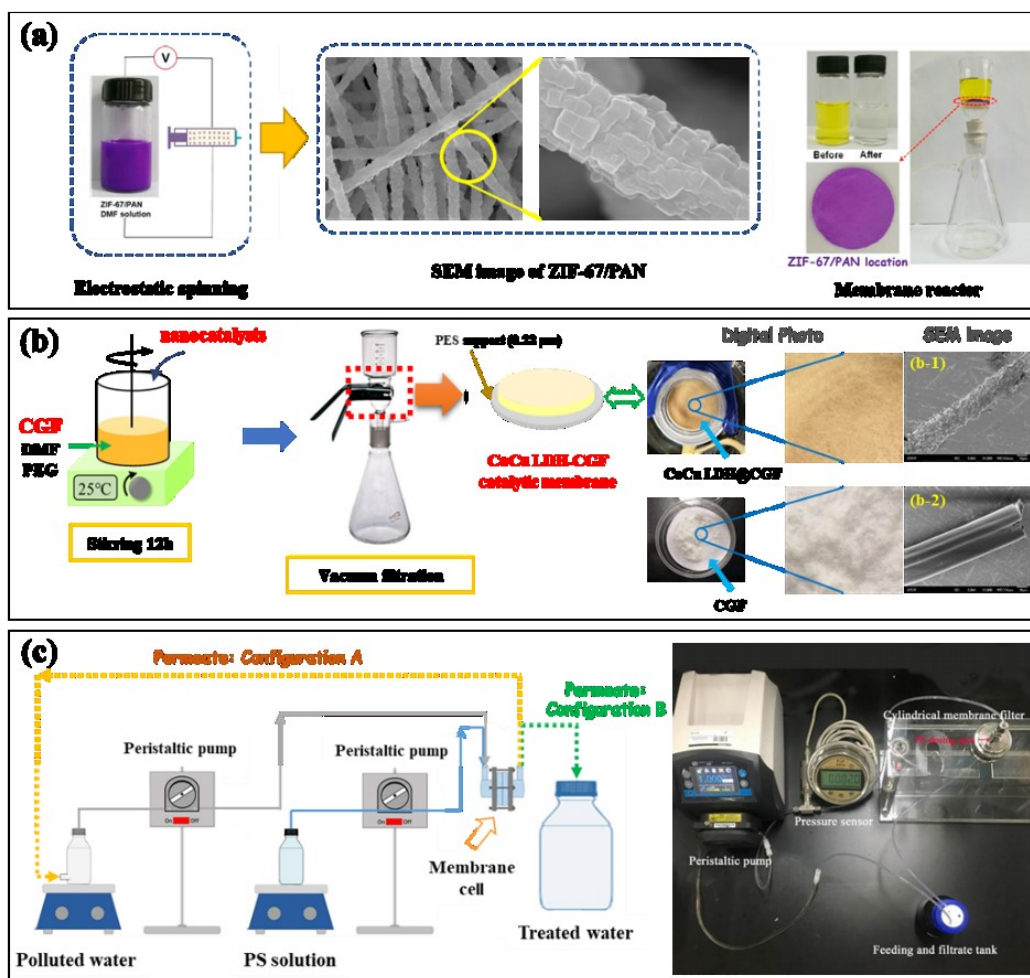
253 Persulfate-AOPs can be used in conjunction with membrane filtration as a
 254 pretreatment stage to degrade organic compounds in the membrane feed stream. This

255 serves as a mixed/one-pot process and a post-treatment stage to demineralize non-
256 rejected micropollutants in the infiltration stream and reduce organics in the
257 concentrated liquid stream. It has been demonstrated that this series of combined
258 processes (i.e., the filtration system in **Fig. 2**) can efficiently remove pollutants [45].
259 These treatment methods represent the latest developments in the field (**Table 2**). The
260 following section discusses several advanced studies on the coupling of membrane
261 filtration and persulfate-AOPs.

262 Wang et al. [46] established an *in situ* growth technique to produce a zeolitic
263 imidazolate framework (ZIF)-67/PAN filter, in which the loading ZIF-67 retained its
264 morphology, structure, and catalytic capacity in comparison to pure ZIF-67 powder. It
265 has been confirmed that Co^{2+} in ZIF-67 can activate PMS to generate ROS for pollutant
266 degradation. Moreover, a piece of ZIF-67/PAN filter (3.5 cm^2) can be installed in the
267 Swinnex syringe filter bracket enabling the syringe pump to drive contaminated
268 solution through the filter, achieving water purification (**Fig. 7(a)**). Likewise, CuCo
269 LDH@PAN and CuCo LDH@calotropis gigantea fiber (CGF) composite membranes
270 have been synthesized through vacuum filtration (**Fig. 7(b)**) by our group to enhance
271 the applicability of highly efficient nanocatalysts [27]. In **Fig. 7(b)** the pure CGF
272 membrane sample is white, and the composite membrane has a generally brown color,
273 indicating a uniform distribution of CuCo LDH on the CGF scaffold. The morphology
274 of the membrane surface changed visibly after the CuCo LDH coating, also indicating
275 successful fabrication of the composite membrane. Results of controlled experiments
276 revealed that the remarkable catalytic performance of both LDH@CGF and

277 LDH@PAN can be attributed to the excellent PMS activation capability of CuCo LDH.
278 Nevertheless, the metal iron leaching property and stability of composite membranes
279 with different nanocatalysts and/or supports warrant further, in-depth investigation.

280 The activation ability of catalytic membranes in dead-end filtration mode has been
281 tested through full recirculation of the filtrate. **Fig. 7(c)** presents the recirculation mode
282 as configuration A, and the continuous (non-recycling) mode experiments as
283 configuration B [23, 47]. In the recycling filtration mode, the filtrate entered the feed
284 tank under vigorous stirring, and samples were taken each membrane filtration cycle.
285 By adjusting the transmembrane pressure and residence time, the nanocomposite
286 membranes were able to control the degree of reaction in a manner that was easy to
287 operate. As a key characteristic of membrane filtration [48], water flux is intimately
288 linked to surface and structural features of the filter layer, which impact treatment
289 efficiency and energy consumption during operation. Sheng et al. [51] illustrated that
290 the water flux of the composite membrane increases in accordance with enhancement
291 of the C/O ratio of the GO/carbon nanotubes (CNTs) mats, with the ratio exhibiting a
292 linear relationship with the reduction degree of rGO flakes (**Table 2**). Furthermore, Fan
293 et al. [49] reported a new integrated system for phenol removal by combining a coal-
294 based carbon tube membrane with persulfate-AOPs.



295

296 **Fig. 7.** Typical composite membranes used in filtration mode reaction systems based on vacuum filtration:

297 (a) synthetic procedure, SEM images, and water treatment method for ZIF-67/PAN membrane (reprinted

298 with permission from [50], copyright 2017 Elsevier); (b) synthetic procedure, SEM images, digital

299 photos and water treatment method for CoCu LDH-CGF membrane and pristine CGF membrane.

300 (reprinted with permission from [27], copyright 2020 Elsevier); and (c) schematic diagram of the

301 experimental setup under recirculation mode (configuration A) and continuous mode (configuration B).

302 (reprinted with permission from [23, 47], copyright 2019 and 2020 Elsevier); the digital photograph

303 depicts elements in the filtration reaction system with recirculation and continuous modes (reprinted with

304 permission from [51], copyright 2020 Elsevier).

305 However, composite membranes prepared by vacuum filtration have poor

306 mechanical properties, which adversely impact on their long-term use in practice. As a

307 possible solution, high-efficiency nanocatalysts with CoFe alloy and CoFe_2O_4

308 encapsulated in N-doped microtubule composites were fabricated and immobilized into
309 PVDF (CFP) membrane [52]. The CFP membrane exhibited excellent
310 superhydrophilicity and high flux (1 463.7 L/(m²·h·bar), in accordance with SEM
311 images (**Fig. 8(a)**). The foregoing indicate that the powder catalysts served as pore-
312 forming agents to the PVDF membrane, thus allowing electrons to be transmitted
313 quickly without being affected by high mass transfer resistance. As evident in **Table 2**,
314 the CFP membrane achieves excellent, stable catalytic performance and low metal
315 leaching. After adding PMS, the CFP membrane not only maintained a high removal
316 rate of tetracycline degradation (more than 90%) in the humus coexistence system but
317 also effectively eliminated the adverse effects of membrane pollution, thus
318 demonstrating that the membrane possessed an excellent catalytic self-cleaning
319 property. As illustrated in **Fig. 8(b)**, biomimetic polydopamine and ZIF-67 decorated
320 polypropylene (PDA/ZIF-67@PP) membrane under Xenon lamp irradiation were
321 filtered with feed solution consisting of contaminants and PMS at 1 bar pressure [53].
322 Abundant active sites, such as carboxyl, amide, and phenolic hydroxyl occur in the
323 PDA layer, which can bind with Co ions during synthesis of ZIF-67. As a result, the
324 membrane exhibited especially desirable properties of recyclability, antifouling, and
325 self-cleaning during pollutant degradation. Hence, integration of catalytic oxidation
326 technology with membrane technology offers a broad prospect for overcoming fouling
327 [52, 53].

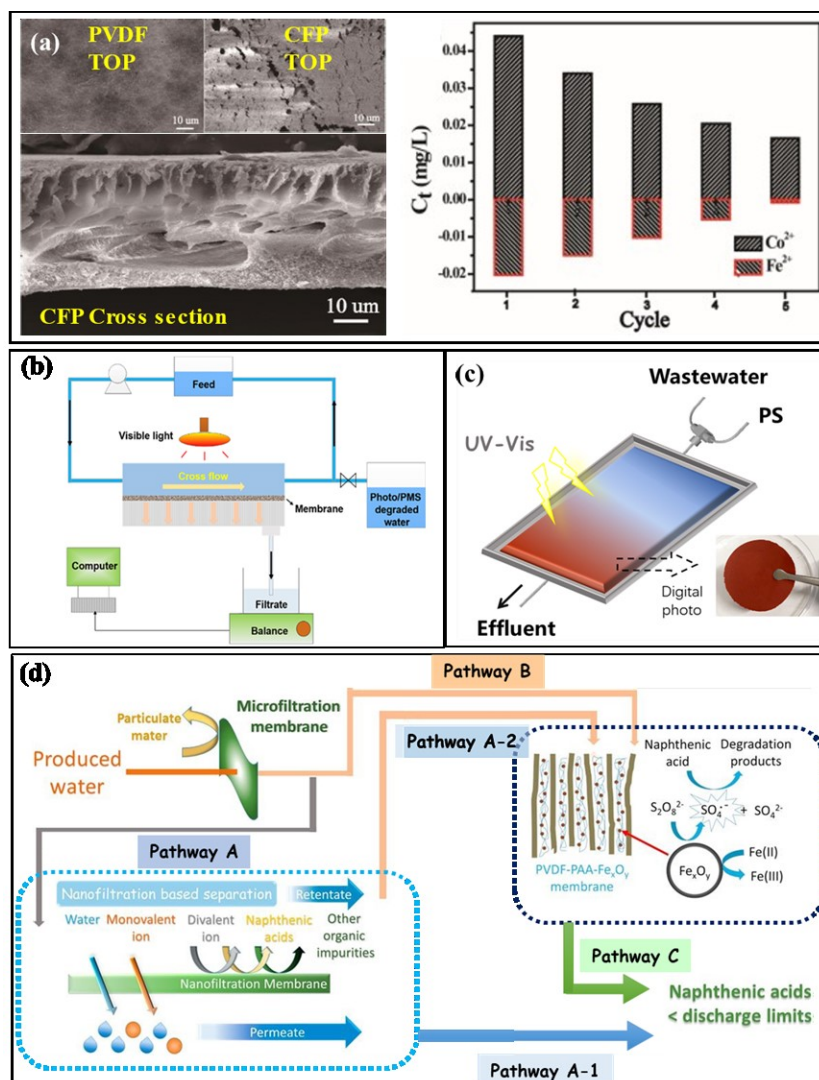
328 Another alternative water treatment unit design strategy is based on a fluidized
329 bed. Zhu et al. [54] demonstrated that an optimized α -Fe₂O₃ nanodisk/bacterial

330 cellulose composite membrane attained excellent PMS photodegradation performance
331 in both ordinary stirring and flowing bed states (**Fig. 8(c)**). Rich hydroxyl groups on
332 the bacterial cellulose benefited the accommodation and dispersion of $\alpha\text{-Fe}_2\text{O}_3$
333 nanodisks and helped enrich dyes on the surface. Furthermore, the membrane retained
334 high catalytic efficiency, especially in the flowing bed condition, and achieved long-
335 term durability over a range of flow rates. Compared to batch mode operation, the Fe_xO_y
336 functionalized membrane/PDS system has been found to have higher degradation
337 efficiency in the pressure filtration mode, as shown in **Fig. 8(d)** pathway A [55], and
338 that the diffusion resistance of the reactants limited accessibility of Fe_xO_y located in the
339 membrane matrix.

340 Apart from direct sewage treatment, functionalized membranes could be used
341 more cost-effectively through combination with nanofiltration membrane-based
342 separation to repair naphthenic acid in water containing highly concentrated total
343 dissolved solids (TDS). As seen in **Fig. 8(d)**, a nanofiltration membrane can remove
344 naphthenic acid from large volumes of produced water via pathway B, resulting in
345 permeation comprised of discharge quality water (<10 mg/L) that leaves the operating
346 unit via pathway A-1. Finally, the retentate stream should be treated by Fe_xO_y
347 functionalized membrane/PDS system (AOP, pathway A-2) to meet the emission
348 standards for naphthenic acid and discharge via pathway C.

349 Pollutants in the feed solution are limited near the catalyst surface when the feed
350 passes through the active layer of the membrane by way of voids between the catalysts.
351 In the surface reaction, the concentration of short-lived ROS is significantly higher than

352 that of the bulk. Thus, the pollutants are constantly and rapidly removed from the
 353 reaction zone, leading to a method of recovery of potable water that is more feasible,
 354 energy-intensive, and cost-effective. However, the amount of Fe leaching was very high
 355 (see **Table 2**). Therefore, further research, including long-term stability tests and
 356 technoeconomic analysis, is needed to verify the feasibility of the combination strategy
 357 in practical application.



358
 359 **Fig. 8.** Typical composite membrane used in filtration mode reaction systems based on cross-flow
 360 filtration: (a) top-section SEM images of pristine PVDF membrane and CoFe-NMTs-800/PVDF
 361 membrane, cross-section SEM image of CoFe-NMTs-800/PVDF membrane, and metal leaching
 362 concentration after five runs in CoFe-NMTs-800/PMS system (reprinted with permission from [52],

363 copyright 2021 Elsevier); (b) schematic representation of integration of nanofiltration membranes and
364 Fe_xO_y functionalized membranes for treatment of naphthenic acid from produced water (reprinted with
365 permission from [55], copyright 2017 Elsevier); (c) schematic depiction of the Flowing Bed Device
366 (reprinted with permission from [54], copyright 2018 ACS); and (d) cross-flow filtration apparatus with
367 light irradiation (reprinted with permission from [53], copyright 2019 Elsevier).

368 The carbon-based catalytic membrane is likely to become a substitute for metal
369 catalysts, thus avoiding secondary pollution arising from metal leaching into the treated
370 water. As discussed above, only three studies have employed carbon-based catalytic
371 membranes in which the catalytically active phase is placed on top of a certain support
372 (Polytetrafluoroethylene (PTFE) [47, 56] or nylon [51]). Vieira et al. [23] conducted a
373 study of N-doped rGO (rGO-N) nanocatalysts, during which rGO-N-PTFE partially
374 disintegrated during continuous operation and/or drying. By contrast, rGO-N-PVDFs
375 exhibited structural and catalytic stability, demonstrating resistance toward fouling
376 phenomena. However, the performance of the treatment process declined dramatically
377 when surface water was used instead of ultrapure water in an early trial.

378 **3. Specific materials systems**

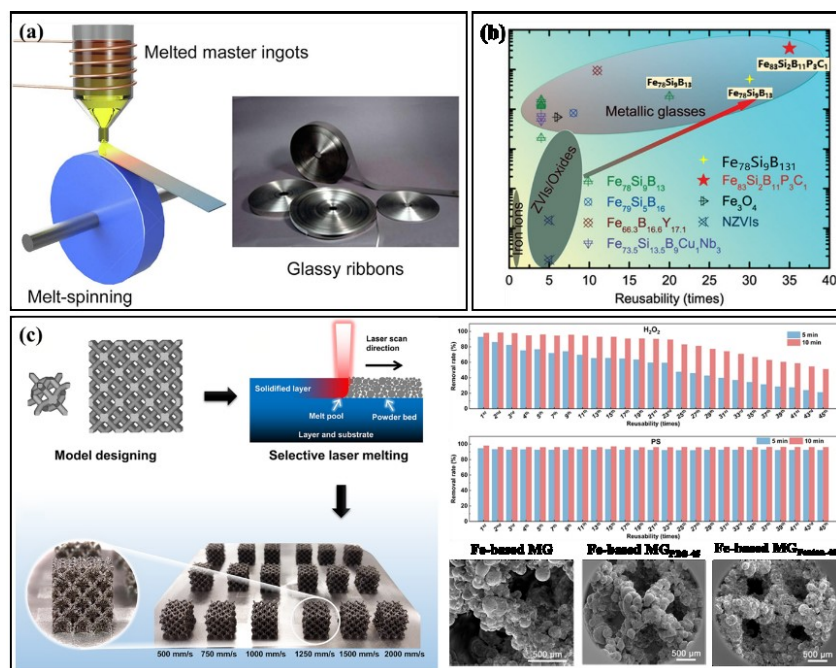
379 Metallic glasses (MGs) have grown in popularity in the field of wastewater
380 remediation catalysis due to their great catalytic activity, high strength, elasticity,
381 superior corrosion and wear resistance properties, and unique soft/hard magnetism [57,
382 58]. MG ribbons prepared by melt-spinning usually exhibit high efficiency, reusability,
383 and sustainability [59]. Moreover, melt-spinning techniques have proved cost-effective
384 when applied to industrial-scale water remediation [57].

385 Liang et al. [60] manufactured various iron-based MGs and applied them to
386 persulfate activation systems. Unlike powder catalysts, MG ribbons present a metallic,
387 flexible appearance (**Fig. 9(a)**) benefiting ease of operation, low cost, and control of
388 excess reaction [60]. Moreover, as-obtained MGs in persulfate-AOPs have outstanding
389 reusability, exceeding $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ MG [61, 62], $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Cu}_1\text{Nb}_3$ MG [63], and
390 $\text{Fe}_{83}\text{Si}_2\text{B}_{11}\text{P}_3\text{C}_1$ MG by factors of 30, 10, and 35 (see **Fig. 9(b)**) [64]. Such a durable
391 and efficient environmental catalyst has great potential in practical wastewater
392 remediation. The exact mechanism by which atoms participate and electrons are
393 transferred in MGs with amorphous structures is poorly understood, especially when
394 MGs are used as a catalyst. Jia et al. [61] stated that persulfate activation can be
395 attributed to ferrous (Fe^{2+}) in solution rather than in solid form in a
396 $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ /PDS/ultraviolet-visible light (UV-Vis) reaction system. Even so, in a more
397 recent study [62], Liang et al. utilized ZVI as an electron donor to activate PDS and
398 generate $\bullet\text{OH}$ and ferrous ions via a four-electron pathway involving water oxidation
399 in $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ MG. Further reaction of Fe^{2+} with persulfate then produced $\text{SO}_4^{\bullet-}$.
400 Similarly, in a $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ /PMS/UV-Vis reaction system, direct surface corrosion of
401 $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ ribbons by PMS generated $\text{SO}_4^{\bullet-}$. As the reaction progressed, ZVI on the
402 $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ MG surface was consumed by persulfate to produce ROS (used for pollutant
403 removal), after which UV-Vis irradiation accelerated the surface corrosive process.
404 Buried Fe was gradually covered by SiO_2 , which in turn gradually changed from Si on
405 the ribbon surface during persulfate activation, thus preventing further iron leaching.
406 During mechanical stirring, SiO_2 was easily shaken off, meaning that $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$

407 ribbons could react with peroxide when necessary, thereby realizing the high reusability
408 of $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ ribbons. However, when the service time was over 30 cycles, the
409 $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ ribbon became gradually exhausted due to the lack of a SiO_2 layer to prevent
410 further iron leaching, causing secondary pollution of the dye solution [61].

411 In recent years, three-dimensional (3D) printing, also known as additive
412 manufacturing, has emerged as a novel method for simplifying the single process of
413 material manufacture. Liang et al. [60] successfully prepared Fe-based MGs with 3D
414 diamond dodecahedron microstructure using selective laser melting (SLM) according
415 to a predesigned 3D computer-aided design model (**Fig. 9(c)**). Their results showed that
416 efficiency remained almost unchanged after being used repeatedly 45 times, and that
417 the surface after use was still as fresh as the original MG matrix composite. The ultra-
418 stable reusability of the MG matrix composite in persulfate-AOPs means that it
419 currently has the greatest reusability and catalytic potential among prospective catalysts.
420 Moreover, it is likely that even higher reusability will be achieved in future.

421 Follow-up studies have focused on optimizing the catalytic performance of MGs
422 by accurately regulating their chemical composition and atomic structure. Even so, the
423 link between structural heterogeneity and catalytic performance of MGs still needs to
424 be confirmed, and the mechanism (or origin) behind their high catalytic performance
425 has yet to be identified.



426
 427 **Fig. 9.** Typical metallic glasses used in persulfate-AOPs: (a) schematic diagram of melt-spinning process
 428 for manufacturing glassy ribbons and an optical photograph of typical product (reprinted with permission
 429 from [57], copyright 2019 Elsevier); (b) comparison of the catalytic stability of different iron-based
 430 materials (reprinted with permission from [64], copyright 2019 Wiley); and (c) synthetic procedure, SEM
 431 images, and reusability of as-produced Fe-based MG matrix composite (Fe-based MG_{PDS-45}: the Fe-based
 432 MG_{PDS-45} after 45-times use in PDS activation process; Fe-based MG_{Fenton-45}: the Fe-based MG_{PDS-45} after
 433 45-times use in Fenton-like reaction process) (reprinted with permission from [60], copyright 2020
 434 Elsevier).

435 Aerogels are a class of highly porous lightweight materials with an average pore
 436 size in the tens of nanometers, and are sublimated from the liquid components of
 437 traditional gels (usually by freeze-drying or critical point drying) [65, 66]. Cellulose
 438 aerogels have wide application prospects due to their high specific surface area, uniform
 439 pore size distribution, biodegradability, recyclability, and low cost [65, 67]. As
 440 indicated in **Table 3**, ZIF-9 and ZIF-12 were decorated on cellulose aerogels with
 441 macroscopic 3D structure and low weight (**Fig. 10(a)**), and the aerogels then used to
 442 activate PMS effectively [68]. Carbon aerogels are a new class of carbonaceous

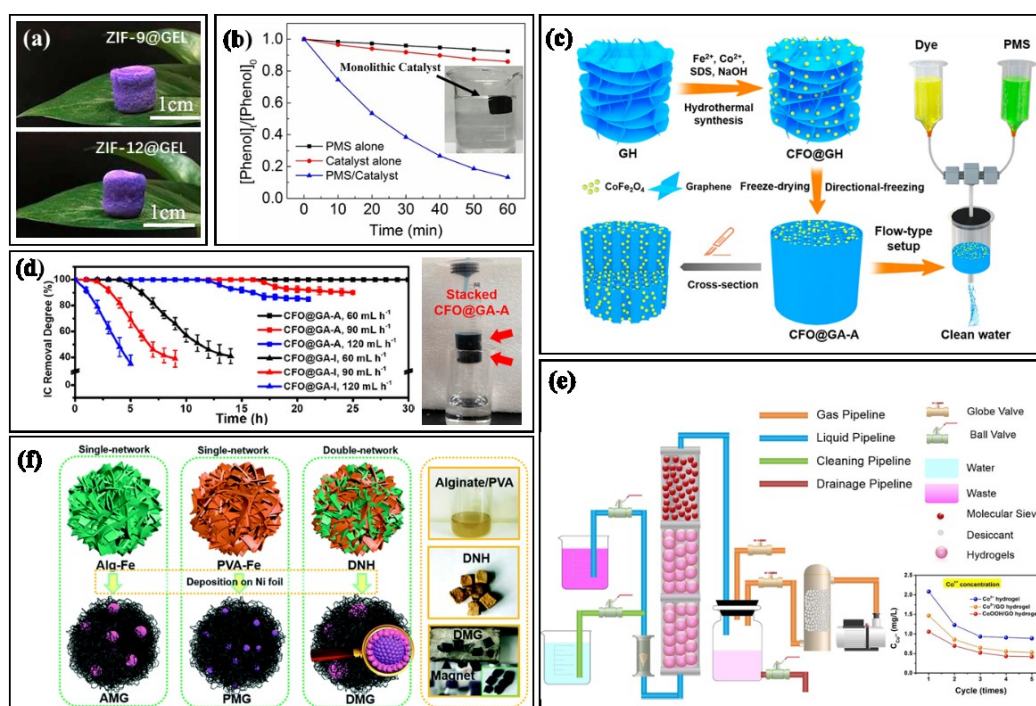
443 materials that feature an interconnected framework, possess large specific surface areas,
444 and have a hierarchical pore structure. Co-doped carbon aerogels (CoCA) activate PMS
445 at lower activation energy, effectively removing organic pollutants while maintaining a
446 low metal ion leaching rate [69] (**Table 3**). As evident in **Fig. 10(b)**, CoCA floats
447 beneath the surface of the aqueous solution and can be completely removed without
448 any change in form.

449 Flow-type configurations are suitable for continuous treatment of wastewater, thus
450 expanding the applicability of aerogels. However, traditional isotropic graphene
451 aerogels and foams contain randomly dispersed graphene sheets, which would cause
452 erosion and seriously reduce the flux. Compared with isotropic CoFe_2O_4 @graphene
453 hybrid aerogels (CFO@GA-I), anisotropic CoFe_2O_4 @graphene hybrid aerogels
454 (CFO@GA-A) have higher flux, lower metal ion leaching concentration, and much
455 better, stable catalytic performance (**Table 3** and **Fig. 10(c)**) [70]. Moreover, CFO@GA
456 aerogels can be stacked together to meet complex application conditions (**Fig. 10(d)**).

457 Hydrogels have rigid but soft elastic networks that permeate one another, giving
458 them higher mechanical strength and strain capacity than aerogels [71]. Among
459 hydrogels, hydrophilic material offers an appropriate support conducive to mass
460 transfer in water treatment, and which reduces the dissolution of metal ions [72].
461 Polyacrylic acid (PAA) is a kind of ionic hydrogel with polar carboxyl groups (-COOH)
462 that exhibit high adsorption efficiency toward metal ions and strong interaction with
463 water. After successfully synthesizing a 3D composite hydrogel based on
464 CoOOH /graphene oxide (CoOOH/GO) and PAA hydrogel precursor, Yi et al. [73]

465 constructed an automatic water treatment system under laboratory conditions (**Fig.**
 466 **10(e)**). Duan et al. [74] discovered the formation of chemical bonds between Co_3O_4 and
 467 graphene in a 3D hierarchical Co_3O_4 /graphene hydrogel composite with high specific
 468 surface area, stable structure, and significantly heterogeneous surface synergistic effect
 469 (**Table 3**). Later, the dual network hydrogel consisted of two interpenetrating networks
 470 with enhanced structural properties [75-77]. Meanwhile, Zhuang et al. [78] prepared a
 471 double-network hydrogel templated FeS /graphene (DMG) based on a double-network
 472 hydrogel containing Fe. This not only facilitated the formation of high-quality graphene
 473 at a low cost but also achieved intensive interactions between Fe and graphene, as
 474 shown in **Fig. 10(f)**.

475 Overall, immobilizing as-prepared nanocatalysts into hydrogel can reduce the
 476 leaching concentration of metal ions based on specific chemical bond formation, thus
 477 avoiding the loss of nanocatalysts from the reactor [78-80].



478
 479 **Fig. 10.** Typical aerogels and hydrogels used in persulfate-AOPs: (a) photographs of ZIF-based hybrid

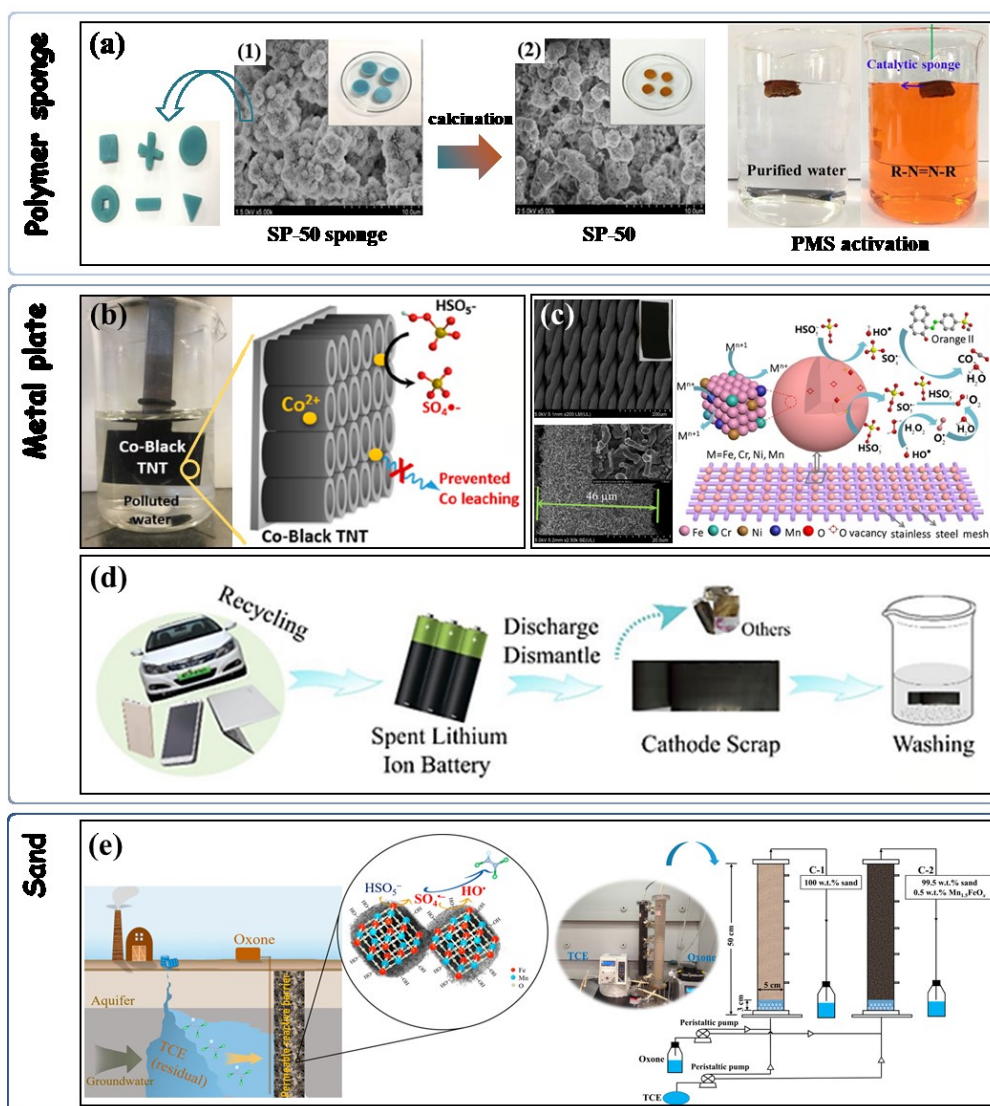
480 aerogels (reprinted with permission from [68], copyright 2018 Elsevier); (b) elimination of phenol under
481 different conditions, and photographs of CoCA in water (inset) (reprinted with permission from [69],
482 copyright 2020 Elsevier); (c) schematic illustration of the preparation of an anisotropic CoFe₂O₄@GA-
483 A and its application for the continuing treatment of wastewater with a flow-type setup (reprinted with
484 permission from [70], copyright 2020 Elsevier); (d) plots of removal efficiencies of organic pollutants
485 for CoFe₂O₄@GA-A and CoFe₂O₄@GA-I at different flow rates, and a photograph of real-time catalytic
486 experiments using CoFe₂O₄@GA-A and stacked CoFe₂O₄@GA-As (each red arrow indicates a piece of
487 CoFe₂O₄@GA-A) (reprinted with permission from [70], copyright 2019 ACS); (e) schematic illustration
488 of degradation equipment flowchart based on CoOOH/GO hydrogel composite (reprinted with
489 permission from [73], copyright 2019 ACS); and (f) preparation routine and photographs of samples
490 (reprinted with permission from [78], copyright 2020 RSC).

491 Apart from the abovementioned support materials, many other uncommon
492 supports, such as polymer sponges [81], metal plates [82-85], and sand [86, 87], have
493 been studied for the immobilization of persulfate catalysts, as listed in **Table 4**. These
494 materials have two benefits: easy procurement in massive quantities and cost-efficiency
495 for large-scale procedures.

496 Using a sponge catalyst composed of polyvinyl alcohol (PVA) as support, a
497 chemically bonded Co₃O₄ nanoflower sponge (SP-50) was prepared with good
498 mechanical and elastic properties, adjustable geometry, multi-porosity, and multi-
499 dimensionality. As shown in **Fig. 11(a)**, the catalytic sponge floats on water and, more
500 importantly, can be easily recycled. Due to the use of bonding materials or organic
501 adhesives that limit contact between catalyst and target matrix, many published works
502 concerning immobilized catalysts for persulfate activation have recently focused on
503 direct *in situ* growth catalysts situated on metal plates. For instance, Hoffmann et al.
504 [83] employed cobalt-doped Black TiO₂ nanotubes (Co-Black TNT) as PMS activators

505 to degrade organic pollutants (**Fig. 11(b)**). Moreover, stainless steel was used for cost-
506 effective bifunctional supports and catalysts after appropriate pretreatment, owing to its
507 mechanical firmness, corrosion resistance, conductivity, and ease of scale-up (**Fig.**
508 **11(c)**) [88]. In another study, waste from a sandwich cathode containing LiMn_2O_4 was
509 directly used as a catalyst to activate PMS for removal of organic pollutants in water,
510 which were then entirely (and easily) collected from the reaction system (**Fig. 11(d)**)
511 [84].

512 As previously remarked, the continuous flow reactor system has two notable
513 characteristics: ease of operation and low energy consumption, thus marking a
514 milestone in the practical use of AOPs. Considering pollutant removal performance and
515 operation process cost (see **Table 4**), CoFe_2O_4 was placed onto a quartz sand support
516 ($\text{CoFe}_2\text{O}_4\text{-QS}$) and packed into a column reactor to activate PMS [86]. Similarly, a
517 systematic study evaluated the feasibility of using a sand column reactor, consisting of
518 BFMO (i.e., $\text{Mn}_{1.5}\text{FeO}_{6.35}$) and sand, to activate PMS *in situ* for the treatment of
519 trichloroethylene-contaminated water (**Fig. 11(e)**) [87]. The current findings indicate
520 that BFMO is a very stable and long-acting catalyst for persulfate-based *in situ* chemical
521 oxidation (ISCO), which may be employed for groundwater remediation.



522

523 **Fig. 11.** Specific materials based on uncommon supports prepared for persulfate activation: (a) digital
 524 images of as-obtained SP-50 sponge cut into different geometrical shapes; SEM images of (1) SP-50
 525 sponge and (2) SP-50; digital photograph of SP-50/PMS reactive process (reprinted with permission
 526 from [81], copyright 2019 Wiley); (b) digital photograph of Co-Black TNT/PMS reactive process and
 527 the activation mechanisms (reprinted with permission from [83], copyright 2019 ACS); (c) SEM images
 528 and activation mechanisms of the stainless-steel/PMS system for degrading organic contaminants
 529 (reprinted with permission from [85], copyright 2020 Elsevier); (d) recycling process of spent lithium-
 530 ion battery (reprinted with permission from [84], copyright 2020 ACS); and (e) schematic illustration of
 531 PMS-based *in situ* chemical oxidation process and the sand columns (5 cm internal diameter × 50 cm
 532 length) working mode (reprinted with permission from [87], copyright 2020 ACS).

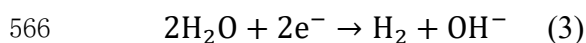
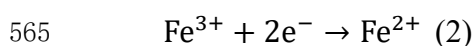
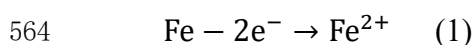
533 4. Electrocatalytic auxiliary systems

534 Electrochemical treatment is conducted by applying a potential to the anode and
535 cathode in a reactor. In this process, influent is used as the electrolyte, with chemicals
536 added as necessary to improve conductivity. Direct degradation of targeted pollutants
537 occurs through charge transfer on the electrode surface. Anode and cathode processes
538 can also indirectly promote the removal of pollutants through reaction with
539 electrochemically generated ROS. Construction of an electrochemically-activated
540 persulfate process can be achieved by means of a sacrificial anode system, electric
541 filtration system, and photoelectrocatalytic system, as shown in **Fig. 2**. These reaction
542 systems improve degradation efficiency while reducing power consumption and cost.
543 They are particularly applicable to decentralized processes because of their efficiency
544 and stability at small scale and ease of automatic control by current/voltage adjustment.

545 Electrochemical systems with addition of iron ions (Fe^{2+} or Fe^{3+}) for persulfate
546 activation were initially implemented to remove organic pollutants [89-91]. It was
547 found unexpectedly that Fe^{2+} can regenerate from the cathodic reduction reaction in
548 Fered-Fenton and other electro-Fenton processes [89], thereby overcoming the problem
549 of Fe^{2+} regeneration after transformation to Fe^{3+} . Thus, the reaction systems could
550 possess continuous persulfate catalytic capability; however, a large amount of iron
551 sludge would inevitably be produced.

552 Later, electrochemical enhancement of persulfate-AOPs, with iron sheets used as
553 sacrificial anodes, was used to promote destruction of organic contaminants (**Table 5**).
554 In the oxidation process, once a current was applied between the anode and cathode, a

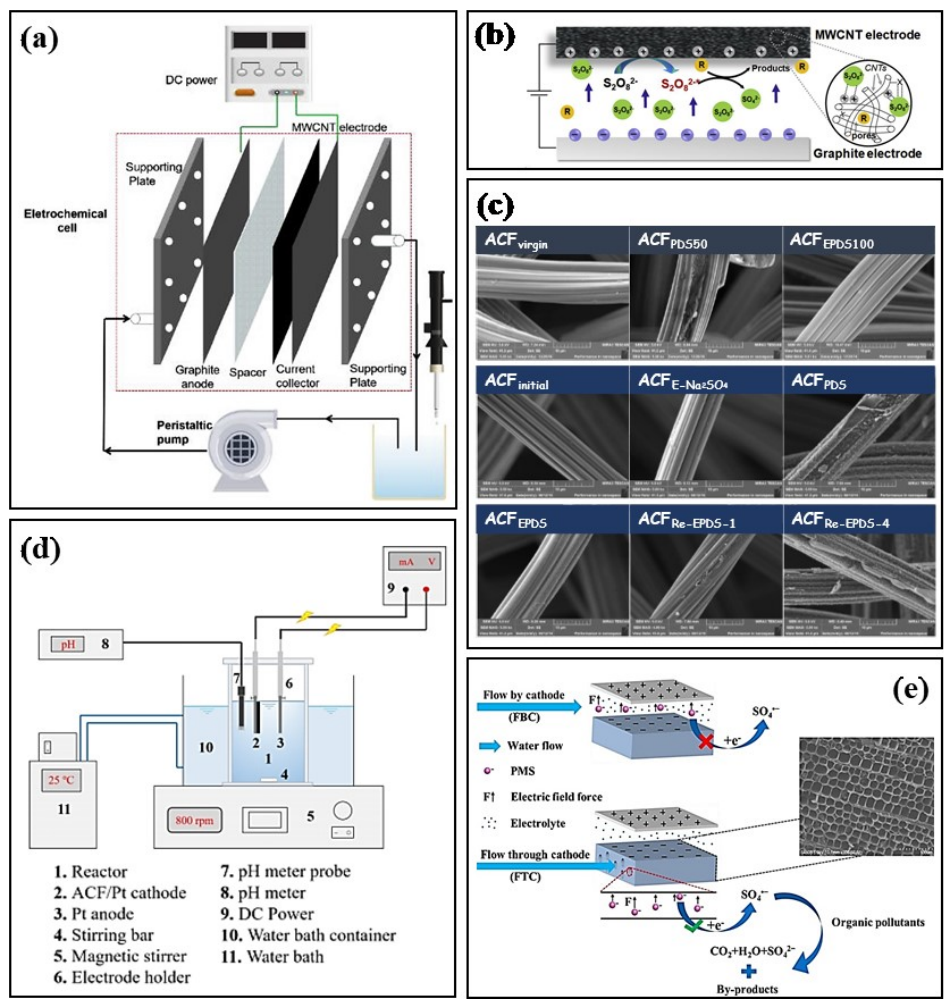
555 predetermined amount of persulfate was then added to the reactor. Ferrous ions
556 produced by sacrificial iron anodes mediated the persulfate decomposition. In **Fig. 2**,
557 the production rate of Fe^{2+} is controlled by the positive current of the iron anode,
558 according to the reaction expressed by Eq. (1). Consumed Fe^{2+} is regenerated on the
559 cathode, satisfying Eq. (2). In turn, OH^- forms and may restore the pH value and redox
560 potential, thus inhibiting heavy metals from leaching into the subsurface, as expressed
561 by Eq. (3). Therefore, the iron electrode can be readily introduced into a polluted region
562 to control persulfate activation *in situ*, thus minimizing the potential loss of persulfate
563 during injection and transportation [92].



567 This sacrificial anode reaction system has several important advantages: low cost,
568 substantially reduced energy consumption, and remarkably increased pollutant
569 degradation. However, the approach has been criticized due to the increased operating
570 cost incurred from disposal of the iron sludge byproduct [93, 94]. Song et al. [95]
571 detected the electrochemical activation of PDS at the Ti/Pt anode, whereas Farhat et al.
572 [96] studied the PDS activation performance of a boron-doped diamond electrode.
573 From the foregoing, it was found that discharge is the dominant factor in the
574 electrochemical activation processes of PDS, which induces the generation of the PDS
575 transition state. Hence, the electrode only plays a role in electron transfer and does not
576 directly participate in persulfate activation.

577 In capacitive deionization (CDI), application of a direct current voltage that is
578 lower than the water breakdown voltage (1.23 V) on the porous electrode can induce
579 ions or charged organic groups in an aqueous solution to gather quickly on the surface
580 of the polarized electrode and attract oppositely charged species to their surfaces; this
581 phenomenon is called the illegal Larch process [97]. Due to their great conductivity,
582 large specific surface area, and chemical stability, CNTs have been widely used as
583 electrode materials for CDI to remove organic pollutants from wastewater [93, 98]. As
584 reported, multi-walled carbon nanotube (MWCNT) cathodes were synthesized by a
585 casting method using PVA as binder and graphite sheet as support [93]. As shown in
586 **Fig. 12(a)**, during each operation, a certain amount of stock liquid was continuously
587 pumped into the cell by a peristaltic pump until the discharged liquid returned to the
588 electrochemical cell. Interaction between persulfate and carbon surface functional
589 groups has been found to play a remarkable role in persulfate-AOPs. Electrochemical
590 reactions usually occur on the electrode surface, and the generated free radicals are
591 usually adsorbed on the electrode surface, although they are difficult to disperse
592 thoroughly in the bulk solution [95]. However, as shown in **Fig. 12(b)**, activation and
593 electro-adsorption of PDS on the surface of a porous carbon electrode can promote
594 electron transfer between the generated active substance and target pollutant, which is
595 conducive to the degradation of pollutants. Correspondingly, the MWCNT electrode
596 reduces the working voltage and enhances PDS activation performance to degrade
597 organic pollutants simultaneously. The results showed that organic compounds on the
598 electrode surface and the generated reaction species helped promote the electron

599 transfer progress through the synergistic effect of electro-adsorption of pollutants and
 600 electrochemical activation of PDS.



601
 602 **Fig. 12.** Electrocatalytic auxiliary systems constructed for persulfate activation: (a) schematic diagram
 603 of electrochemical activation of PDS and aniline degradation experiment (reprinted with permission from
 604 [93], Copyright 2018 Elsevier); (b) proposed mechanism of organic pollutant removal by asymmetric
 605 quasi capacitive deionization (AQCDI)/PDS/1.2V system (R represents the organic molecule and X
 606 represents the active sites in MWCNTs) (reprinted with permission from [98], copyright 2019 Elsevier);
 607 (c) SEM images of the ACF in different reaction systems (reprinted with permission from [99, 100],
 608 copyright 2018 and 2020 Elsevier); (d) schematic representation of ACF Regeneration experimental
 609 setup (reprinted with permission from [101], copyright 2020 ACS); and (e) schematic diagram of the E-
 610 PMS activation mechanism via FTC and FBC strategy (reprinted with permission from [102], copyright
 611 2020 ACS).

612 Likewise, Han et al. [103] investigated an enhanced electric activated carbon fiber

613 (ACF)/ferric iron/PDS (ACF-E/Fe³⁺/PDS) process in which ACF served as a cathode.

614 The results showed that the ACF cathode did not play a substantial role in activating

615 PDS, and a large number of iron ions were deposited on the cathode surface, indicating

616 good adsorption performance. Liu et al. [100] investigated the influence of operational

617 conditions, including pH, electrode potential temperature, peroxydisulfate

618 concentration, and water matrix. As listed in **Table 5**, ACF-E/PDS achieved a high

619 pollutant removal rate of 98.78% in 30 min with high PDS concentration [103], proving

620 that sufficient PDS can efficiently and quickly degrade pollutants. Therefore, in the

621 ACF-E/PDS system, the economic benefits and environmental effects of PDS

622 consumption or iron sludge disposal require further research. As depicted in **Fig. 12(c)**,

623 SEM images of ACF_{virgin} (virgin ACF) and ACF_{EPDS100} (electro PDS (E-PDS) reacted

624 ACF after reutilization of 100 times) presented relatively neat surfaces, except that PDS

625 oxidation caused the surface of ACF_{PDS50} to become cracked and rough (the case

626 corresponding to PDS reacted ACF after 50-times reutilization). This finding may be

627 attributed to electrons on the cathode reducing damage by ROS or PDS to ACF while

628 maintaining continuous generation of SO₄^{•-} without depleting the electron supply

629 residues of ACF. Furthermore (see **Table 5**), addition of PMS evidently improved the

630 current in the MnFe₂O₄/carbon fiber paper (CFP) electrode [104] as well as in the

631 PDA/CF cathode [105], indicating that the reaction between PMS and MnFe₂O₄/CFP

632 or PDA/CF was energetically favorable. Moreover, the applied bias and photogenerated

633 electrons of the photoanode facilitated the formation of different valence state ions in

634 MnFe₂O₄, which activated PMS for SO₄^{•-} induction and catalytic stability of the

635 $\text{MnFe}_2\text{O}_4/\text{CFP}$ cathode [104].

636 This kind of cathodic catalyst protection phenomenon also exists in cathodic
637 material regeneration, such as the *in situ* regeneration of phenol-saturated ACF by an
638 electro-PDS process [99]. The surface of ACF_{PDS} (virgin ACF immersed in the PDS
639 system for 180 min) was attacked and became covered with a mass of attachments
640 because ACF acted as a catalyst rather than an initiator. Compared with ACF_{PDS} , the
641 morphological characteristics and pore texture ACF_{EPDS} (virgin ACF immersed in PDS
642 with 1 A current applied for 180 min) and $\text{ACF}_{\text{initial}}$ coincided, such that the pore
643 remained almost unchanged.

644 By comparison with conventional electrochemical regeneration, the E-PDS
645 process can regenerate exhausted ACF and mineralized desorption pollutants
646 simultaneously by activating PDS with much lower energy consumption (1/6).
647 However, a large number of oxides and oligomers produced by anodic oxidation can be
648 re-adsorbed to carbon, resulting in a regeneration efficiency of only about 60%. What
649 is worse is that, compared with $\text{ACF}_{\text{Re-E-PDS-1}}$ (phenol-saturated ACF regenerated in the
650 E-PDS process for one cycle), the structure of $\text{ACF}_{\text{Re-E-PDS-4}}$ (phenol-saturated ACF
651 regenerated in E-PDS process for four cycles) deteriorated severely, as shown in the
652 SEM image in **Fig. 12(d)**. Therefore, after undergoing regeneration four times, the
653 regeneration efficiency decreased to less than 40%. As reported, the electro-PMS (E-
654 PMS) treatment progress is more suitable for the regeneration of activated carbon [101].
655 Phenol-saturated activated CF was regenerated *in situ* using an electro PMS reaction
656 system, as shown in **Fig. 12(d)**. This reaction system mineralized the desorbed

657 contaminants (81.90%) while consuming only one-tenth of the energy. Even after ten
658 cycles, regeneration remained effective at around 60% of the initial value, and cathodic
659 polarization during E-PMS regeneration effectively protected the physical structure and
660 chemical properties of ACF. Nevertheless, ACF had a minor impact on PMS self-
661 decomposition, and its role in E-PMS was distinct from that of the E-PDS process.
662 Therefore, there is an urgent need to conduct more systematic, deeper studies on the
663 performance, experimental setup, and reaction mechanisms of combined
664 electrochemical and persulfate activation, which is considered a sustainable, efficient,
665 low-toxicity technique for the remediation of contaminated water.

666 Several studies have activated persulfate on a plate cathodic surface, but achieved
667 poor performance (see e.g. Zhang et al. [102]). Electrostatic repulsion tends to drive
668 persulfate anions away from the cathode because both anions and cathode are
669 negatively charged. Given the poor breakdown of persulfate and the low creation of
670 radicals, the contaminants then degrade slowly. Two possible approaches to
671 overcoming this problem are to shorten the diffusion distance and to increase collision
672 and contact between persulfate anions and the cathode. Zhang et al. used carbonized
673 wood with well-ordered channels as the cathode (**Table 5**), and performed a set of
674 comparative experiments for a flow-by cathode (FBC) and a flow-through cathode
675 (FTC) (**Fig. 12(e)**) to confirm that the microchannels of the FTC could boost the
676 creation of radicals, and organics degradation. Cycling tests revealed that this FTC was
677 quite stable. As a result, activating persulfate in FTC is an effective technique for
678 increasing radical yield and availability.

679 The electro-activated persulfate process mainly involves an electron transfer
680 reaction. Increases in current density and residence time tend to improve the number of
681 electrons transferred and enhance the efficiency of the electrochemical activation.
682 Several issues remain unresolved for all electrochemical–persulfate reaction systems.
683 Future research should consider energy consumption, electrode manufacturing costs,
684 power consumption, persulfate consumption, and loss in treatment capacity. Future
685 research should also consider how to avoid secondary pollution by excess PMS and its
686 associated reaction products, and how to recycle principal byproducts such as SO_4^{2-} .
687 Furthermore, such studies should not only be conducted in the laboratory but also
688 expanded to pilot scale.

689 **5. Challenges and outlook**

690 The integration of various conventional research disciplines, such as materials
691 science for the creation of purpose-driven catalysts and water treatment engineering for
692 the construction of practical reactors, has led to the effective application of
693 nanoparticle-based AOPs for water remediation. Correspondingly, rapid advances have
694 been achieved over the past few years in the emerging field of persulfate-based
695 immobilized-catalyst systems. This review article summarizes current developments
696 concerning nanocatalyst immobilization in persulfate-AOPs for target contaminant
697 removal. Various immobilization techniques onto supports, including membrane-based
698 reaction systems (immersion mode, filtration mode), electrocatalytic auxiliary systems,
699 and other supports (metallic glasses, aerogels, and hydrogels, or specific materials), are

700 discussed.

701 Compared with common nanocatalyst reaction systems, the immobilized-catalyst
702 system can bypass the separation problem to reduce scour and prevent aggregation by
703 anchoring nanoparticles onto porous or large-particle carriers. As a result, great effort
704 has been devoted to exploring suitable support substances for nanocatalysts and
705 designing reactors that cope with the changing environment for targeted pollutant
706 removal. Meanwhile, a series of studies have been carried out to gain insight into the
707 persulfate activation mechanism. Even so, considerable challenges remain regarding
708 high-performance reactors and the practical applications of persulfate-based AOPs.

709 To ensure excellent activation performance and high reusability of next-generation
710 multifunctional treatment systems, it is necessary to develop advanced reactors,
711 incorporating advances in materials science and a fundamental understanding of key
712 mechanisms. For example, direct evidence is still lacking for the outer- and inner-sphere
713 connection between nanocatalysts and supporting materials. Meanwhile, interactions
714 remain uncertain among catalysts, persulfate, and targeted pollutants. Although
715 laboratory studies have been undertaken to develop immobilized catalysts with simple
716 recycling operation and excellent catalytic performance, the application and
717 commercialization of such technology is quite low in more complicated situations.
718 Future studies are expected to employ persulfate-AOPs at pilot and semi-industrial
719 scales with the goal of reactor design and the focus on engineering issues.

720 In terms of the prospects for persulfate-based immobilized-catalyst systems, we
721 propose the following foci:

722 (1) *Determine a universal design principle by which to optimize the structure and*
723 *catalytic performance of heterogeneous catalysts.* In practice, the optimization of
724 electronic characteristics and elemental composition of nanoparticles plays a
725 remarkable role in catalytic processes. Through careful material design and theoretical
726 calculations, it is possible to prepare a catalyst with amazing performance. Furthermore,
727 reaction active sites and reaction pathways to the catalyst can be fully understood.
728 Theoretical calculation and *in situ* characterization are two powerful techniques to
729 advance reaction mechanisms, both of which are instructive in determining design and
730 preparation rules for high-performance materials. Moreover, many state-of-the-art
731 nanoparticles are notable for environmental applications, but have yet to make a
732 significant impact in the field of water treatment. Covalent organic frameworks (COFs),
733 for example, are an attractive new form of porous organic nanomaterials with desirable
734 properties, including a completely organic metal-free backbone, low mass density, well-
735 defined topology, structural variety, high heat resistance, and permanent porosity. An
736 effective, facile method for fabricating flexible, free-standing pure COF membranes
737 has been described in a previous study, thus allowing development of new forms of
738 membrane-based persulfate-AOPs [106]. Furthermore, based on the mononuclear
739 nature of the catalytic site, single-atom catalysts possess superior atomic utilization
740 efficiency, thus inheriting the advantages of homogeneous and heterogeneous catalysts.

741 (2) *Optimize the combination of active materials and supporting substances.* The
742 catalyst preparation stage pertains to reactor design and systems engineering. Here the
743 activity and stability of catalysts are only two of the key factors. The goal is to improve

744 the effective utilization of persulfate-AOPs. In most cases, immobilized-catalyst
745 systems are inherently mass transfer-limited. Correspondingly, the approach is based
746 on nanocatalysts with outstanding, stable catalytic capability, which exploit the
747 maximized surface area of the nanoscale active material and the support material
748 architecture. Additional studies should thus reveal the relationship between the
749 excellent catalytic performance of nanocatalysts and the structural properties of their
750 supports in order to guide reactor design in systems engineering. Given their
751 widespread applications, the as-expected immobilized catalysts must be manufactured
752 at industrial scale (in tons), resulting in a stable, mature market. All the foregoing
753 advances, including catalytic performance, stability, flexibility, and cost-efficiency, are
754 aimed at the development of new reactors.

755 (3) *Solve problems of decreased performance in various complex water matrices*
756 *and formation of reaction byproducts.* Most of the studies examined in this review
757 detected the removal effect of target pollutants using synthetic water to evaluate the
758 catalytic capability of catalysts, hence, the lack of background organic content.
759 However, due to competitive adsorption onto catalyst surfaces and radical scavenging
760 in an aqueous solution, natural organic matter (NOM) is commonly recognized to
761 reduce persulfate-AOP performance. The remarkable spatiotemporal changes that take
762 place in water quality parameters (e.g. target pollutant concentration, turbidity, various
763 coexisting ions, and pH) are inherent challenges that have often been overlooked at
764 laboratory scale. Despite efforts to recreate realistic settings, the absence of defined
765 experimental methodology has made it difficult to obtain a quantitative evaluation of

766 the actual processing effect of persulfate-AOPs. In turn, this has limited effective
767 technology transfer and commercialization. It should be noted that the majority of the
768 research reviewed herein focused on the degradation of single or a few types of
769 pollutants. In actual sewage, many types of pollutants co-exist, and so the cooperative
770 inhibition of different types of pollutants merits further in-depth research. Hence, future
771 studies are expected to employ persulfate-AOPs at pilot- and semi-industrial scales,
772 aimed at improved reactor design while focusing on engineering aspects.

773 (4) *Reasonable evaluation of treatment effect of the reaction system.* Much work
774 has yet to be done in properly assessing the viability and industrialization of
775 immobilized catalysts in terms of cost and life-cycle impacts (which are mostly
776 unpredictable and unclear at this early stage of research). Although new studies on
777 persulfate-based AOPs for water treatment are often reported nowadays, these
778 numerous studies and proposed technology combinations pose great challenges for the
779 assessment of AOPs. The challenges include operating costs (e.g., energy consumption,
780 and chemical inputs), general practicality (e.g., physical footprint, oxidation byproduct
781 production, and impact on multiple microbial subsistence), and sustainability (e.g.,
782 resource use, and carbon footprint). Future studies are likely to confirm the economic
783 benefits and environmental consequences of persulfate-based AOPs. For this purpose,
784 life-cycle analysis is required, which involves evaluating energy usage, natural
785 resources, and chemical products related to emissions to air, soil, and water, as well as
786 considering potential trade-offs in actual environmental remediation.

787

788 **Declaration of Interest Statement**

789 The authors declare that they have no known competing financial interests or
790 personal relationships that could have appeared to influence the work reported in this
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792

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1161 **Figure captions**

1162 **Fig. 1.** Heterogeneous activation mechanism of persulfates, and challenges to
1163 nanocatalysts in persulfate-based-AOPs

1164 **Fig. 2.** Construction strategy for persulfate activation systems based on immobilized
1165 nanocatalysts

1166 **Fig. 3.** Typical composite membrane prepared via ceramic and polymeric substances, and
1167 then used in immersion mode reaction systems: (a) synthetic procedure for PAN-Co
1168 ceramic membrane, with SEM surface images of (a-1) initial Al₂O₃ membrane, and (a-2)
1169 functionalized PAN-Co-C membrane, and SEM cross-section images of (a-3) initial
1170 Al₂O₃ membrane, and (a-4) functionalized PAN-Co-C membrane (reprinted with
1171 permission from [26], copyright 2019 Elsevier); (b) synthetic procedure for LDH@PVDF
1172 membrane (reprinted with permission from [27], copyright 2020 Elsevier); and (c)
1173 synthetic procedure for NSC-Fe@PVDF membranes, with (c-1) digital photograph of
1174 NSC-Fe@PVDF membrane and (c-2) color changes of Orange II in NSC-
1175 Fe@PVDF/PMS system (reprinted with permission from [28], copyright 2017 Elsevier).

1176 **Fig. 4.** Typical composite membrane prepared from nanofibers through filtration, and
1177 used in immersion mode reaction systems: (a) synthetic procedure, (b) SEM image of
1178 Co/Fe bi- MOFs/CNFs membrane (reprinted with permission from [32], copyright 2020
1179 Elsevier); and (c) schematic representation of magnetic nanocellulose membrane
1180 preparation and PMS activation process (reprinted with permission from [33], copyright
1181 2020 Elsevier).

1182 **Fig. 5.** Typical composite membrane prepared from electrospun nanofibers, and used in
1183 immersion mode reaction systems: (a) synthetic procedure for metallic Cu-doped C/SiO₂

1184 nanofibers (CINMs) by sol-gel electrospinning method; (b) SEM image of α -Fe@carbon
1185 ENFs (reprinted with permission from [38], Copyright 2017 RSC); (c) SEM image of
1186 CINMs; and (d) optical photograph showing that the CINMs could be folded into a paper
1187 crane without any fracturing (reprinted with permission from [39], copyright 2019 RSC).

1188 **Fig. 6.** Schematic illustration of reaction mechanism for organic removal by (a) Co/Fe bi-
1189 MOFs/cellulose NFs membrane/PMS system (reprinted with permission from [32],
1190 copyright 2020 Elsevier), and (b) NSC-Fe@PVDF/PMS system (reprinted with
1191 permission from [28], copyright 2017 Elsevier).

1192 **Fig. 7.** Typical composite membranes used in filtration mode reaction systems based on
1193 vacuum filtration: (a) synthetic procedure, SEM images, and water treatment method for
1194 ZIF-67/PAN membrane (reprinted with permission from [50], copyright 2017 Elsevier);
1195 (b) synthetic procedure, SEM images, digital photos and water treatment method for
1196 CoCu LDH-CGF membrane and pristine CGF membrane. (reprinted with permission
1197 from [27], copyright 2020 Elsevier); and (c) schematic diagram of the experimental setup
1198 under recirculation mode (configuration A) and continuous mode (configuration B).
1199 (reprinted with permission from [23, 47], copyright 2019 and 2020 Elsevier); the digital
1200 photograph depicts elements in the filtration reaction system with recirculation and
1201 continuous modes (reprinted with permission from [51], copyright 2020 Elsevier).

1202 **Fig. 8.** Typical composite membrane used in filtration mode reaction systems based on
1203 cross-flow filtration: (a) top-section SEM images of pristine PVDF membrane and CoFe-
1204 NMTs-800/PVDF membrane, cross-section SEM image of CoFe-NMTs-800/PVDF
1205 membrane, and metal leaching concentration after five runs in CoFe-NMTs-800/PMS
1206 system (reprinted with permission from [52], copyright 2021 Elsevier); (b) schematic
1207 representation of integration of nanofiltration membranes and Fe_xO_y functionalized

1208 membranes for treatment of naphthenic acid from produced water (reprinted with
1209 permission from [55], copyright 2017 Elsevier); (c) schematic depiction of the Flowing
1210 Bed Device (reprinted with permission from [54], copyright 2018 ACS); and (d) cross-
1211 flow filtration apparatus with light irradiation (reprinted with permission from [53],
1212 copyright 2019 Elsevier).

1213 **Fig. 9.** Typical metallic glasses used in persulfate-AOPs: (a) schematic diagram of melt-
1214 spinning process for manufacturing glassy ribbons and an optical photograph of typical
1215 product (reprinted with permission from [57], copyright 2019 Elsevier); (b) comparison
1216 of the catalytic stability of different iron-based materials (reprinted with permission from
1217 [64], copyright 2019 Wiley); and (c) synthetic procedure, SEM images, and reusability of
1218 as-produced Fe-based MG matrix composite (Fe-based MG_{PDS-45}: the Fe-based MG_{PDS-45}
1219 after 45-times use in PDS activation process; Fe-based MG_{Fenton-45}: the Fe-based MG_{PDS-45}
1220 after 45-times use in Fenton-like reaction process) (reprinted with permission from [60],
1221 copyright 2020 Elsevier).

1222 **Fig. 10.** Typical aerogels and hydrogels used in persulfate-AOPs: (a) photographs of ZIF-
1223 based hybrid aerogels (reprinted with permission from [68], copyright 2018 Elsevier); (b)
1224 elimination of phenol under different conditions, and photographs of CoCA in water (inset)
1225 (reprinted with permission from [69], copyright 2020 Elsevier); (c) schematic illustration
1226 of the preparation of an anisotropic CoFe₂O₄@GA-A and its application for the
1227 continuing treatment of wastewater with a flow-type setup (reprinted with permission
1228 from [70], copyright 2020 Elsevier); (d) plots of removal efficiencies of organic pollutants
1229 for CoFe₂O₄@GA-A and CoFe₂O₄@GA-I at different flow rates, and a photograph of
1230 real-time catalytic experiments using CoFe₂O₄@GA-A and stacked CoFe₂O₄@GA-As
1231 (each red arrow indicates a piece of CoFe₂O₄@GA-A) (reprinted with permission from

1232 [70], copyright 2019 ACS); (e) schematic illustration of degradation equipment flowchart
1233 based on CoOOH/GO hydrogel composite (reprinted with permission from [73],
1234 copyright 2019 ACS); and (f) preparation routine and photographs of samples (reprinted
1235 with permission from [78], copyright 2020 RSC).

1236 **Fig. 11.** Specific materials based on uncommon supports prepared for persulfate
1237 activation: (a) digital images of as-obtained SP-50 sponge cut into different geometrical
1238 shapes; SEM images of (1) SP-50 sponge and (2) SP-50; digital photograph of SP-
1239 50/PMS reactive process (reprinted with permission from [81], copyright 2019 Wiley);
1240 (b) digital photograph of Co-Black TNT/PMS reactive process and the activation
1241 mechanisms (reprinted with permission from [83], copyright 2019 ACS); (c) SEM images
1242 and activation mechanisms of the stainless-steel/PMS system for degrading organic
1243 contaminants (reprinted with permission from [85], copyright 2020 Elsevier); (d)
1244 recycling process of spent lithium-ion battery (reprinted with permission from [84],
1245 copyright 2020 ACS); and (e) schematic illustration of PMS-based *in situ* chemical
1246 oxidation process and the sand columns (5 cm internal diameter × 50 cm length) working
1247 mode (reprinted with permission from [87], copyright 2020 ACS).

1248 **Fig. 12.** Electrocatalytic auxiliary systems constructed for persulfate activation: (a)
1249 schematic diagram of electrochemical activation of PDS and aniline degradation
1250 experiment (reprinted with permission from [93], Copyright 2018 Elsevier); (b) proposed
1251 mechanism of organic pollutant removal by asymmetric quasi capacitive deionization
1252 (AQCDI)/PDS/1.2V system (R represents the organic molecule and X represents the
1253 active sites in MWCNTs) (reprinted with permission from [98], copyright 2019 Elsevier);
1254 (c) SEM images of the ACF in different reaction systems (reprinted with permission from
1255 [99, 100], copyright 2018 and 2020 Elsevier); (d) schematic representation of ACF

1256 Regeneration experimental setup (reprinted with permission from [101], copyright 2020
1257 ACS); and (e) schematic diagram of the E-PMS activation mechanism via FTC and FBC
1258 strategy (reprinted with permission from [102], copyright 2020 ACS).

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Table 1. Summary of recent studies on catalytic membranes for persulfate activation in batch mode

Catalytic component and support material	Experimental conditions	Pollutant removal	Metal leaching (mg/L)	Fabrication method	Regeneration method	Reaction mode
Co embedded carbon (dip-coating) Al ₂ O ₃ (20 nm pore size) [26]	Membrane weight: 100 mg Transmembrane pressure: 1 bar [Sulfamethoxazole] ₀ =10 mg/L [PMS] ₀ =0.1 g/L <i>T</i> =room temperature pH _{solution} =not reported <i>t</i> =60 min	Over 90%	[Co]=0.05	Dip-coating and carbonization method	Not studied	Batch mode Immersion
NSC-Fe PVDF [28]	[Orange II] ₀ =20 mg/L <i>V</i> =250 mL [PDS] ₀ =0.6 g/L <i>T</i> =25 °C pH _{solution} (unadjusted) <i>t</i> =150 min Single piece of membrane (24 cm ²)	98% (in 1 st cycle) ~78% (in 4 th cycle)	[Fe]=0.037	Phase inversion technique	Filtered and washed with ultrapure water after each cycle	Batch mode Magnetic stirring
CoCu LDH PVDF [27]	[Sulfamethoxazole] ₀ =10 mg/L <i>V</i> =100 mL [PMS] ₀ =150 mg/L <i>T</i> =25 °C pH _{solution} =5.77 (unadjusted) <i>t</i> =60 min Single piece of membrane (5×10 cm ²) (catalyst)	Over 90% (from 1 st cycle to 10 th cycle)	[Co]=0.044, [Cu]=0.026 (nanocatalysts) [Co]=0.157, [Cu]=0.174	Phase inversion technique	Washed with deionized water and ethanol after each cycle	Batch mode Magnetic stirring

	7.00 wt.%)					
CuO@CuS PVDF [107]	[Organics] ₀ =10 mg/L <i>V</i> =100 mL [PDS] ₀ =0.4 g/L <i>T</i> =25 °C pH _{solution} =7.34 (unadjusted) <i>t</i> =60 min Single piece of membrane (5×5 cm ²) (catalyst 20.00 wt.%)	83.4% (Tetracycline), about 50% (Enrofloxacin), about 45% (Ciprofloxacin), 40.8% (Lomefloxacin)	[Cu]=1.664 (nanocatalysts [Cu]=2.147)	Phase inversion technique	Washed with ethanol after each cycle	Batch mode Magnetic stirring
Co/Fe bi-MOFs CNFs as fiber support and unspecified organic substrate (0.22 μm pore size) as membrane support [32]	Single piece of membrane with 20 mg catalyst <i>V</i> =100 mL [Tetrabromobisphenol A] ₀ =50 mg/L [PMS] ₀ =0.1 mM <i>T</i> =room temperature pH _{solution} =7.5 <i>t</i> =30 min	100% (in 1 st cycle) 60% (in 5 th cycle)	Not reported	Vacuum filtration	Rinsed and freeze-dried	Batch mode Immersion
Fe₃O₄ CNFs [33]	<i>V</i> =100 mL [Rhodamine B] ₀ =20 mg/L [PMS] ₀ =1.0 g/L <i>T</i> and pH _{solution} not reported <i>t</i> =300 min	Not reported	Not reported	<i>In situ</i> co- precipitation method and filtration	Not studied	Batch mode Magnetic stirring
α-Fe@carbon composite NFs [38]	Membrane weight=10 mg [Methyl blue] ₀ =10 mg/L <i>V</i> =100 mL	100% (in 1 st cycle) 90% (in 5 th cycle)	Not reported	Electrospinning method and carbonization in an	Not illustrated	Batch mode Magnetic stirring

			[PMS] ₀ =0.5 g/L T=25 °C pH _{solution} (unadjusted) t=15 min			N ₂ atmosphere environment		
Metallic nanofibers (CINMs) [39]	Cu-doped C/SiO₂	Membrane weight=0.3 g/L [Tetracycline] ₀ =50 mg/L V=10 mL [PDS] ₀ =0.3 g/L T=55 °C pH _{solution} =9 (adjusted) t=40 min	95% (in 1 st cycle) Over 90% (in 5 th cycle)	[Cu]=0.18 (pH=7, after 10 min) [Cu]=0.37 ((pH=7, after 40 min)	Electrospinning method and carbonization in an N ₂ atmosphere environment	Washed with deionized water and ethanol, dried in an air-circulating	Batch mode Magnetic stirring	
Co–Al₂O₃ NFs membrane [41]		Membrane weight=10 mg (catalyst 11.00 wt.%) [Bisphenol A] ₀ =20 mg/L V=10 mL [PMS] ₀ =1 mM T=25 °C pH _{solution} =7 (buffered) t=40 min	100%	[Co]=0.10 ± 0.4 [Al]=0.09 ± 0.09	Electrospinning method	Not studied	Batch mode Mechanical stirring	
Pt–Al₂O₃ NFs membrane [42]		Membrane weight=1.0 g/L (catalyst 6 wt.%) V=10 mL [Bisphenol A] ₀ =20 mg/L [PMS] ₀ =2 mM T=room temperature pH _{solution} =7.0 (buffered) t=20 min	100% 97% and 88% (in the 1 st , 2 nd and 3 rd cycle, respectively) 100% (stored for one week) 97% (stored for one month)	No Pt leaching [Al]=0.37	Electrospinning method	Not illustrated	Batch mode Rotary shake	

		87% (stored for one year)				
	Membrane weight=1.0 g/L (catalyst 6 wt.%) $V=10$ mL [Bisphenol A] ₀ =20 mg/L [PMS] ₀ =2 mM T =room temperature $\text{pH}_{\text{solution}}=7.0$ (buffered) $t=20$ min	100%	Not reported	Electrospinning method	Not illustrated	Batch mode Mechanical stirring
Ag-LCF Initial spinning mixture composed of Ag-LCF powder, polyethersulfone (PESF), and 1-methyl-2-pyrrolidinone (NMP) [43]	Membrane 30 cm long (catalyst 61.5 wt.%) [Methyl blue] ₀ =10 ppm $Q=26$ mL/min [PMS] ₀ =0.6 mM T , t , and $\text{pH}_{\text{solution}}$ not reported	Over 90% (in the 1 st to 4 th cycles) Less than 70% (in 5 th cycle)	Not reported	Combined phase inversion and sintering method	Not illustrated	Batch mode Surface flow

Table 2. Summary of recent studies on catalytic membranes for persulfate activation in a filtration system

Catalytic component and support material	Experimental conditions	Pollutant removal	Metal leaching (mg/L)	Fabrication method	Regeneration method	Filtration mode
ZIF-67 PAN (Mw = 150,000) [46]	Membrane weight=40 mg (catalyst 50 wt.%) [Acid yellow-17] ₀ =500 mg/L <i>V</i> =200 mL [PMS] ₀ =0.5 g/L <i>T</i> =25 °C pH _{solution} (unadjusted) <i>t</i> =10 min	95.1% (in 1 st cycle) 93.9% (in 5 th cycle)	Not reported	In situ electrospinning method	Not illustrated	Batch mode Magnetic stirring
CoCu LDH CGF as fiber support and PES as membrane support [27]	About 60 s with -0.8 MPa <i>V</i> =100 mL [Sulfamethoxazole] ₀ =10 mg/L [PMS] ₀ =500 mg/L, pH _{solution} =5.77 (unadjusted) <i>T</i> =25 °C Single piece of membrane (12 cm ²)	92.9% (about 60 s) 92.3% (about 60 s, in 10 th cycle)	[Co]=1.605, [Cu]=1.919 (nanocatalysts [Co]=0.157, [Cu]=0.174)	Vacuum filtration	Washed with deionized water and ethanol after each cycle	Batch filtrating mode Pressure filtration
CoCu LDH PAN as fiber support and PES as membrane support [30]	About 60 s with -0.8 MPa <i>V</i> =100 mL [Sulfamethoxazole] ₀ =10 mg/L [PMS] ₀ =0.65 mM pH _{solution} =5.77 (unadjusted) <i>T</i> =25 °C Single piece of membrane (12 cm ²)	95.81% (about 60 s) 94.66% (about 60 s, in 8 th cycle) 94.96% (about 60 s, in 10 th cycle)	[Co]=0.037, [Cu]=0.023 (nanocatalysts [Co]=0.157, [Cu]=0.174)	Vacuum filtration	Washed with deionized water and ethanol after each cycle	Batch filtrating mode Pressure filtration

Ni-Co embedded carbon spheres	[Nimesulide] ₀ =5 mg/L <i>V</i> =50 mL	94% (after 10 min) 81% (6 th cycle)	[Ni]=0.05 [Co]=0.15	Vacuum filtration	Washed with deionized water and ethanol after each cycle	Batch filtrating mode Pressure filtration
Unspecified organic substrate (0.22 μm pore size) as membrane support [108]	[PDS] ₀ =0.4 g/L <i>T</i> =25 °C pH _{solution} =7 <i>t</i> =10 min					
Mn₃O₄ embedded g-C₃N₄	[4-Chlorophenol] ₀ =12.9 mg/L <i>V</i> =20 mL	90% (after 60 min) 80% (5 th cycle)	[Mn]=9.9	Vacuum filtration	Washed with deionized water and ethanol after each cycle	Batch filtrating mode Pressure filtration
PTFE (0.22 mm pore size) as membrane support [109]	[PMS] ₀ =0.15 g/L <i>T</i> =25 °C pH _{solution} not reported <i>t</i> =60 min					
Ni-Co encapsulated N-doped CNTs	[Ibuprofen] ₀ =500 μg/L <i>V</i> =200 mL	~70% (after 20 min) 100% (after 80 min)	[Ni]=0.13 [Co]=0.18	Vacuum filtration	Washed with deionized water after each cycle; after the third cycle, the used catalyst was heated in argon at 350 °C for 3 h.	Semi-continuous mode (under recirculation) Under gravity
PTFE (0.45 mm pore size) as membrane support [110]	[PMS] ₀ =0.1 g/L <i>T</i> =25 °C pH _{solution} =7.2 (buffered) <i>t</i> =20 min (each recirculation)	~70% (after 80 min, in 4 th cycle)	(after 80 min)			
N-doped rGO	[Phenol] ₀ =5 mg/L or [Oxalic acid] ₀ =30 mg/L <i>Q</i> =1.5 mL/min	Phenol 30% (after 6.5 h)	Metal free	Vacuum filtration	Without regeneration	Continuous mode

membrane support [47]	[PDS] ₀ =238 mg/L $T=25\text{ }^{\circ}\text{C}$ $\text{pH}_{\text{solution}}=\text{inherent pH}$ (~7.0 for phenol; 3.0 for oxalic acid) $t=6.5\text{ h}$	Oxalic acid 65% (after 6.5 h)			treatment	Pressure filtration
rGO/CNTs nylon substrate as membrane support [51]	[Sulfamethoxazole] ₀ =500 $\mu\text{g/L}$ $Q=1.0\text{ mL/min}$ [PDS] ₀ =1190 mg/L $T=25\text{ }^{\circ}\text{C}$ $\text{pH}_{\text{solution}}$ not reported $t=3\text{ h}$	77% (after 3 h)	Metal free	Vacuum filtration	Without regeneration treatment	Continuous mode Pressure filtration
N-doped rGO PTFE (0.45 mm pore size) as membrane support [56]	[Phenol] ₀ =47 mg/L $Q=1.5\text{ mL/min}$ [PDS] ₀ =238 mg/L $T=25\text{ }^{\circ}\text{C}$ $\text{pH}_{\text{solution}}=6.5$ $t=3\text{ h}$	~80% (after 3 h)	Metal free	Vacuum filtration	Washed with deionized water	Continuous mode Pressure filtration
rGO-ion nanoparticle PVDF membrane support [111]	[Trichloroethylene] ₀ =0.2 mM Transmembrane pressure=0.4 bar [PDS] ₀ =2 mM $T=23\text{ }^{\circ}\text{C}$ $\text{pH}_{\text{solution}}=7$ $t=3\text{ h}$	~85(over 17h)	Iron leaching was around 8%	Vacuum filtration	Without regeneration treatment	Continuous mode Pressure filtration

Co-TPML PVDF membrane support [45]	[Bisphenol A] ₀ =0.2 μM Transmembrane pressure=0.5 bar [PMS] ₀ =10 mM T=20 °C pH _{solution} =3.5 (unadjusted) t=1 h	>90%	[Co]<0.1 μg/L	Vacuum filtration	Not illustrated	Continuous mode Pressure filtration
CoFe alloy and CoFe₂O₄ nanoparticles encapsulated in N-doped microtube composites (CoFe-NMTs) PVDF as membrane substrate [52]	V=100 mL [Tetracycline, Bisphenol A or Phenol] ₀ =30 mg/L or [Orange G] ₀ =50 mg/L [PMS] ₀ =0.3 g/L pH _{solution} not reported T=30 °C [catalyst] ₀ =0.1 g/L	Tetracycline 99.2% (70 min), Bisphenol A 98.7% (60 min), Phenol 99.5 (70 min) and Orange G 100% (50 min) Tetracycline over 95% (60 min, in 5 th cycle)	[Co]=0.015, [Fe]=0.004	Phase invasion technique	Washed with deionized water and ethanol and then dried in a vacuum after each cycle	Batch filtrating mode Pressure filtration
ZIF-67 PP membrane support [53]	Membrane weight no reported (catalyst 31.8 wt.%) Filtration pressure=0.1 MPa Light source: Xenon lamp (300 W) [Methyl blue or Methyl orange] ₀ =20 mg/L V=300 mL [PMS] ₀ =0.3 mM T, t and pH _{solution} not reported	TOC removal efficiency of 82.2% (Methyl blue) and 83.5% (Methyl orange) (in 1 st cycle) 73.3% (Methyl blue) and 82.0% (Methyl orange) (in 1 st cycle)	Not reported	<i>In situ</i> self-assembly approach	Without regeneration treatment	Semi-continuous mode (under recirculation) Pressure filtration
α-Fe₂O₃	Membrane, 3.8×1.6 cm ² , with catalyst of ~7.5	100% (Q=3 mL/h, after	Not reported	Vacuum filtration	Without	Continuous

bacterial cellulose	mg	84 h)			regeneration	flowing bed
[54]	$Q=3, 6, 9$ mL/h [Rhodamine B] ₀ =10 mg/L each [PMS] ₀ =0.4 g/L Light source: Xenon lamp with a 400 nm cutoff filter T, t and pH_{solution} not reported	93% ($Q=6$ mL/h, after 62 h) More than 87% ($Q=9$ mL/h, after 42 h)			treatment	state
Fe_xO_y	Time: 24 h (for 8 h in a cycle)	50% (in 1 st cycle)	Iron leaching was	<i>In situ</i>	Not illustrated	Batch mode
PVDF as membrane substrate	$V=50$ mL [Naphthenic acids] ₀ =48 mg/L [PDS] ₀ =17 mM $pH_{\text{solution}}=5$ $T=23$ °C Single piece of membrane (13.2 cm ² , Iron loading: 12 g/m ²)	15% (in 2 nd cycle)	around 14.4%, 12.3%, and 16.2% in three cycles, respectively.	polymerization, ion exchange, reduction, and controlled oxidation		Surface flow
[55]	Average flux=2 LMH [Naphthenic acids] ₀ =48 mg/L [PDS] ₀ =5000 mg/L (added in every cycle) $pH_{\text{solution}}=5$ $T=23$ °C Single piece of membrane (13.2 cm ² , Iron loading: 12 g/m ²)	44% (in 1 st pass) 42% (in 2 nd pass)	Not reported	<i>In situ</i>	Not illustrated	Continuous mode Pressure filtration
rGO-N	Membrane weight=23 mg (catalyst 6.4 wt.%)	54% (Ofloxacin), 77% (Ciprofloxacin) and	[Mn]=9.9	Knife cast technique	Without regeneration	Continuous mode
PVDF as membrane substrate	$Q=0.1$ mL min ⁻¹					

[23]	[Ofloxacin, Ciprofloxacin and Enrofloxacin, simultaneously] ₀ =100 µg/L each [PDS] ₀ =25 mg/L <i>T</i> =room temperature pH _{solution} =inherent pH (5.9) <i>t</i> =24 h	91% (Enrofloxacin) (after 24 h)	treatment	Pressure filtration
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Table 3. Recent studies on hydrogels and aerogels in persulfate-AOPs system

Catalytic component and support material	Experimental conditions	Catalytic Performance and Stability	Regeneration method	Metal leaching (mg/L)
ZIF-9 Cellulose aerogels [68]	[P-nitrophenol] ₀ =20 mg/L	About 90% (from 1 st to 3 rd cycle)	Washed with deionized water	[Co]=0.60 (the 1 st cycle)
	[PMS] ₀ =600 mg/L			[Co]=0.50 (the 2 nd cycle)
	[ZIF-9@GEL] ₀ =600 mg/L			[Co]=0.30 (the 3 rd cycle)
	pH _{solution} =6 (adjusted) <i>t</i> =130 min <i>T</i> =25 °C			
ZIF-12 Cellulose aerogels [68]	[P-nitrophenol] ₀ =20 mg/L	About 85% (from 1 st to 3 rd cycle)	Washed with deionized water	[Co]=0.75 (the 1 st cycle)
	[PMS] ₀ =600 mg/L			[Co]=0.60 (the 2 nd cycle)
	[ZIF-12@GEL] ₀ =600 mg/L			[Co]=0.45 (the 3 rd cycle)
	pH _{solution} =6 (adjusted) <i>t</i> =130 min <i>T</i> =25 °C			
Cobalt and Co₃O₄ Carbon aerogels [69]	[Phenol] ₀ =20 mg/L	87% (in 1 st cycle)	Without regeneration treatment	[Co]=0.014 (the 1 st cycle)
	[PMS] ₀ =2.6 mM	84% (in 2 nd cycle)		[Co]=0.011 (the 2 nd cycle)
	[Composite] ₀ =1.0 g/L	67% (in 3 rd cycle)		[Co]=0.004 (the 3 rd cycle)
	pH _{solution} =7.5 (adjusted and buffered) <i>t</i> =60 min <i>T</i> =25 °C			

CoFe₂O₄			[Indigo carmine] ₀ =50 ppm	100% (30 h, 60 mL/h)	Without regeneration	Not reported
Anisotropic	graphene	Hybrid	[PMS] ₀ =0.2 g/L	91% (25 h, 90 mL/h)	treatment	
Aerogels			[CFO@GA-A] ₀ =165.1 mm ² ×11.4 mm	85% (21 h, 120 mL/h)		
[70]			pH _{solution} unadjusted			
			<i>T</i> not reported			
CoFe₂O₄			[Indigo carmine] ₀ =50 ppm	100% (4 h, 60 mL/h) and 41%	Without regeneration	Not reported
Isotropic	graphene	Hybrid	[PMS] ₀ =0.2 g/L	(subsequent 10 h, 60 mL/h)	treatment	
Aerogels			[CFO@GA-I] ₀ =165.1 mm ² ×11.4 mm	Drop to 35% (within 5 h, 120 mL/h)		
[70]			pH _{solution} unadjusted			
			<i>T</i> not reported			
BiOI			[Methylparaben] ₀ =50 mg/L	99% (90 min, with light irradiation)	Without regeneration	Not reported
p(HEA-APTMs) hydrogel			[PMS] ₀ =30 mM	More than 80% (180 min, in dark)	treatment	
[71]			[Composite] ₀ =2.0 g/L			
			Xenon lamp (500 W)			
			pH _{solution} and <i>T</i> not reported			

CoOOH/GO PAA hydrogel [73]	[Rhodamine B] ₀ =20 mg/L <i>V</i> =1 L [PMS] ₀ =0.15 mM 200 mg Co(NO ₃) ₂ ·6H ₂ O was used for CoOOH preparation pH _{solution} =6.0 (unadjusted) Flow rate=200 mL/min <i>t</i> =5 min <i>T</i> not reported	About 85% (in 1 st cycle) Above 60% (in 10 th cycle)	Calcination treatment	In Fig. 10(e)
Co₃O₄ Graphene hydrogel [74]	[Orange II] ₀ =0.2 mM [PMS] ₀ =1 mM [Composite] ₀ =0.05 g/L Neutral pH _{solution} (buffered) <i>t</i> =90 min <i>T</i> not reported	100% (from 1 st to 5 th cycle)	Dried in a vacuum oven overnight without any treatment	[Co]=0.360
Carbon black nano-spheres (CBNS)/Fe₃O₄ Calcium alginate hydrogel matrix [80]	[Acetaminophen] ₀ =0.1 mM [PMS] ₀ =1.0 mM [Composite] ₀ =0.3 g/L pH _{solution} =5.5 (unadjusted) <i>t</i> =60 min <i>T</i> not reported	76.8% (in 1 st cycle) 66.8% (in 5 th cycle)	Not illustrated	No metal

FeS	[Tetracycline] ₀ =100 mg/L	92.2% (in 1 st cycle)	Shaken in distilled water for 6 h	Not reported
Graphene hydrogel	[PMS] ₀ =2 mM	88.3% (in 5 th cycle)		
[78]	[Composite] ₀ =1.0 M			
	pH _{solution} =6 (unadjusted)			
	<i>t</i> =120 min			
	<i>T</i> =25 °C			

Table 4. Recent studies on persulfate-AOPs with unusual materials as activators

Catalytic component and support material	Experimental conditions	Catalytic Performance and Stability	Regeneration method	Metal leaching (mg L ⁻¹)
Co₃O₄ Polymer sponge [81]	[Acid Orange 7] ₀ =0.3 mM [PMS] ₀ =3 mM [Composite] ₀ =0.6 g/L pH _{solution} =7 (adjusted and buffered) T=25 °C	100% (15 min, in 4 th cycle) 100% (21 min, in 6 th cycle) 100% (24 min, in 8 th cycle)	Washed with distilled water and ethanol and dried in a vacuum after each cycle	[Co]=0.0118–0.066 (over eight runs)
TiO₂ Ti plate [82]	[Ciprofloxacin] ₀ =10 mg/L [PMS] ₀ =0.5 mM Xenon lamp (300 W) pH _{solution} =6.3 (No description) t=90 min T not reported	99.16% (from 1 st to 5 th cycle) 92% (in 6 th cycle)	Dried	Not reported
Co-Black TNT Ti plate [83]	[4-chlorophenol] ₀ =100 μM [PMS] ₀ =1 mM pH _{solution} =7.0 (buffered) t=30 min T not reported	100% (from 1 st to 15 th cycle)	Without regeneration treatment	[Co]=0
Recycled active LiMn₂O₄ Al foil in spent lithium-ion batteries [84]	[Ortho-phenylphenol] ₀ =20 mg/L [PMS] ₀ =0.3 g/L pH _{solution} not reported t=60 min T=25 °C	100% (in 1 st cycle) 94.8% (in 10 th cycle)	Washed with deionized water	Not reported

Surface-etched and N ₂ -annealed stainless-steel mesh	[Orange II] ₀ =10 mg/L [PMS] ₀ =0.25 g/L pH _{solution} unadjusted t=40 min T=25 °C	100% (from 1 st to 3 rd cycle)	Washed with ethanol after each cycle.	Not reported
CoFe ₂ O ₄ Quartz sand [86]	V=1 L [Sulphachloropyridazine sodium] ₀ =20 mg/L [PMS] ₀ =75 mg/L [Composite] ₀ =0 g (1.0% CoFe ₂ O ₄ loading) pH _{solution} =6.8 (adjusted) Flow rate=6 mL/min T not reported	Fresh composite: Over 80% (from 0 to 360 min) Over 75% (from 360 to 480 min) Regenerated composite: Over 80% (from 0 to 120 min)	Calcined in the muffle furnace at 300 °C for 4 h.	Contrary to the batch reactor, the continuous flow reactor exhibited about a quarter lower cobalt leaching.
Mn _{1.5} FeO _{6.35} Sand [87]	[Trichloroethylene] ₀ =20 mg/L [PDS] ₀ =8 mM Column reactor (porosity of 25.7%) packed with sand (99.5 wt.%) and the BFMO catalysts (0.5 wt.%) pH _{solution} =7.0 Flow rate=1.47 L/d T not reported	BFMO remained stable in the sand column throughout 115-day continuous flow test period.	Not reported	Not reported

Table 5. Recent studies on electro-assistance persulfate-AOPs

Anode	Cathode	Ref.	Experimental conditions	Catalytic performance and stability
Fe sheet (4.2 cm×3 cm×0.5 cm, 25.2 cm ²)	Fe sheet (4.2 cm×3 cm×0.5 cm, 25.2 cm ²)	[112]	[Pentachlorophenol] ₀ =0.10 mM	75% (Mineralization efficiency)
			[PMS] ₀ =9.9×10 ⁻⁵ M	
			[NaCl]=1.7 mM	
			<i>t</i> =10 min	
			pH _{solution} =4.5 (unadjusted)	
			Current density=90 mA	
			<i>T</i> not reported	
			[Pentachlorophenol] ₀ =0.10 mM	About 60% (mineralization efficiency)
			[PDS] ₀ =9.9×10 ⁻⁵ M	
			[NaCl]=1.7 mM	
			<i>t</i> =20 min	
			pH _{solution} =6.5 (unadjusted)	
			Current density=90 mA	
			<i>T</i> not reported	
Fe sheet (10 cm ²)	Graphite bar	[113]	[2,4,5-Trichlorophenoxyacetic acid] ₀ =0.10 mM	About 100%
			[PMS] ₀ =0.25 mM	
			[Na ₂ SO ₄]=50 mM	
			<i>t</i> =30 min	
			pH _{solution} not reported (unadjusted)	
			Current=10 mA	
			<i>T</i> =23 ± 2 °C	
Fe sheet (Cast gray iron, 76 mm×9.5 mm×3.2 mm)	Mixed metal oxide sheet (85 mm×15 mm×1.8 mm, IrO ₂ /Ta ₂ O ₅ coating on titanium mesh type)	[92]	[Trichloroethylene] ₀ =0.4 mM	More than 99%
			[PDS] ₀ =5 mM	
			<i>t</i> =20 min	
			pH _{solution} =5.6 (unadjusted)	
			Current=+100 mA	
			<i>T</i> not reported	
Graphite sheet (4.5 cm×4.5 cm)	MWCNTs coating graphite sheet cathode (with active)	[93]	[Aniline] ₀ =0.45 mM	98% (in the 1 st cycle)
			[PDS] ₀ =5.55 mM	89% (in the 9 th cycle)
			<i>t</i> =150 min	
			pH _{solution} not reported	

	materials of ~ 85 mg, 4.5 cm×4.5 cm)			Working voltage=-0.6 V <i>T</i> not reported	
Graphite sheet (4.5 cm×4.5 cm)	MWCNTs coating graphite sheet cathode (with active materials of ~ 10 mg, 4.5 cm×4.5 cm)	[98]		[Acyclovir] ₀ =0.45 mM [PDS] ₀ =11.1 mM <i>t</i> =120 min (positive polarization) <i>t</i> =180 min (negative polarization) pH _{solution} not reported Working voltage=1.2 V <i>T</i> not reported	Above 95% (from 1 st to 3 rd cycle, negative polarization) Above 95% (from 1 st to 11 th cycle, negative polarization)
Ti/Pt (50 mm×35 mm×1 mm)	ACF coating Titanium plate cathode (50 mm×35 mm×1 mm)	[103]		[Carbamazepine] ₀ =0.04 mM [PDS] ₀ =2 mM [Fe ³⁺]=0.4 mM [Na ₂ SO ₄]=50 mM <i>t</i> =30 min pH _{solution} =3 (adjusted) Current density=7.14 mA/cm ² <i>T</i> =25 °C	97.76% (in 1 st cycle) above 97% (in 10 th cycle)
Pt-plating titanium (50 mm×35 mm)	ACF coating Pt-plating titanium cathode (50 mm×35 mm)	[100]		[Carbamazepine] ₀ =0.042 mM [PDS] ₀ =100 mM <i>t</i> =30 min pH _{solution} =3 (adjusted) Working voltage=6 V <i>T</i> =25 °C	98.78% (in 1 st cycle) 97.35% (in 100 th cycle)
BiVO₄ photoanode (1 × 1 cm ²)	MnFe₂O₄ coating Carbon paper (CFP) cathode	[104]		[Bisphenol A] ₀ =10 mg/L [PMS] ₀ =1 mM <i>t</i> =90 min pH _{solution} not reported Working voltage=1 V <i>T</i> =20 °C Xenon lamp (300 W)	100% (in 1 st cycle) About 85% (in 5 th cycle)
BiVO₄ photoanode (16 cm ²)	PDA coating carbon felt (CF) cathode (16 cm ²)	[105]		[Ofloxacin] ₀ =0.04 mM [PMS] ₀ =2 mM <i>t</i> =120 min pH _{solution} =5 (buffered) Working voltage=1.5 V <i>T</i> not reported	100% (in 1 st cycle) above 90% (in 5 th cycle)

			Xenon lamp (300 W)	
Platinum-plated titanium (5.0×3.5 cm)	ACF coating Pt-plating titanium cathode (0.2 g, 5.0 cm×3.5 cm×3 mm)	[99]	[Phenol] ₀ =1600 mg/L	66% (in 1 st cycle)
			[PDS] ₀ =100 mM	34.12% (in 4 th cycle)
			[Na ₂ SO ₄]=0.2 M	
			<i>t</i> =6 h	
			pH _{solution} not reported (unadjusted)	
			Current intensity=1 A	
			<i>T</i> =25 °C	
Not reported	Carbonized wood cathode (4.0 cm×2.0 cm×0.8 cm)	[102]	[Phenol] ₀ =20 mg/L	97.9% (in 1 st cycle)
			[PMS] ₀ =6.51 mM	98.4% (in 2 nd cycle)
			[Na ₂ SO ₄]=50 mM	98.0% (in 3 rd cycle)
			<i>t</i> =10 min	97.6% (in 4 th cycle)
			pH _{solution} =2.87 (unadjusted)	97.9% (in 5 th cycle)
			Current density=2.75 mA/cm ²	
			<i>T</i> =25 °C	
			Flow rate=0.5 mL/min	