

Efficient activation of peroxymonosulfate by sulfur-coordinated iron-based two-dimensional composite membrane (S-Fe@G) via sulfur doping and nanoconfined catalysis

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ABSTRACT:

The combination of nanoconfined catalysis, sulfate radicals based-advanced oxidation processes (SR-AOPs) and membrane filtration processes, can remove organic pollutants efficiently while eliminating the need for secondary recovery of heterogeneous catalysts. In this study, sulfur-doped iron-based carbonaceous two-dimensional composite nanoconfined catalytic membranes (S-Fe@G membranes) were prepared to rapidly activate peroxymonosulfate (PMS) for efficient water purification. The best performing 2S-20Fe@G catalytic membrane/PMS system achieved an ultra-rapid (158.7 ms retention time) removal (94.9%) and high mineralization (> 66.7%) of tetracycline (TC, 20 mg L⁻¹) due to the generation of ¹O₂, Fe(IV)=O and •OH. The introduction of sulfur was found to significantly improve the electronic structure and electron transfer efficiency of S-Fe@G. This enhancement promoted the activity of Fe reaction sites and increased the multivalent distribution of Fe. Additionally, sulfur incorporation lowered the reaction energy barrier for PMS dissociation and accelerated the Fe(II)/Fe(III) cycle. These combined effects resulted in the rapid degradation of pollutants and ensured the stable operation of the catalytic system over extended periods. In addition, the nanoconfined space composed of the two-dimensional carbonaceous structure was conducive to the accumulation of pollutants and the rapid activation of PMS. The 2S-20Fe@G catalytic membrane achieved a high selective removal of TC (> 94.5%) and substantial mineralization of pollutants (> 52.1%) in both simulated (Humic acid + TC) and real (Lake water + TC) waters, demonstrating its potential for practical applications.

KEYWORDS : PMS activation; Tetracycline degradation; Two-dimensional catalytic membrane; Reduced sulfur species; Water treatment

1. Introduction

With the rapid development of the pharmaceutical industry and human living standards, antibiotics have become the most widely used class of prescription drugs [1], but a large quantity of these antibiotics, which are not fully absorbed by the human body during use, pass into the environment, posing a serious potential threat to the aquatic environment and human health [2]. Recent studies have detected antibiotics in Chinese surface waters at concentrations ranging from ng/L to $\mu\text{g/L}$, with peaks up to $26\text{ }\mu\text{g/L}$, where tetracycline, sulfamethoxazole, and ciprofloxacin were the most prevalent [3,4]. Globally, a study analyzing 1052 water samples from 258 rivers across 104 countries found that 9 of 13 targeted antibiotics repeatedly exceeded safe thresholds for aquatic organisms [5]. Even at trace levels, these persistent contaminants pose significant risks, including the potential to drive antibiotic resistance. To date, a range of practical wastewater treatment technologies have been developed and applied, including biodegradation [6], adsorption [7], membrane filtration [8] and advanced oxidation processes (AOPs) [9]. Sulfate radicals based-advanced oxidation processes (SR-AOPs) have attracted attention as a promising strategy for the rapid degradation of emerging contaminants under mild conditions over a broad pH range and under complex water matrix conditions by employing both free and non-free radical pathways (such as $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$, $^1\text{O}_2$, and $\text{O}_2^{\bullet-}$) [10,11]. In practical applications, peroxymonosulfate (PMS) is one of the most widely studied sulfate oxidants owing to its asymmetric molecular structure (favoring rapid bond breaking to generate the active substance) [12], stability, non-toxicity, low cost and high solubility in water [13].

In order to accelerate the reaction of activated PMS, researchers have been exploring the use of various transition metal-based catalysts in recent years, mainly incorporating Fe, Co, Cu and Mn [14]. Among these catalysts, Fe has been employed as the transition metal of choice for environmental applications due to its environmental properties (viz. it is abundant and non-toxic, making it an environmentally friendly choice for remediation techniques compared to other heavy metal elements) [15], cost-effectiveness and ability to efficiently activate PMS [16]. Iron oxides [17–19] (FeO , Fe_2O_3 , and Fe_3O_4) have been commonly investigated as catalysts in SR-AOPs over the past decades. However, since the consumption of Fe(II) is much faster than

the rate of Fe(III) reduction to produce Fe(II) during the activation of PMS, the catalytic activity and stability of iron oxides will decrease with the consumption of Fe(II). [20] Therefore, the construction of a Fe(II)/Fe(III) redox cycle is the key to improve the catalytic activity and reuse of catalysts [21].

In recent years, the modification of the reducing element sulfur has been shown to be a potentially viable method of solving the catalytic deterioration problem. Previous studies have demonstrated that sulfur doping can modulate the electron arrangement and change the electronic configuration around transition metals, promoting the enhancement of active sites [22,23]. Hu. et al. [24] found that S doping modulated the electronic structure of Co atoms in the material, forming electron-rich Co sites with a stronger chemisorption capacity and electron utilization, lowering the energy barriers of the adsorption state of PMS, thereby increasing the utilization of PMS and the yield of reactive substances ($\text{SO}_4^{\bullet-}$ and high valent metal-oxo species (HVMS)). During advanced oxidation, sulfur can convert to multiple valence states, facilitating electron transfer between the oxidant and the iron substance on the surface of the material [25,26], which accelerates the reduction of Fe(III). It had been demonstrated [27] that FeS_2 can be converted to fresh FeS_n , thereby speeding up the Fe(III)/Fe(II) cycle with the help of S^{2-} . However, the loss of effective sulfur and the occurrence of the homogeneous Fenton reaction, caused by the leaching of large amounts of the ions, also lead to a decrease in the activity and stability of the catalyst.

In attempting to solve the problem of metal dissolution, researchers have developed strategies such as carrier effect [28], interface effect [29], and nanoconfined effect [30]. Some studies have shown that combining cobalt with suitable carriers can reduce metal leaching and increase its catalytic capacity [31]. Interfacial effects such as strong electronic coupling between the modifying material and the metal sites (e.g. PANI and FeCo-MS) [32] or the construction of surface coatings (e.g. rGO and Se-based materials) [33] can prevent the leaching of metals and improve chemical stability. Meanwhile, the encapsulation of metal nanoparticles (NPs) in a carbonaceous matrix with a restricted structure not only facilitates the enrichment of reactive species (RS), but also reduces the leaching of metal ions, thereby improving the catalytic activity [34]. For example, Yang. et al. [35] investigated the catalytic activation of PMS by encapsulating Fe in nitrogen-doped graphene, and found that

sulfamethoxazole (5 mg/L) could be completely degraded within 20 min, and the encapsulation of the porous carbon significantly reduced the leaching of iron ($\leq 0.023 \text{ mg L}^{-1}$). In addition, constructing nanoconfined catalytic membranes is a promising strategy to realize the nanoconfined effect. Under nanoconfinement, molecules (pollutants and PMS) are accumulated in the nanoscale space, effectively accelerating collisions (molecule-to-molecule, molecule-to-active-site), improving the mass transfer rate and enhancing the reaction rate, resulting in a significant improvement in catalytic performance and protection of the catalyst [36,37]. The immobilization of nanocatalysts onto a membrane surface, provides a straightforward method for the fabrication of nanoconfined catalytic membranes [38]. Currently, researchers have concentrated on employing a variety of simple carbonaceous materials, such as graphene [39], MXene [40], and CNT [36], to construct nanoconfined membranes for water treatment.

Among the carbonaceous materials, reduced graphene oxide (rGO) has good electron transfer ability [41,42], hydrophilicity [43,44], and high specific surface area [45,46], so that it can be used as a carrier for catalysts to effectively enhance the performance of the composite catalysts, and its unique two-dimensional lamellar structure realizes the tunability of the catalyst morphology [47,48]. Despite the vast potential promise of nanocatalysts, complex post-treatment processes (the additional operations of separating and washing out the nanocatalysts from the treated water) are still the current challenge for the large-scale application of nanocatalysts [49–52]. The nanoconfined catalytic membrane process resulting from the coupling of SR-AOPs with nanoconfined membrane technology can achieve multiple benefits by simultaneously realizing the efficient and continuous degradation of pollutants, alleviating the contamination problem on the membrane surface, and eliminating the need for subsequent treatment of the catalyst [52].

In this study, sulfur-coordinated iron-based carbonaceous (GO and rGO) two-dimensional (2D) nanosheets (S-Fe@G NSs) were simply synthesized using a one-step method for in situ sulfurization and catalytic nano membranes (S-Fe@G membranes) were prepared by vacuum filtration stacking. The researchers enhanced the performance of iron-activated peroxymonosulfate (PMS) through sulfur doping. The catalyst was encapsulated with a carbonaceous structure, which provided a domain-limited framework and significantly reduced

iron (Fe) leaching. Moreover, by coupling sulfate radical-based advanced oxidation processes (SR-AOPs) with membrane separation technology, they achieved efficient and long-term degradation of a wide range of pollutants in aqueous environments. Various characterization methods, such as scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD) and X-ray photoelectron spectroscopy (XPS), were employed to investigate the chemical composition and morphology of the S-Fe@G membranes. Density Functional Theory calculations (DFT) were utilized to demonstrate that the introduction of sulfur can change the electron distribution near the catalytic site thereby promoting the dissociation of PMS. The performance of the S-Fe@G membrane for the degradation of tetracycline (TC) (a common antibiotic) was systematically evaluated in terms of its efficiency, resilience to interference by solution conditions (e.g. pH, anions and water source) and stability, and its broad applicability for the degradation of other representative pollutants (dyes and pharmaceuticals) was investigated. The catalytic mechanism, including the reaction mechanism and analysis of intermediates, was thoroughly investigated using RS quenching experiments, electron paramagnetic resonance (EPR) spectroscopy, XPS and liquid chromatography-mass spectrometry (LC-MS) spectrometry.

2. Experimental – methods and materials

2.1. Materials and reagents

The polyethersulfone (PES) membrane (pore size 0.22 μm) was purchased from JinTeng (China). The aqueous colloidal suspension of graphene oxide (GO suspension, 98%) was purchased from Soochow Tanfeng Graphene Technology Co., Ltd. (Chian). Sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, GR), sodium sulfate (Na_2SO_4 , AR) and potassium peroxymonosulfate (KHSO_5 , PMS, $\geq 98\%$) were obtained from Macklin Biochemical Co., ltd. (Shanghai, China). Iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, AR), tetracycline (TC, 98%), 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 97%), carbamazepine (CBZ, $\geq 98.0\%$), crystal violet (CV, AR), methyl orange (MO, 96%), rhodamine B (RhB, AR), methyl blue (MB, AR), methylene blue (MNB, $\geq 70.0\%$), sodium nitrate (NaNO_3 , AR), humic acid (HA, AR), tert-butyl alcohol (TBA, $\geq 99.5\%$) and 2,2,6,6-tetramethylpiperidine (TEMP, $\geq 98.0\%$) were purchased from Aladdin Chemistry Co., ltd. (Shanghai, China). Hydrochloric acid (HCl, AR) was obtained from Merck (Germany). Furfuryl alcohol (FFA, 98%) and p-benzoquinone (pBQ, 99%) were provided by Meryer (Shanghai, China) Biochemical Technology Co., Ltd. Sodium hydrogen carbonate (NaHCO_3 , AR), sodium chloride (NaCl , AR), sodium hydroxide (NaOH , AR) and sodium carbonate anhydrous (Na_2CO_3 , AR) were obtained from Beijing Beihua Fine Chemicals Co., Ltd. (Beijing, China). Methanol (MeOH , AR) and sodium phosphate dibasic (Na_2HPO_4 , 99%) were purchased from Beijing Daishi Zede Technology Development Co., Ltd. (Beijing, China) and J&K Scientific Co., Ltd. (Beijing, China). The real water samples were taken from the North Lake of Liangxiang Campus of Beijing Institute of Technology (Beijing, China).

2.2. Fabrication of S-Fe@G membranes

The S-Fe@G membrane was prepared using a combination of hydrothermal and vacuum filtration methods as shown in **Figure 1**. To prepare the catalytic composite membrane, we used a commercial polyethersulfone (PES) membrane (0.22 μm) as a support membrane. Typically, 2 mg of GO nanosheets were added to the prepared $\text{Fe}(\text{OH})_3$ colloidal solution (iron source, prepared as shown in the Supporting Information (SI) (Text S1, 20 mL) and the

Fe(OH)₃/GO mixed solution was sonicated for 1 h. Then, Na₂S₂O₃·5H₂O (sulfur source, 2 mmol) was added to the solution and ultrasonicated for 10 min for homogeneous dispersion. Afterwards, the solution was transferred to a 50 mL polytetrafluoroethylene-lined stainless steel autoclave and subjected to hydrothermal reaction at 60°C for 1 h. After cooling to room temperature, a 2S-20Fe@G membrane was prepared by vacuum filtration. Various xS-yFe@G (x represents the amount of Na₂S₂O₃·5H₂O, and y represents the volume of Fe(OH)₃ colloid) membranes were prepared by changing the amount of iron and sulfur sources. For comparison, additional catalytic membranes were synthesized by the same procedure but without the addition of Fe(OH)₃, Na₂S₂O₃·5H₂O or both chemicals, and these were denoted as: S@G membrane, Fe@G membrane and GO-Heat membrane. A pure GO membrane was fabricated by filtering 10 mL of 0.2 mg/L GO suspension through the support membrane.

Figure 1.

2.3. Characterization

Scanning electron microscopy (SEM, QUANTA FEG 250, FEI, USA) provided surface and cross section images of the microstructure of the ‘as-prepared’ membranes. The elemental compositions were obtained by energy dispersive spectroscopy (EDS, Oxford Ultim Max 65). X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific, America) was used to reveal the relative elementary composition. 20 nm was chosen as the depth of surface etching, which can avoid surface carbon pollution to the greatest extent and help understand the internal structure of the 2S-20Fe@G sample. The phase composition was characterized by X-ray diffractometer equipment (XRD, Rigaku UltimaIV, Cu-K α radiation, 45 kV, 50 mA, Japan). Fourier transform infrared spectroscopy (FT-IR, BRUKER, ALPHA-P, USA) was used to explore the content of oxygen-containing function groups of the membranes. The hydrophilic nature of various GO based membranes were indicated by water contact angle measurements (WCA, OCA15ED, Dataphysics, Germany) of membrane surfaces using the sessile drop method. A solid-surface zeta potential analyzer (SurPASSTM 3, Anton Paar, Germany) was employed to analyze the surface charge properties of the membrane and an average zeta potential value for the samples was determined at pH 7 from 3 measurements. The hydroxyl radicals, sulfate and singlet oxygen in aqueous solutions were detected using electron

paramagnetic resonance (EPR, Bruker EMXplus) analysis with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) as spin traps.

2.4. Catalytic degradation experiments

The compound degradation performance of the catalytic membranes was studied using a dead-end filtration device as shown in the SI (Fig. S1). The experimental apparatus consisted of a filter extraction cup, a glass sand core, a filter extraction bottle and a pump. During the degradation reaction, a mixed solution containing contaminants and peroxymonosulfate (PMS) was poured into the upper filter cup, and a pressure of 0.1 MPa was supplied by the pump to allow the solution to permeate through the catalytic membrane and be collected in the lower filter bottle. Samples were collected from the bottles at regular intervals and the mixed solution was then filtered through a 0.22 μm PTFE membrane for subsequent measurement of pollutant concentrations. The removal efficiency R (%) can be calculated by the following equation:

$$R = \frac{C_F - C_P}{C_F} \times 100\% \quad (1)$$

where C_F (mg/L) and C_P (mg/L) are the concentrations of the organic pollutant in the feed and permeate, respectively.

The effect of water retention time on the pollutant removal performance was analyzed by operating the membrane at different applied pressures (0.5–2.5 bar). The water retention time (ms) in the S-Fe@G membrane was calculated using the following equation:

$$r_m = \frac{V_m \times M_m}{J \times S \times P} \quad (2)$$

where V_m , M_m , J , S and P are the specific pore volume (cm^3/g), the total mass of membrane (g), the water permeance ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{MPa}^{-1}$), the effective membrane filtration surface area (m^2 , $d = 40$ mm), and the applied pressure (MPa), respectively.

The PMS concentrations were determined by adding 100.0 μL samples into a 10 mL aqueous solution containing KHCO_3 (0.05 g) and KI (0.4 g). After reacting for 15 min, the mixed solution was then analyzed by UV–visible spectroscopy at 352 nm. The PMS decomposition efficiency, D (%), was calculated using:

$$D = \frac{A_0 - A_t}{A_0} \times 100\% \quad (3)$$

where A_0 is the absorbance of the original PMS test solution, and A_t is the absorbance of the sample solution at the specified time, t .

Tetracycline was chosen as a model pollutant owing to its widespread use in agriculture, animal husbandry, and human medicine, which has led to its presence as a common contaminant in water and soil [4,53,54]. Specifically, TC is one of the most frequently detected antibiotics in surface water, with concentrations ranging from ng/L to $\mu\text{g/L}$ [3,4,55], and it is known to contribute to the development of antibiotic resistance genes (ARGs) [56,57]. Additionally, TC's complex chemical structure and resistance to conventional degradation processes make it a representative compound for evaluating the efficiency of advanced oxidation processes (AOPs) in pollutant removal [58,59]. Also, other selected compounds, namely carbamazepine (CP), crystal violet (CV), methyl orange (MO), rhodamine B (RhB), methyl blue (MB), and methylene blue (MNB), which had the same initial concentration as TC, were investigated to validate the catalytic performance of the membranes. The effects of PMS concentration, initial pH of the solution (adjusted by addition of NaOH and HCl), common inorganic anions, simulated/natural organics, and water quality conditions were evaluated. In the quenching experiments, methanol (MeOH, 20 mM, quenches $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$), tert-butanol (TBA, 20 mM, quenches $\bullet\text{OH}$), furfuryl alcohol (FFA, 20 mM, quenches $^1\text{O}_2$), and p-benzoquinone (p-BQ, 20 mM, quenches $\text{O}_2^{\bullet-}$) were added to the initial solution separately. NaCl, Na_2HPO_4 , Na_2CO_3 , NaHCO_3 , Na_2SO_4 and NaNO_3 were used to simulate the presence of anions in real water. In the absence of specific instructions, the default experimental conditions for this study were a PMS concentration of 1 mM, a membrane pressure of 0.1 MPa, an initial TC concentration (C_0) of 20 mg/L (a pH of 4.44) at room temperature. Detailed information of the analytical methods for characterization or quantification of substances is given in the SI (Text S3).

3. Results and discussion

3.1. Characterization of 2D catalytic membranes

As shown in **Figure 1b**, the pure GO membrane showed a fluctuating surface with typical wrinkles and no obvious visible cracks. Compared to the pure GO membranes, Fe@G

membranes showed larger wrinkles shapes and a reduced distribution density (**Figure 1c**), while for the S@G membrane the wrinkles increased and nanoparticles were distributed over it (**Figure 1d**), which were revealed through correlation with S by EDS mapping (SI, Fig. S2). In contrast, the 2S-20Fe@G membrane doped with Fe and S exhibited a distinctly wrinkled morphology, and moderate-sized nanoparticles were uniformly distributed among the layers, which were inferred to be iron sulfides by EDS mapping (**Figure 1e**). The uniformly distributed nanoparticles not only help to accelerate the rate of water flow through the layer and improve the water permeance [60], but also help the contaminant solution containing PMS to fully contact with the catalyst to achieve efficient catalytic degradation [61]. In addition, EDS mapping verified the uniform distribution of the elements C, O, Fe, and S on the membrane surface, in which C, O, Fe, and S accounted for 48.93%, 33.45%, 10.56%, and 7.06%, respectively, as shown in the SI (Fig. S3). The cross-sectional images of the 2S-20Fe@G membrane (**Figure 1f** and SI, Fig. S4) reveal a well-defined laminar structure with a uniform thickness of approximately 2.5 μm . The uniform interlayer gaps, which serve as nanoconfined spaces for catalytic reactions, are clearly visible. The two-dimensional layered structure created a nanoconfined structure that restricted the catalyst particles to the nanospaces. With the increase of the Fe/S source, the extent of wrinkles of the composite membrane became more obvious, but the accompanying pinholes and holes indicated that the structure of the two-dimensional membrane was gradually destroyed (SI, Fig. S5). This was attributed to the increase in the Fe/S source leading to larger iron sulfide particles between the layers of the composite membranes, which resulted in cracks in the surface structure of the membranes.

The structures of the 2S-20Fe@G membrane and 2S-20Fe NP were characterized by XRD analysis (**Figure 1g**). The diffraction peak of the 2S-20Fe@G membrane at $2\theta = 21.21^\circ$ was attributed to the (002) crystalline surfaces of graphene [62,63]. In the XRD pattern of 2S-20Fe NP, the peaks of $2\theta = 28.6^\circ$, 32.2° , 36.7° , 40.7° and 56.7° belong to FeS_2 [64,65], the peaks of $2\theta = 15.5^\circ$, 30.5° , 47.7° and 52.3° correspond to Fe_3S_4 [65,66], the peaks of $2\theta = 27.0^\circ$ and 38.3° are related to FeS [67] and Fe_3O_4 [67], respectively, and the peaks of $2\theta = 44.4^\circ$ and 59.2° are assigned to Fe^0 [68]. This shows that the main components of iron sulfide in the 2S-20Fe@G membrane were FeS_2 and Fe_3S_4 , accompanied by some FeS , Fe_3O_4 and Fe^0 . A variety of iron sulfides are beneficial to efficiently catalyze the rapid degradation of pollutants by PMS. In

addition, the peak of S ($2\theta = 21.3^\circ$) was able to be observed[67]. However, only diffraction peaks of FeS_2 [64,65] ($2\theta = 35.2^\circ$), Fe_3O_4 [67] ($2\theta = 38.3^\circ$), and Fe^0 [68] ($2\theta = 44.4^\circ, 59.2^\circ$) were visible on the 2S-20Fe@G membrane, which was attributed to the weak XRD peaks caused by the encapsulation of C. According to the XRD pattern of the GO-Heat membrane, the peaks at $2\theta = 10.3^\circ$ and 19.8° correspond to the lattice (001) and (002) of graphene, respectively (SI, Fig. S6a). XRD characterization of the S@G membrane can confirm the distribution of S between the membrane layers ($2\theta = 6.5, 23.2^\circ$) [67], while the peaks at $2\theta = 15.2^\circ$ and 29.0° are assigned to the (002) and (100) of graphene (SI, Fig. S6b). The weakly broad peaks at 35.9° and 62.7° in the XRD pattern of the Fe@G membrane indicated the presence of Fe(III) [69], which was predominantly $\text{Fe}(\text{OH})_3$, and that the peak at 20.3° represented the (002) of graphene (SI, Fig. S6b). According to the sharpness of the (002) peak of graphene, the degree of reduction of GO can be corroborated in one aspect. As can be observed in Fig. S6, the peaks of Fe@G membrane, S@G membrane, and 2S-20Fe@G membrane gradually sharpened, which proved that the ratio of its GO/rGO decreased. At the same time, we used XRD for analyzing the interlayer spacing of membranes through the Bragg equation (SI, Fig. S6c). The GO-Heat membrane showed a diffraction peak at 10.29° corresponding to a layer spacing of 0.850 nm. When Fe/S was modified individually, the layer spacing of the Fe@G membrane was almost constant (0.848 nm), and the layer spacing of S@G membrane was reduced to 0.757 nm; however, as Fe and S were co-doped, the layer spacing of the 2S-20Fe@G membrane was increased to 0.947 nm. When Fe(III) was added individually, cross-linking only with GO nanosheets resulted in almost constant spacing of the membrane layers; whereas low-valent S^{2-} (both S^{2-} and S^{4+} in $\text{Na}_2\text{S}_2\text{O}_3$) modification caused part of the GO nanosheets to undergo a deoxidation reduction reaction to rGO nanosheets, resulting in orderly stacking of nanosheets to reduce the spacing of the layers. However, when Fe and S were co-incorporated, S^{2-} undergoes a redox reaction partly with the Fe(III) and the GO nanosheets, and the resulting iron sulfides lead to disordered stacking between the nanosheets, thereby increasing the spacing of the layers. However, the nanoscale layer spacing within the 2S-20Fe@G membrane still offers a nanoconfined space. The optical photographs (SI, Fig. S7) also revealed that the Fe-doped GO membrane (Fe@G) exhibited the distinctive red hue of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ colloids, while the incorporation of S (S@G) predominantly

reduced the GO from yellow (GO) to black (rGO). Ultimately, the 2S-20Fe@G membrane also appeared black with characteristic rGO properties. Therefore, changing the dosage of the Fe/S source can also regulate the proportion of reduced GO.

The physicochemical properties of the various types of membranes were further analyzed. Fourier transform infrared (FTIR) spectroscopy was applied to study the functional groups of the GO membranes, GO-Heat membranes, S@G membranes, and Fe@G membranes with 2S-20Fe@G membranes (**Figure 2a**). Absorption peaks attributed to C-H, C-O-C, C=C, C=O and -OH were observed in the FTIR spectra of the five membranes at 830, 1097, 1630, 1729, 1394 and 2890-3660 cm^{-1} respectively [70]. Among them, the -OH absorption peak of the Fe@G membrane was enhanced due to the presence of iron hydroxide. Owing to the joint action of Fe/S, most of the GO inside the 2S-20Fe@G membrane was reduced to rGO, which resulted in the reduction of O-H tensile vibration inside the membrane. This weakens the interaction between oxygen-containing functional groups and water molecules, thereby increasing the water permeance. The FTIR spectra of the 2S-20Fe@G membrane displayed absorption peaks at 446 and 1578 cm^{-1} , which were attributed to Fe-O bonding [71] and S=O bonding [72], respectively, proving the successful introduction of Fe/S.

BET analysis was performed to determine the specific surface area (S_{BET}) and pore size distribution of the 2S-20Fe@G membrane. The nitrogen adsorption-desorption isotherms of the 2S-20Fe@G membrane were classified as type III (**Figure 2b**). The specific surface area and total pore volume of the 2S-20Fe@G membrane were 38.09 m^2/g and 0.093 cm^3/g , respectively. The pore size distribution, calculated using the Horvath-Kawazoe (HK) model for micropores (<2 nm) and the Barrett-Joyner-Halenda (BJH) model for mesopores (2–36.55 nm), ranged from 0.936 to 36.55 nm (Inset to **Figure 2b**), with a peak pore size of 2.78 nm. This suggests that the 2S-20Fe@G membrane contained numerous inter- and intra-layer nanochannels, which facilitated nanoconfinement catalysis within the membrane and allow rapid water passage [73].

X-ray photoelectron spectroscopy (XPS) was performed to determine the surface chemistry of the 2S-20Fe@G membrane and to compare this with the GO membrane. As shown in the SI (Fig. S8), the appearance of Fe and S peaks in the composite membrane proved the successful loading of both elements. Compared with the C 1s of the GO membrane (**Figure**

2c), in addition to the C-C[74], C-O/C-O-C[75], and C=O/HO-C=O[76] bonds, the composite membrane also appeared to have C-S bonds (285.6 eV)[77]. This indicated that the S from doping was not only bonded with Fe, but also to the C on GO, improving the coordination environment of C on GO; it also reinforced the connection between Fe and GO, limiting the leaching of metal ions. The doping of Fe/S resulted in the partial conversion of sp^3 hybridized carbon to sp^2 hybridized carbon, confirming the partial reduction of GO to rGO, which was consistent with the XRD results. This is conducive to enhancing the surface activity of GO nanosheets, which can facilitate charge transfer and improve the electron transfer rate. The introduction of Fe/S doping can significantly affect the electron configuration of PMS, leading to the weakening of its terminal O-O bond [78,79]. Such weakening facilitates the decomposition of PMS, accelerating the generation of RS, which are highly reactive and beneficial for the efficient degradation of pollutants [23]. Furthermore, the doping of Fe/S induces a partial transformation of sp^3 hybridized carbon to sp^2 hybridized carbon, which enhances the electronic conductivity of the GO nanosheets. The presence of sp^2 carbons improves the electron transfer efficiency, as sp^2 carbon atoms in graphene oxide have a higher density of states at the Fermi level and a more delocalized π -electron cloud, making them more favorable for charge transfer processes [80,81]. The electrons on the catalyst could be effectively excited by the covalent bonding of sp^3 hybridized carbon into the conjugated system of neighboring sp^2 hybridized carbon, generating a denser electron population while transferring electrons to the PMS molecule and boosting the non-radical pathway [82]. These structural modifications not only accelerate the electron transfer rate but also promote the generation of reactive species (RS), improving the catalytic efficiency in advanced oxidation processes (AOPs) [23,82–84]. The O 1s of 2S-20Fe@G membrane (**Figure 2d**) showed the characteristic groups of GO nanosheets [85–87]. In this case, the ratio of C=O/C-O-C was decreased by S doping. The peak at 529.7 eV indicated the appearance of oxides of Fe[88], while the binding energy of 530.3 eV was attributed to the lattice oxygen of Fe-O[89], which together with the surface oxygen on C-OH accelerated the electron transfer and provided electrons with the promotion of PMS conversion. The deconvolution of Fe 2p for the 2S-20Fe@G membrane (**Figure 2e** and SI, Table S3) displayed the presence of three valence states of Fe^0 , Fe(II), and Fe(III) in the material, where both Fe(II) and Fe(III) were bonded to S and

O, and the results corresponded to those of the XRD analysis. The two convolution peaks at 707.3 and 720.1 eV corresponded to Fe 2p_{3/2} and Fe 2p_{1/2} of Fe⁰, [90] which accounted for about 7.77%. Fe(II) consisted of Fe(II)-S (deconvolution of 708.3 and 721.3 eV, which accounted for 16.69%) [91] and Fe(II)-O (deconvolution of 709.9 and 723.1 eV, which accounted for (24.31%) [92], accounting for 41%. Fe(III) was composed of Fe(III)-S (deconvolution of 711.8 and 725.3 eV, which accounted for 14.19%) [93] and Fe(III)-O (deconvolution of 713.9 and 727.7 eV, which accounted 9.84%) [94], with a percentage of 24.03%. Multiple valence states of Fe facilitated the rapid activation of the catalytic membrane for PMS to produce active substances to catalyze the degradation of pollutants. Deconvolution of S 2p revealed the presence of different forms of S within the 2S-20Fe@G membrane (**Figure 2f**). The proportions of monosulfides (S²⁻, 161.4 and 162.6 eV) [64,95] and disulfides (S₂²⁻, 161.8 and 163.1 eV) [96] were 15.65% and 51.32%, respectively; also, the peaks at 163.8 and 164.9 eV represented the presence of S⁰ (with a proportion of 25.64%) [64]. The presence of strongly reducing polysulfides in the membrane facilitate the cyclic conversion of Fe(II)/Fe(III) in the 2S-20Fe@G membrane/PMS system. Additional analysis of the C 1s, O 1s, Fe 2p and S 2p XPS results for the GO membrane and 2S-20Fe@G membrane can be found in the SI (Table S2 and Table S3).

Figure 2g summarizes the comparative Raman spectra of the GO, GO-Heat, S@G, Fe@G and 2S-20Fe@G membranes. Two characteristic peaks appeared at 1350 cm⁻¹ (D band) and 1580 cm⁻¹ (G band), which can be attributed to amorphous or defective carbon and associated graphitic carbon, respectively. Furthermore, the intensity ratio of I_D/I_G as a crucial parameter was generally employed to evaluate the number of defects. It was found that the ratios of the GO, GO-Heat, S@G, Fe@G and 2S-20Fe@G membranes were 1.69, 1.66, 1.74, 1.82, and 1.88, respectively, which indicated that the co-doping of S/Fe resulted in composite membranes with a higher concentration of defects. Since the I_D/I_G ratio can only provide a basic assessment of defects in the graphene network, we deconvoluted the D and G bands into five distinct peaks — D_{sep}, G_{sep}, and three additional peaks (D*, D'', and D') (SI, Fig. S9a-e) — to extract more detailed information from the Raman spectra [97,98]. Previous studies [98,99] have shown that the position of the D'' and D* peaks is shifted to lower and higher wavenumber values, respectively, when oxygen content decreases. Therefore, these behaviors suggest that it is

possible to consider the position of these bands as a suitable parameter to estimate the reduction degree of GO. The red shift of the D" peak and the blue shift of the D* peak (SI, Fig. S9f) indicated that GO in 2S-20Fe@G was highly reduced among above materials, consistent with the XRD results (SI, Fig. S6).

The results of the initial water contact angle can indicate the characteristics of the micro-structure and hydrophilicity of material surfaces and this technique has been effectively used to analyze the physicochemical properties of the GO based membranes. The results summarized in **Figure 2h** showed that the introduction of Fe favored the increased hydrophilicity of the Fe@G membrane (31.13°) compared to the GO membrane (45.56°) and the GO-Heat membrane (39.11°). This phenomenon could be attributed to the easy coordination between electron-deficient Fe and H₂O (electron-rich O atoms)[100]. In contrast, the initial water contact angle of the 2S-20Fe@G membrane was increased partly due to the increase in hydrophobicity caused by the binding of S to the end-group oxygen on the GO membrane surface[101], and partly due to the hydrophobicity of the iron sulfides. The hydrophobicity of the 2S-20Fe@G membrane facilitated the prolongation of the retention time of the pollutants and PMS as they passed through the membrane and promoted the catalytic degradation of pollutants. The GO membrane exhibited a negative Zeta potential with a value of -18.8 mV. The Zeta potential of the S@G membrane decreased to -62.4 mV due to the electronegativity of S. Although electro-neutralization resulted in an increase in the Zeta potential of the Fe@G membrane to -5.33 mV, the 2S-20Fe@G membrane was still negatively charged (-41.3 mV) owing to the strong electronegativity of S (**Figure 2i**). Negatively charged catalytic membranes tended to favor the adsorption of positively charged contaminants (e.g., CBZ, etc.) and repel to intercept negatively charged contaminants (e.g., TC) on the basis of the mutual attraction of dissimilar charges.

Figure 2.

3.2. Performance of the S-Fe@G membrane/PMS system

The catalytic performance of the S-Fe@G membrane was evaluated by filtering a feed solution at pH 4.44 containing a model contaminant (TC, 20 mg/L) and PMS (1 mM). First,

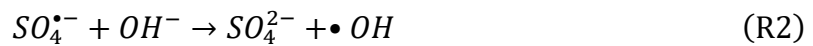
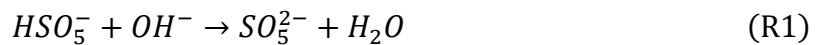
the combined effects of different S/Fe doping amounts on the TC removal efficiency and membrane permeance of the S-Fe@G membrane were investigated (**Figure 3a** and SI, Fig. S10a). When the concentration of $\text{Fe}(\text{OH})_3$ was greater than 4.62 mM or the $\text{Na}_2\text{S}_2\text{O}_3$ dosage was greater than 2 mM, the removal rate increased with the reduction of Fe/S addition. This was attributed to the high concentration of Fe/S forming larger particles with reduced surface area (SI, Fig. S5). For membranes with defects or a lack of active sites, water tends to pass through the larger defects, resulting in a lower catalytic efficiency. In contrast, the removal efficiency of TC was able to reach more than 90% in 2 h when the concentration of $\text{Fe}(\text{OH})_3$ colloid was < 4.62 mM, or the $\text{Na}_2\text{S}_2\text{O}_3$ dosage was < 2 mM. However, with the decrease of Fe/S doping, the water permeance of the membrane decreased substantially due to the increase of solution resistance caused by the diminution of the intercalated particles. We investigated the impact of different catalyst loadings (with the same Fe/S ratio) on the catalytic performance within the 2D membrane (SI, Fig. S10b). The greatest TC degradation efficiency and suitable water permeance were observed at a catalyst loading of 5.4 mg (2 mmol $\text{Na}_2\text{S}_2\text{O}_3$ and 4.62 mM $\text{Fe}(\text{OH})_3$ in 20 mL). This result was attributed to a reduction in the catalyst's effective active sites when the loading was decreased, which lowered the activation efficiency of PMS. Additionally, a reduction in the number of membrane pores decreased the water permeance. As the loading increased, the number of pore channels within the membrane also increased, which enhanced the water permeance but reduced the PMS residence time, thereby decreasing the TC degradation efficiency. Therefore, the 2S-20Fe@G membrane with a $\text{Na}_2\text{S}_2\text{O}_3$ dosage of 2 mmol and $\text{Fe}(\text{OH})_3$ colloidal concentration of 4.62 mM (20 mL) was selected as the optimal treatment condition because it provides optimal removal efficiency (94.9% of TC in 2 h) and water permeance ($124.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{MPa}^{-1}$) while retaining the structural integrity of the membrane.

The performance of various catalytic membranes in activating PMS to degrade TC is shown in **Figure 3b**. The removal efficiency of TC in the 2S-20Fe@G membrane/PMS system remained above 90% throughout the test period (0 – 120 min). In the absence of PMS, the final removal efficiency of the 2S-20Fe@G membrane was only about 30% due to adsorption saturation and a small percentage of retention. Meanwhile, PMS alone only removed 22.4% of TC. These results indicated that membrane adsorption and retention as well as PMS alone

catalytic degradation played a limited role in the 2S-20Fe@G membrane/PMS system. In addition, the ability of 2S-20Fe NP and 2S-20Fe@G NS to activate PMS was examined. The degradation of TC by 2S-20Fe NP (7.4 mg, same loading as on 2S-20Fe@G membrane) and 2S-20Fe@G NS (7.4 mg, same loading as on 2S-20Fe@G membrane) was only 55.9% and 75.2% within 120 min, respectively. Based on the results, it was hypothesized that the nanoconfined effect caused by GO (rGO) nanosheets would be conducive to the activation of PMS by the catalyst [36], and at the same time, two-dimensional membranes were made to enrich TC and PMS in the nanoconfined space, which would shorten the delivery paths of the active substances and further improve the degradation efficiency [102,103]. This process enhances the effective collision of organics and PMS on the 2S-20Fe@G membrane layer, and promotes the subsequent TC degradation [104,105]. Meanwhile, the retention (reaction) time of the pollutant was calculated to further illustrate the pollutant degradation performance of the 2S-20Fe@G membrane with rapid activation of PMS. The 2S-20Fe@G membrane achieved greater than 90% TC removal within a retention time of 158.7 ms. The kinetics of the 2S-20Fe@G membrane/PMS system were calculated using the pseudo-first-order reaction kinetics formula, yielding a rate constant of 1443 min^{-1} . This rate constant was 4-5 orders of magnitude greater than that of batch PMS-activation mode for the 2S-20Fe NP and 2S-20Fe@G NS, highlighting that the rapid catalytic degradation of TC by RS is enhanced in the nanoconfined state (**Figure 3b** and SI, Fig. S11a). In addition, a comparison of the kinetic rate constants for the 2S-20Fe@G membrane with those of the 2S@G membrane (220.3 min^{-1}) and 20Fe@G membrane (500.5 min^{-1}) demonstrated that sulfur doping significantly accelerates the catalytic membrane activation of PMS, leading to the rapid degradation of pollutants (SI, Fig. S11a). In addition, the 2D membranes with nanoconfined space exhibited higher PMS utilization compared to non-nanoconfined catalysts, and the sulfur-modified iron-based composite membrane (2S-20Fe@G M) demonstrated the highest PMS utilization (SI, Fig. S11b). This was attributed to the synergistic effect of nanoconfined structures and the pressure-driven membrane filtration process, which enhanced mass transfer. The above results demonstrated that the 2S-20Fe@G membrane/PMS system had an excellent catalytic degradation performance.

Figure 3c showed that the removal efficiency of TC remained between 96.3% and 91.0%

when the initial pH was in the range of 4 to 10 in 60 min. The results indicated that the 2S-20Fe@G membrane/PMS system has a wide range of applications in solutions with different pH values. However, when the pH was increased to 12, the removal efficiency decreased substantially to only ~40%. It is likely that alkalinity reduces the activity of the 2S-20Fe@G membrane through the reaction between excess OH⁻ and HSO₅⁻ (R1) [106]. Meanwhile, the reaction of SO₄^{•-} with excess OH⁻ can be converted to shorter-lived •OH (R2). High concentrations of OH⁻ may also generate Fe(OH)₃ precipitates to plate the membrane leading to structural collapse, which can lead to a significant decrease in the removal efficiency of TC. In addition, previous studies have demonstrated that alkaline environments catalyze the autolytic decomposition of activated PMS, leading to the production of RS [107]. To investigate how the autolytic decomposition of PMS in alkaline environments affects pollutant degradation, we compared the decomposition efficiencies of PMS across various pH levels without any external catalyst (SI, Fig. S12). The self-decomposition efficiency of PMS was lower at neutral (pH 7). As the pH increased, the self-decomposition efficiency of PMS enhanced to varying degrees. However, at pH 12, the increase in active substances from the self-decomposition of PMS (R1) in an alkaline environment cannot counterbalance the quenching of free radicals by OH⁻ (R2-R3) and the negative impact on the catalyst (R4). As a result, the 2S-20Fe@G membrane/PMS system exhibits poor degradation efficiency at this pH. When the pH was reduced to 2, the removal efficiency dropped to ~80%. In acidic solutions, the high concentration of H⁺ can bind to the peroxides of PMS and inhibit the interaction between PMS and the 2S-20Fe@G membrane [108]. In addition, H⁺ can stabilize PMS, making it more difficult to activate [109].



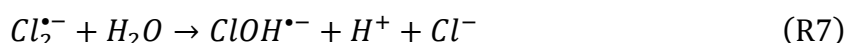
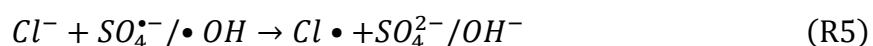
To further assess the mechanical strength and stability of 2S-20Fe@G membranes under acidic and alkaline conditions, the apparent stability, crystal structures, and functional groups were characterized and compared to those of the untreated 2S-20Fe@G membranes at pH 4, pH 7, and pH 10, respectively (SI, Fig. S13). We immersed 2S-20Fe@G membranes in the

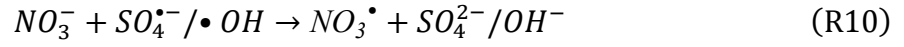
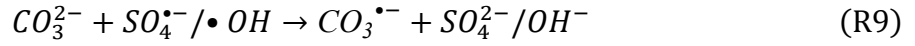
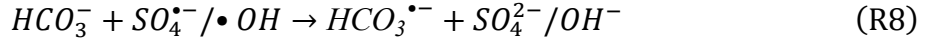
three pH solutions for an extended period to assess their apparent stability. Fig. S13a showed that all membranes remained intact without significant disintegration for 30 days under acidic (pH 4), neutral (pH 7), and alkaline (pH 10) conditions, demonstrating good mechanical stability. The XRD spectra of both the original and treated membranes showed similar peak positions, indicating that the interlayer and crystal structures remained largely unchanged (SI, Fig. S13b). FTIR spectra revealed no significant alterations in the functional groups of the membranes after 30 days of immersion in solutions with varying pH (SI, Fig. S13c). These results demonstrate that the 2S-20Fe@G membranes retain good mechanical properties and stability under both acidic and alkaline conditions. It is plausible to infer that the presence of iron sulfides primarily contributes to the enhanced stability, with the iron sulfides in the interlayers strengthening the cross-linking between the nanosheets.

In addition, to evaluate Fe leaching from different materials, we compared the Fe^{3+} concentrations in the leachates of the 2S-20Fe@G membrane, 2S-20Fe@G NS, and 2S-20Fe NP under different conditions (after 1 h of PMS addition and TC reaction) (SI, Fig. S14). Under control conditions (pH = 4.44), the Fe leaching concentration from the 2S-20Fe@G membrane was $70.9 \mu\text{g L}^{-1}$, which is below the WHO Guidelines for Drinking Water Quality ($300 \mu\text{g L}^{-1}$); whereas that of 2S-20Fe@G NS and 2S-20Fe NP increased to $361.5 \mu\text{g L}^{-1}$ and $550.6 \mu\text{g L}^{-1}$ (both exceeding the WHO guideline), respectively. The GO nanosheet carriers dispersed and immobilized Fe, reducing ion leaching, while the nanoconfined structure in the 2S-20Fe@G membrane anchored Fe within the membranes, significantly decreasing its leaching. Under strong acidic conditions (pH = 1), Fe leaching increased in all three systems; however, the stable nanoconfined structure in the 2S-20Fe@G membrane resulted in the lowest Fe leaching, demonstrating its excellent resistance to strong acidity.

In aquatic environments, inorganic ions coexist with pollutants such as TC. Here, we explored the removal efficiency of TC in a 2S-20Fe@G membrane/PMS system in the presence of anions (Cl^- , HPO_4^{2-} , CO_3^{2-} , HCO_3^- , SO_4^{2-} and NO_3^-) (**Figure 3d**). The results showed that the presence of 15 mM Cl^- slightly hindered the removal efficiency of TC, and the removal efficiency gradually decreased with the increasing concentration of Cl^- (SI, Fig. S16a). Cl^- can combine with $\text{SO}_4^{\bullet-}$ or $\bullet\text{OH}$ to form secondary chlorine radicals (i.e., $\text{Cl}\bullet$, $\text{Cl}_2^{\bullet-}$ and $\text{ClOH}^{\bullet-}$) with low oxidation potentials (R5, R6 and R7), causing inhibition of pollutant

removal from the reaction system. The presence of only weak inhibition in the 2S-20Fe@G membrane/PMS system corroborated the diversity of active substances produced in this system. Similar to Cl^- , the anions CO_3^{2-} and HCO_3^- can readily interact with $SO_4^{\bullet-}$ or $\bullet OH$ to form $HCO_3^{\bullet-}$ or $CO_3^{\bullet-}$ at lower oxidation potentials (R8-R9)[110]. In the system of the 2S-20Fe@G membrane/PMS, the removal efficiency of TC showed a high level (~88.0%) at 15 mM HCO_3^- , and remained high, at 66.0%, as the concentration increased to 50 mM (SI, Fig. S16c), which demonstrated that the free radicals and the non-free radicals together dominated the degradation of pollutants in the system. The hydrolysis of CO_3^{2-} resulted in a strongly alkaline pH of the solution, leading to a substantial decrease in TC removal efficiency (SI, Fig. S16b). In addition, NO_3^- can also react with $SO_4^{\bullet-}$ or $\bullet OH$ to form $NO_3^\bullet$ (R10), thus effectively scavenging free radical substances from the system without affecting the non-free radical pathway[111]. Apparently, no significant inhibitory effect of NO_3^- on the system was observed in the concentration range of 0-50 mM (SI, Fig. S16d). Previous studies have revealed that SO_4^{2-} cannot react with radical species to generate secondary radicals. As a result, the TC removal efficiency was almost unaffected in SO_4^{2-} solutions at concentrations of 0-35 mM, but decreased to ~70.3% as the concentration was increased to 50 mM (SI, Fig. S16e). In addition to the scavenging effect of anions, inhibition can be caused by their competition for the catalyst active sites, also leading to a decrease in the performance of the reaction system[112]. The surface hydroxyl groups of transition metal sulfides have been confirmed as adsorption sites for sulfates[113]. Therefore, the high concentration of SO_4^{2-} in the reaction system would compete with PMS for the surface hydroxyl groups of the 2S-20Fe@G membrane, leading to a reduction in performance. The inhibition of the system by HPO_4^{2-} may be attributed also to competition for the active sites. In aqueous solution, HPO_4^{2-} can rapidly complex with the surface hydroxyl groups of the 2S-20Fe@G membrane and occupy the active sites[114]. The removal efficiency of the system was high at ~ 72.2% at a phosphate concentration of 15 mM, and remained essentially unchanging with increasing concentration (SI, Fig. S16f), which demonstrated the strong adaptability of the 2S-20Fe@G membrane/PMS process.





The concentration of TC in natural waters is generally low (below 20 mg/L), which may reduce the degradation efficiency of PMS [115]. To evaluate the degradation stability of the 2S-20Fe@G membrane/PMS system under more realistic conditions (micro-antibiotic environment) [116], the feed solution (10 mg/L TC + 0.5 mM PMS) was continuously passed through the membrane. The system maintained a stable TC removal efficiency of > 85.4% after 50 h of continuous flow operation, with the membrane permeance varying in the range of 115-125 L·m⁻²·h⁻¹·MPa⁻¹ (**Figure 3e**). However, the TC removal efficiency of the Fe@G membrane decreased to ~54% after 7 h of operation (**Figure 3e**), indicating that the introduction of low-valent iron (e.g., Fe⁰) and multivalent sulfur species (e.g., S²⁻, S₂²⁻ and S⁰) through S doping improved the degradation stability of the membrane. As a consequence of its stable structure, the 2S-20Fe@F membrane had sufficient active sites and was able to prevent deactivation from aggregation of the Fe_xS_y nanocatalysts, thus maintaining high stability under continuous flow operation. Meanwhile, the leaching concentration of iron in the permeate solution initially increased from 70.9 µg/L at 1 h to a stable concentration of ~ 120 µg/L (lower than the 300 µg/L recommended in the WHO Guidelines for Drinking Water Quality) after 50 h of continuous operation (SI, Fig. S17). These results demonstrated that the 2S-20Fe@G membrane had a greater stability compared with the Fe@G membrane. To further assess the long-term stability of the 2S-20Fe@G membrane, we characterized the membrane after 50 h of operation (SI, Fig. S18). The FTIR spectra before and after the extended operation exhibited similar peak positions, indicating that the functional groups of the membranes remained largely unchanged (SI, Fig. S18a). However, it is possible that the Fe-O bonds weakened due to the cycling of Fe during PMS activation. Similarly, XRD spectra revealed that the membrane structure remained largely intact before and after the reaction (SI, Fig. S18b), though the peak intensities were weakened due to partial oxidation of Fe⁰ into the Fe(II)/Fe(III) cycle during operation (SI, Table S3). Raman spectroscopy further confirmed that there were no significant changes in the structural defects of the membranes, highlighting the stability of the membrane structure (SI, Fig. S18c). Additionally, SEM images of the membrane surface before and after

long-time operation showed that the membrane retained its typical folded, two-dimensional structure (SI, Fig. S18d and e).

The 2S-20Fe@G membrane/PMS system also achieved high removal efficiencies (80% ~ 100%) for most of the organic pollutants, selected in this study, demonstrating the broad applicability of this 2D membrane in water treatment (**Figure 3f**). The particular physical and chemical properties of CBZ and MO resulted in removal efficiencies of only 61.6% and 69.8%, respectively. Control experiments confirmed that the degradation of these organic compounds was slightly lower using PMS only, while their removal efficiency using the 2S-20Fe@G membrane alone (without PMS) was mainly derived from low levels of membrane retention and membrane adsorption. Additionally, we compared the removal efficiency and reaction kinetics of the 2S-20Fe@G membrane with those of other membrane-based catalysts. The results show that the sulfur-coordinated iron-based nanoconfined catalytic membranes we developed exhibited superior reaction kinetics (**Figure 3g** and SI, Table S5).

Figure 3.

3.3 The reaction mechanism in the S-Fe@G membrane/PMS system

3.3.1. Identification of the RS

Catalyst-mediated electron transfer is a unique non-radical pathway in which the catalyst serves as an electron transfer bridge, while PMS and the pollutant function as electron acceptors and donors, respectively [108]. The existence of this pathway can be confirmed by monitoring the i-t curve changes after adding PMS and pollutants [117]. As shown in SI (Fig. S19a), a sharp increase in current was observed after adding PMS, indicating rapid electron transfer between the 2S-20Fe@G and PMS. However, after adding TC, the current did not change significantly, indicating no electron transfer between TC and the 2S-20Fe@G, thus refuting the existence of a catalyst-mediated electron transfer pathway [108]. To directly verify the existence of an electron transfer pathway, a galvanic oxidation process (GOP) system was constructed (SI, Fig. S20). Continuous pollutant degradation in the GOP system would indicate electron transfer [118]. However, the TC concentration decreased slightly within the first 30 min due to adsorption by the electrodes and remained unchanged over the next 180 min,

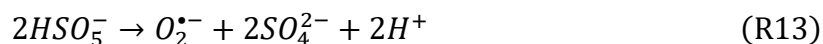
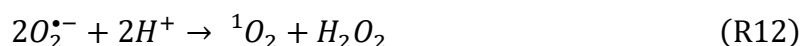
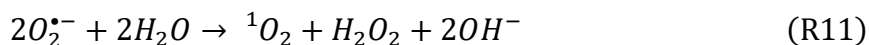
demonstrating that the 2S-20Fe@G membrane cannot mediate electron transfer from TC to PMS.

It is worth mentioning that the current change amplitude of Fe@G was much smaller than that of 2S-20Fe@G, indicating that S doping could improve the electron transfer rate of the catalyst [119]. This may be attributed to the introduction of thiophene sulfur (C-S-C) via S doping, which enhances the intra-membrane electron transfer capability (**Figure 2c**) [23]. The open-circuit potential (OCP) test showed a greatly raised OCP of the 2S-20Fe@G electrode upon PMS addition (SI, Fig. S19b), implying the surface binding and activation of PMS via electron transfer. A more profound change in potential (ΔE , after adding PMS) was observed for 2S-20Fe@G (0.14 V) than for Fe@G (0.009 V). A larger activation potential difference is the driving force for rapid electron transfer and swift consumption of PMS [120]. This suggested an enhanced PMS adsorption on 2S-20Fe@G, forming metastable and reactive complexes with higher potentials [121], thereby reinforcing PMS adsorption and electron transfer within the 2S-20Fe@G.

EPR and RS quenching experiments were employed to detect the active reactive species involved in the 2S-20Fe@G membrane/PMS system and to confirm the contribution of different RS to TC removal. Typically, DMPO can capture $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ radicals in aqueous systems and $\text{O}_2^{\bullet-}$ in methanol systems, while TEMP can trap $^1\text{O}_2$ in aqueous systems [122]. No significant signal peak was detected when only PMS was used as the control. A clear quadratic linear signal (1:2:2:1) of DMPO- $\bullet\text{OH}$ ($A_N = 14.86$ G, $A_H = 14.86$ G) was observed in **Figure 4a**, which was also accompanied by weak DMPO- $\text{SO}_4^{\bullet-}$ signals ($A_N = 14.86$ G, $A_{\alpha H} = 12.90$ G, $A_{\beta H} = 2.35$ G, $A_{\gamma H} = 0.98$ G), indicating that the system produced a certain amount of $\bullet\text{OH}$ and a small amount of $\text{SO}_4^{\bullet-}$. In the SI, Fig. S21a shows the EPR spectra using DMPO as a trapping agent in the methanol system, and it was found that the 2S-20Fe@G membrane/PMS system had a weak signal of DMPO- $\text{O}_2^{\bullet-}$, an adduct of DMPO with $\text{O}_2^{\bullet-}$, which indicated the production of $\text{O}_2^{\bullet-}$. TEMP- $^1\text{O}_2$ (1:1:1) was also observed in the reaction system (**Figure 4b**), confirming the occurrence of $^1\text{O}_2$. The contribution of each RS recognized in the 2S-20Fe@G membrane/PMS system was investigated by introducing different quenching agents. MeOH was used to remove $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, while TBA was used to specifically remove $\bullet\text{OH}$ [123]. When MeOH and TBA were added to the feed reaction solution,

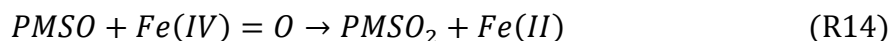
the removal efficiency of TC was only 55.6% and 50.7%, respectively (SI, Fig. S22). In addition, the removal efficiency decreased by 57.1% and 56.2% with the addition of FFA ($^1\text{O}_2$ quencher) and p-BQ ($\text{O}_2^{\bullet-}$ quencher), respectively.

The mechanism of $^1\text{O}_2$ production was investigated through O_2 or N_2 aeration experiments and EPR analysis following p-BQ quenching (**Figure 4c**). It was observed that neither O_2 nor N_2 affected TC degradation, and an absence of the TEMP- $^1\text{O}_2$ signal in the EPR spectra after the capture of $\text{O}_2^{\bullet-}$. These results demonstrated that the $\text{O}_2^{\bullet-}$ was the essential precursor in the formation of $^1\text{O}_2$ through proton-promoted disproportionation reactions (R11-R12), and this also explained the pattern of EPR results [102,120,124,125]. Additionally, the weak DMPO- $\text{O}_2^{\bullet-}$ signal detected may be due to the rapid conversion of $\text{O}_2^{\bullet-}$ as a reaction intermediate to either $^1\text{O}_2$ or H_2O_2 (R11-R12). It also demonstrated that the production of $\text{O}_2^{\bullet-}$ was not related to O_2 and originated from PMS (R13) [36].



To detect high-valent metal-oxo species (HVMS) in the system, we used dimethyl sulfoxide (DMSO) as a quencher, given its high reaction rate with HVMS [126]. Fig. S22 showed a reduction in TC removal efficiency to 48.8% after DMSO addition, highlighting the crucial role of HVMS in pollutant removal in this system. In situ Raman analysis was conducted to monitor the interactions during PMS activation (**Figure 4d**). The PMS solution exhibited characteristic peaks corresponding to HSO_5^- at 878 cm^{-1} and 1060 cm^{-1} , as well as the peak of SO_4^{2-} at 982 cm^{-1} [127]. Following the addition of 2S-20Fe@G, a new peak emerged at 843 cm^{-1} , which was attributed to the highly active high-valent iron species, Fe(IV)=O [128]. Upon the introduction of the contaminant (TC), Fe(IV)=O and HSO_5^- were consumed through the oxidation of TC, leading to a reduction in the intensity of the peaks associated with Fe(IV)=O and HSO_5^- . This observation confirmed the critical role of Fe(IV)=O and HSO_5^- in the degradation of TC. To further confirm, an investigation was conducted using phenylmethyl sulfoxide (PMSO) as a probe. Under acidic or neutral conditions, PMSO can be used as a probe molecule that can be selectively oxidized by high-valent iron species (Fe(IV)=O) to form PMSO_2 (R14) [129]. Previous studies [130] have found that $\text{SO}_4^{\bullet-}$ and

•OH can oxidize PMSO to different products compared to Fe(IV). In the 2S-20Fe@G/PMS system, we found that PMSO₂ was formed after the oxidation of PMSO, indicating the presence of Fe(IV). As shown in **Figure 4e** PMSO was completely degraded, but the generation rate (η) of PMSO₂ was only 67.4%. This indicated that in addition to Fe(IV), other reactive species, such as SO₄^{•-} and •OH, may also react with PMSO or PMSO₂, causing them to degrade and form other substances.



Kinetic constants were calculated by varying the different hydraulic residence times by changing the operating pressure through the membrane (SI, Text S5 and Fig. S23). In the absence of a quenching agent, the pseudo first-order kinetic constant of TC removal by the 2S-20Fe@G membrane/PMS system was 24.05 s⁻¹ (1443 min⁻¹), which was 4-5 orders of magnitude greater than the non-nanoconfined PMS catalytic system (2S-20Fe@G NS (0.102 min⁻¹)), demonstrating the ultra-rapid removal of pollutants in nanoconfined conditions. With the addition of different RS quenching agents, the kinetics were decreased by various degrees (**Figure 4f**). These RS quenching experiments indicated that •OH, ¹O₂ and Fe(IV)=O were the reactive species that mainly contributed to TC degradation in the 2S-20Fe@G membrane/PMS system.

Figure 4.

3.3.2 Activation mechanism of PMS in S-Fe@G membrane/PMS system

The effect of S doping before and after was elucidated for the performance of the catalytic membrane on PMS activation using DFT calculations (calculations shown in the SI, Text S7). We developed both Fe@G and Fe-S₄@G models for probing the adsorption and dissociation of PMS (HO-SO₃). Bader charge and charge density differences were analyzed in order to determine the adsorption sites of PMS on the catalyst and to study the effect of sulfur coordination on the electronic structure. The results given in the SI (Fig. S24) showed the differences in the Bader charge distributions of Fe-S@G and Fe@G, with and without PMS adsorption, where the yellow and blue regions represented charge accumulation and depletion, respectively. The results in **Figure 5a** showed that Fe atoms were in an electron-loss state in Fe@G, whereas in Fe-S₄@G, both S and Fe atoms were in an electron-loss state, with Fe losing

less charge upon S doping. This suggests that Fe was in a lower oxidation state after S doping, which is consistent with the XPS characterization of the 2S-20Fe@G membranes, where a higher content of low-valence Fe was observed (SI, Table S3). Both Fe and S atoms were positively charged, but Fe atoms carried more positive charge than S atoms, so the negatively charged PMS tended to adsorb on the Fe atom sites.

The reaction kinetics of PMS dissociation at the catalyst active site is crucial for the catalytic reaction process [131]. The maximum energy barrier to be overcome during the transition from reactants to products in a reaction path is defined as the reaction energy barrier for that path, which is related to the kinetic information of the reaction [132]. Therefore, the study employed the transition state search method (TS) to evaluate the reaction energy barriers for PMS dissociation, while the CI-NEB method modified by G. Henkelman was used to search for transition states [132]. The calculated reaction energy barriers are shown in **Figure 5b**, which displayed three structural profiles of the TS reaction [133], specifically: adsorption of PMS, transition intermediate structure, and PMS dissociation. The predominant adsorption of PMS to the Fe site has been discussed earlier, and so by default the final structure of the dissociated PMS similarly tended to be adsorbed to the Fe site. When the reaction energy barrier was below 21 Kcal/mol (i.e., 0.9 eV), the reaction can be carried out at room temperature [133]. The free energy of dissociation of HO-SO₃ over Fe-S₄@G was calculated to be only 0.04 eV, which was slightly lower than that of the S-free structure (0.07 eV), demonstrating the kinetic advantage of realizing PMS dissociation over sulfur-coordinated catalysts. This result corresponded to the 2S-20Fe@G membrane with a higher kinetic rate constant (SI, Fig. S11a). Meanwhile, the adsorption free energy of -OH and -SO₃ formed by PMS after dissociation on Fe-S₄@G was lower and more stable, which proved that the doping of S not only reduced the dissociation energy barrier, but also the whole reaction was able to release more heat, favoring the reaction. In view of the above calculations, Fe-S₄@G has significant advantages in both reaction thermodynamics and reaction kinetics compared to Fe@G. Sulfur doping facilitates the improvement of the electronic structure and electron transfer efficiency of S-Fe@G, which results in the formation of highly active Fe sites conducive to the activation of PMS.

It is well known that the Fe(II) sites and Fe⁰ are the main active sites in the activation

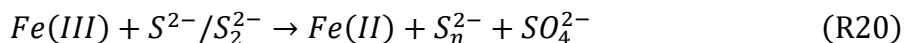
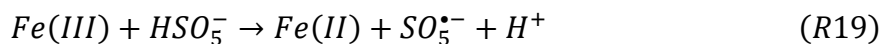
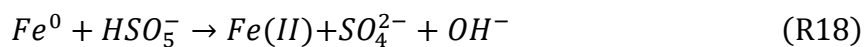
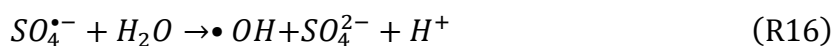
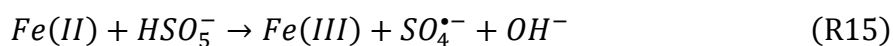
process of iron-heterogeneous catalysts [65,134]. Also, the involvement of sulfur species plays an important role for the activation of PMS by S-doped metal catalysts [52,135]. In order to investigate the possible transformations of Fe(II), S, and rGO inside the 2S-20Fe@G membrane, the chemical valence changes of Fe, S, C, and O before, and after, the use of the membrane were investigated by XPS (**Figure 5** and SI, Fig. S24e). As shown in **Figure 5c**, the major elements inside the membrane did not vary before and after the reaction catalyzing the degradation of TC by PMS. The percentages of Fe⁰, Fe(II), Fe(III), and Fe satellite peaks were 7.77%, 41.0%, 24.03%, and 27.2%, respectively, of the total Fe content in the fresh 2S-20Fe@G membrane, as reported previously (SI, Table S3). For the Fe 2p spectra in the used 2S-20Fe@G membrane, the relevant amount of Fe⁰ decreased to 3.12% and the relative content of Fe(II) and Fe(III) increased to 41.45% and 33.22%, respectively (**Figure 5d**, and SI, Table S3). The results indicated that Fe⁰, Fe(II) and Fe(III) were involved in PMS activation and that Fe⁰ transformed and participated in Fe(II)/Fe(III) cycling inside the 2S-20Fe@G membrane. This change suggested that the doping of sulfur species favored the acceleration of the Fe(II)/Fe(III) cycle.

As shown in **Figure 5e** and Table S3, the relative amount of reducible sulfur species (S²⁻ and S₂²⁻) decreased and the relative amount of S⁰ increased at the end of the reaction, suggesting that sulfur species are involved in the transfer of electrons in the catalyzed reaction. At the same time, a decrease in S²⁻ and an increase in S⁰ indicated the presence of sulfur cycling within the membrane. The reducible sulfur species serve as electron donors, facilitating Fe(II) regeneration and thereby promoting the rapid activation of PMS [22]. The XPS results of Fe 2p (**Figure 5d**) confirmed that the conversion of Fe(III) to Fe(II) was favored by the supply of electrons from sulfur species. The S doping facilitated the conversion of Fe(III), and promoted the Fe(II)/Fe(III) cycling during PMS activation.

The XPS spectra of C 1s and O 1s combined with fresh and used 2S-20Fe@G membranes are shown in the SI (Fig. S24). After the reaction, the relative content of oxygen of Fe rose and the relative content of lattice oxygen (Fe-O) decreased (SI, Table S2). This demonstrated that lattice oxygen on graphene oxide nanosheets (GO) or reduced graphene oxide (rGO) was involved in the reaction of activated PMS[136] and provided oxygen atoms that accelerated the transfer of electrons.

Figure 5.

According to the above results and discussion, a possible mechanism was proposed for the heterogeneous degradation of TC in the 2S-20Fe@G membrane/PMS system, as set out in the reactions shown in **Figure 6**. First, the 2S-20Fe@G membrane catalyzed the generation of a certain amount of $SO_4^{\bullet-}$ by single electron transfer, while Fe(II) was converted to Fe(III) (R15). Meanwhile, most of the $SO_4^{\bullet-}$ was rapidly converted to $\bullet OH$ radicals (R16). The recovery of Fe(II) was realized by using Fe^0 as a reductant (R17), and Fe^0 reacted with HSO_5^- to generate Fe(II) intermediates (R18) [137]. At the same time, there was a slow process of reduction of Fe(III) to Fe(II) by direct reaction with PMS (R19). In addition, the lattice S (S^{2-}/S_2^{2-}) of the sulfur ferrites in the 2S-20Fe@G membrane was able to mediate the transfer of electrons to Fe(III), thus accelerating the regeneration of Fe(II) and the conversion of S (R20). Then, S_n^{2-} underwent a disproportionation reaction to regenerate S^{2-} to realize the cycling of sulfur species (R21). Meanwhile, previous studies have demonstrated that $O_2^{\bullet-}$ radicals can be generated by PMS (R13) [36]. More importantly, the activation of PMS by 2S-20Fe@G membrane also involved non-radical processes (i.e., the singlet oxygen pathway). Regarding the pathway of $^1O_2$ production, previous studies[124,138] have revealed that $^1O_2$ can be generated by $SO_5^{\bullet-}$ (R22) and $O_2^{\bullet-}$ (R11). As discussed in the previous section, the conversion of $O_2^{\bullet-}$ was the main pathway for the generation of $^1O_2$ in the 2S-20Fe@G membrane/PMS system. Subsequently, Fe(II) was further activated to generate Fe(IV)=O species (R23) [19]. Finally, owing to the synergistic effect between the dominant $\bullet OH$, Fe(IV)=O and $^1O_2$ species and the supporting $SO_4^{\bullet-}$ and $O_2^{\bullet-}$ radicals, TC/pollutants can be efficiently degraded into smaller organic substrates (R24).



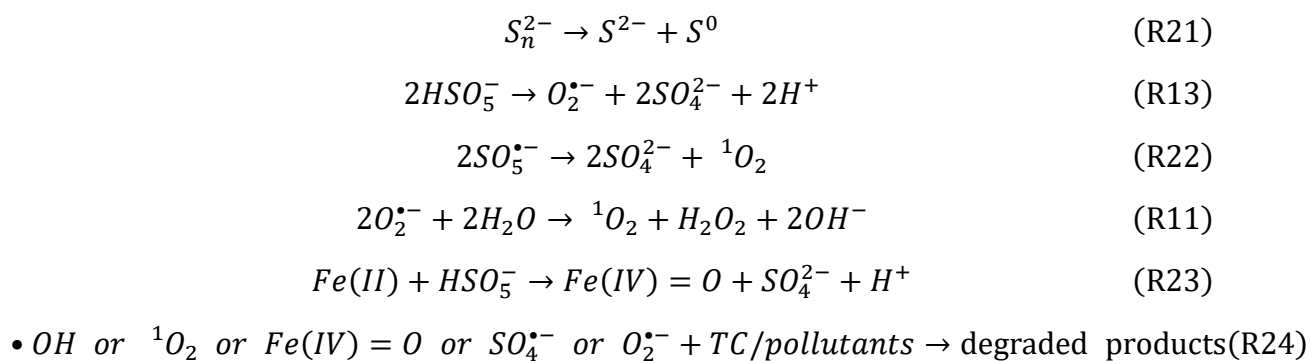


Figure 6.

3.4. Degradation pathway and toxicity of intermediate products

By utilizing LC-MS, we detected intermediates that may be formed during TC degradation, as detailed in the SI (Table S4). The MS spectra corresponding to these intermediates are also shown in Fig. S25. The degradation of TC may occur by one of the two pathways outlined in **Figure 7a**. In pathway I, the TC molecule suffered a loss of functional groups (e.g., through demethylation, hydroxylation, or dihydroxylation) to generate P1 ($m/z = 387$)[139]. Then P1 underwent deamination and cyclization to generate P2 ($m/z = 365$), which was further converted to P3 ($m/z = 251$) by severe ring breakage and dehydroxylation[140]. Thereafter, P3 was degraded to P4 ($m/z = 221$), P5 ($m/z = 205$), and P6 ($m/z = 183$) by deamidation, drastic ring breakage, and hydroxylation. Pathway II involved demethylation of the TC molecule by $\bullet OH$ and $SO_4^{\bullet-}$ radical attack, leading to the formation of P7 ($m/z = 413$)[141]. Subsequently, P7 was converted to P8 ($m/z = 238$) by dehydration, deamidation, ring cleavage and action. Then, double bonds, hydroxyl and carboxyl groups were generated by oxidation on the benzene ring and further dehydration occurred to form P9 ($m/z = 203$). After this, P9 underwent reductive hydroxylation to produce P10 ($m/z = 175$). Finally, several of the aforementioned products continued to decompose into smaller components (P11 ($m/z = 155$), P12 ($m/z = 122$), P13 ($m/z = 117$), P14 ($m/z = 83$), P14' ($m/z = 83$), P15 ($m/z = 81$), P16 ($m/z = 59$), and P17 ($m/z = 42$), and then further oxidized to form CO_2 and H_2O molecules (SI, Table S4).

The 3D EEM technique operates on the principle that the molecular structure of a substance corresponds to the characteristic fluorescence intensity[142], and it is commonly

used to detect intermediates with fluorescence effects produced during degradation. The positions of the different peaks in the spectrum represent different substances.[143,144] The electron-withdrawing groups of the TC molecule resulted in no detectable fluorescent signal in the original TC solution (SI, Fig. S26a) [145]. As can be seen in Fig. S26b, there were no fluorescence peaks evident when only the TC stock solution passed through the membrane. However, when the TC and PMS mixture passed through the catalytic membrane, three major fluorescence peaks and some weak fluorescence signals were observed in the filtrate, at $E_x/E_m = (200 - 250)/(400 - 460)$ nm, $E_x/E_m = (275 - 325)/(400 - 450)$ nm and $E_x/E_m = (210 - 240)/(280 - 310)$ nm, respectively, which corresponded to the presence of humic acid, fulvic acid-like substances, and other small molecules during the reaction (SI, Fig. S26c) [19,146,147]. This variation in solution fluorescence reveals to some extent the transformation process of TC macromolecules during TC degradation. The partial decomposition of TC into small- and medium-sized molecular intermediates with fluorescent properties further supports the consistency between the 3D EEM and the LC-MS results presented in this study.

To assess the potential toxicity of intermediates produced in the 2S-20Fe@G membrane/PMS system, as indicated by fathead minnow LC_{50} (96 h), developmental toxicity, and mutagenicity, we utilized the Quantitative Structure-Activity Relationship (QSAR) method implemented in the Toxicity Estimation Software Tool (T.E.S.T., version 5.1.2) [148]. Fathead minnow LC_{50} (96 h) refers to the dose of the substance that causes the death of half of the fathead minnows within 96 h and represents the acute toxicity of the intermediates. The LC_{50} (96 h) value for TC of fathead minnow was 0.9 mg/L. Encouragingly, most of the identified degradation products, except P3, P4 and P7, exhibited higher LC_{50} values than TC, indicating a significant reduction in acute toxicity (**Figure 7b**). Furthermore, the developmental toxicity values of P1-P5 and P7 were greater than TC, whereas the rest of the developmental toxicity was lower than TC (**Figure 7c**). Meanwhile, as shown in **Figure 7d**, the mutagenicity of TC was positive (with a coefficient of 0.6), except for P1, P3, P7, P17, and P14, where the mutagenicity of the intermediate products was converted to negative. From the above analysis, it can be concluded that most of the products were less toxic than TC.

Figure 7.

3.5. Decontamination Performance with Different Water Sources

To test the broad applicability of the 2S-20Fe@G membrane/PMS system, different water quality backgrounds were used to test its ability to remove TC. In this study, humic acid (20 mg/L) dissolved in DI was regarded as a simulated real water body (HA), and North Lake water was considered as a representative of a real water source (RW). Based on the test results, it can be seen (**Figure 8a** and SI, Fig. S27, Table S6) that the retention and adsorption performance of the 2S-20Fe@G membrane for TC (~ 48%) and its ability to catalyze the degradation of TC by the PMS were essentially unaffected in different water qualities, and the average removal efficiencies at 60 min were maintained at > 94.9%. The above results demonstrated that the 2S-20Fe@G membrane was unaffected by the quality characteristics of the different solutions and able to achieve an efficient removal of TC.

In order to investigate the capability of the 2S-20Fe@G membrane/PMS system to mineralize organic pollutants, the changes in the total organic carbon (TOC) concentration [149], MW distributions (SEC analysis) [150] and 3D EEM [151] spectra of the solutions before and after membrane passage were determined. As can be seen from **Figure 8b**, the removal efficiency of TOC before and after the addition of PMS increased from 10.0% to 56.9% in pure HA solution, which proved that HA was partly mineralized, and degraded into small molecules according to the SEC and 3D EEM analyses (SI, Fig. S28a, d-f). It can be seen clearly that substances with molecular weights of around 10,000 Dalton were degraded into small molecules, with most of the spikes appearing at 2000-3000 Dalton corresponding to the PMS (**Figure 8c** and SI, Fig. S28a). The fluorescence peak of $E_x/E_m = (200 - 325)/(380 - 550)$ nm, which was attributed to humic acid-like substances [152], did not reduce, in general, after membrane passage alone, but with the addition of PMS, the fluorescence weakened and the position of the peak ($E_x/E_m = (210 - 275)/(350 - 450)$ nm) was shifted, indicating that humic acid degraded into small substances, such as proteins [153,154]. At the same time, the results demonstrated that the 2S-20Fe@G membrane/PMS system was also able to achieve 43.3% removal efficiency of TOC for pollutants in the real water (**Figure 8b**), and reduce the molecular weight of organic components in the real water (SI, Fig. S28b). 3D EEM spectra also demonstrated the degradation of aromatic protein-like [155] and tyrosine-like [156]

substances in the real water, whose fluorescence peaks were greatly attenuated ($E_x/E_m = (330 - 380)/(200 - 250)$ nm and $E_x/E_m = (330 - 380)/(250 - 300)$ nm) (**Figure 8d-f**). The above results indicated that the 2S-20Fe@G membrane/PMS system had a substantial degradation and mineralization effect on the pollutants in both simulated and real waters.

To investigate the mineralization of TC in the presence of other water quality constituents, the removal efficiency of TOC in different solutions (DI, HA and RW) was determined. The 2S-20Fe@G membrane/PMS system showed a 66.7% removal efficiency of TOC for TC in deionized water, which indicated that the system exhibited a high degree of mineralization of TC (**Figure 8b**). However, the mineralization rate of TC in HA and real water was reduced due to the competitive consumption of RS by anions and natural organic matter. With the TC in the simulated real water (containing HA), its removal efficiency of TOC was slightly reduced (61.0%), indicating that the system had a good selectivity for TC (**Figure 8b**). No obvious peaks other than the characteristic PMS peaks in the SEC analysis (**Figure 8c**), and only weak fluorescence peaks attributed to small MW humic acid analogs (similar to SI, Fig. S26c) in the 3D EEM spectra, were observed (**Figure 8i**), indicating that the 2S-20Fe@G membrane/PMS system achieved a greater mineralization of both TC and HA. The degradation performance of the 2S-20Fe@G membrane/PMS system resulted in a decrease in the size of the MW distribution of organic matter in RW+TC (SI, Fig. S28c). Lastly, the removal efficiency of TOC for TC was 52.1% for the real water sample (**Figure 8b**). Owing to the variety of natural organic compounds in RW, some of these will form complexes with TC leading to bright fluorescence peaks in the 3D EEM[157] spectra (**Figure 8j**). The three characteristic fluorescence peaks that appeared when TC was degraded (similar to SI, Fig. S26c) can be clearly seen in **Figure 8j-l**, indicating the highly selective degradation of TC and the universal nature of pollutant degradation by the 2S-20Fe@G membrane.

Figure 8.

4. Conclusions

Novel S-Fe@G nanoconfined catalytic membranes were designed to activate PMS for

944 ultra-rapid TC degradation, achieving a first-order rate constant of 1443 min^{-1} (4-5 orders of
945 magnitude higher than non-nanoconfined systems). Sulfur doping enhanced Fe(II)/Fe(III)
946 cycling by optimizing Fe's electronic structure (via DFT), enabling sustained efficiency ($>85\%$
947 TC removal over 50 h) and broad applicability (pH 4–10, multiple pollutants). Quenching
948 experiments identified multiple reactive species ($\bullet\text{OH}$, $^1\text{O}_2$, Fe(IV)=O , $\text{SO}_4^{\bullet-}$ and $\text{O}_2^{\bullet-}$),
949 with $\bullet\text{OH}$, $^1\text{O}_2$ and Fe(IV)=O dominating the degradation. LC-MS revealed two degradation
950 routes, and toxicity assessment confirmed reduced environmental risks. The membrane
951 achieved $>94\%$ TC removal and $>52\%$ mineralization in real water, demonstrating a scalable
952 performance for sulfur-coordinated iron-based catalytic membranes in practical water
953 treatment.

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977 **Notes**

978 The authors declare no competing financial interest.

979

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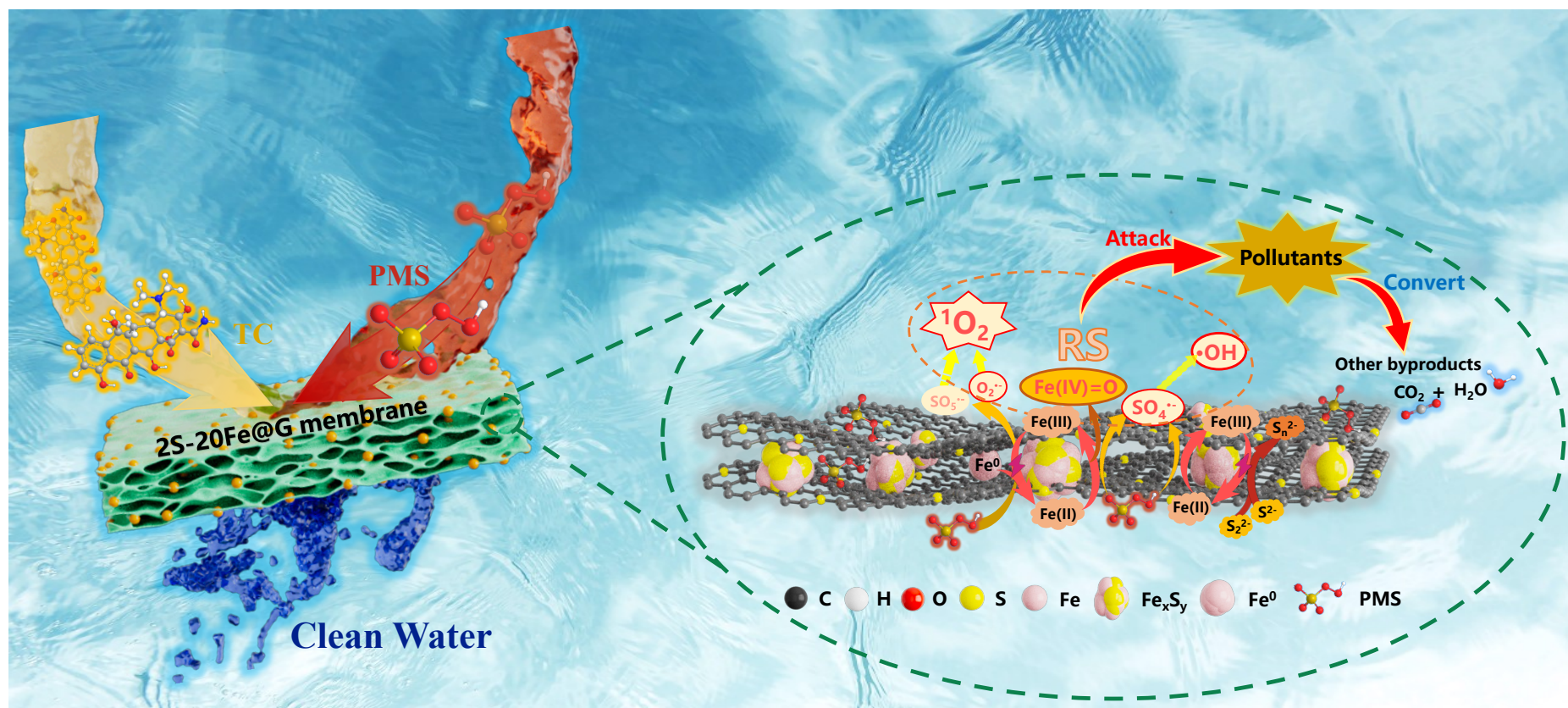
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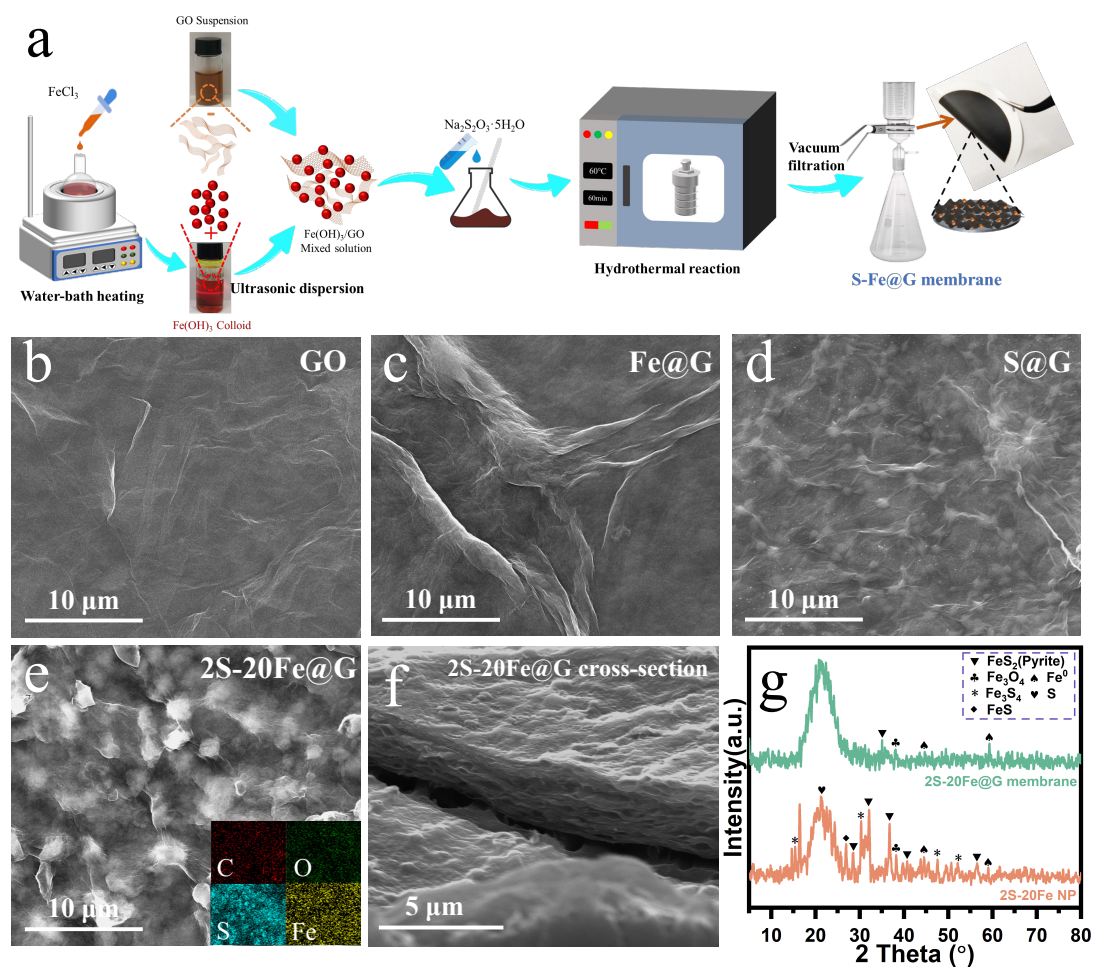


Figure 1. Illustration of the preparation of the S-Fe@G membrane (a); SEM images of pure GO membrane (b), Fe@G membrane (c), S@G membrane (d), 2S-20Fe@G membrane with the energy dispersive spectroscopy (EDS) mappings (e) and the cross section of the 2S-20Fe@G membrane (f); XRD spectra of 2S-20Fe@G membrane and 2S-20Fe NP (g).

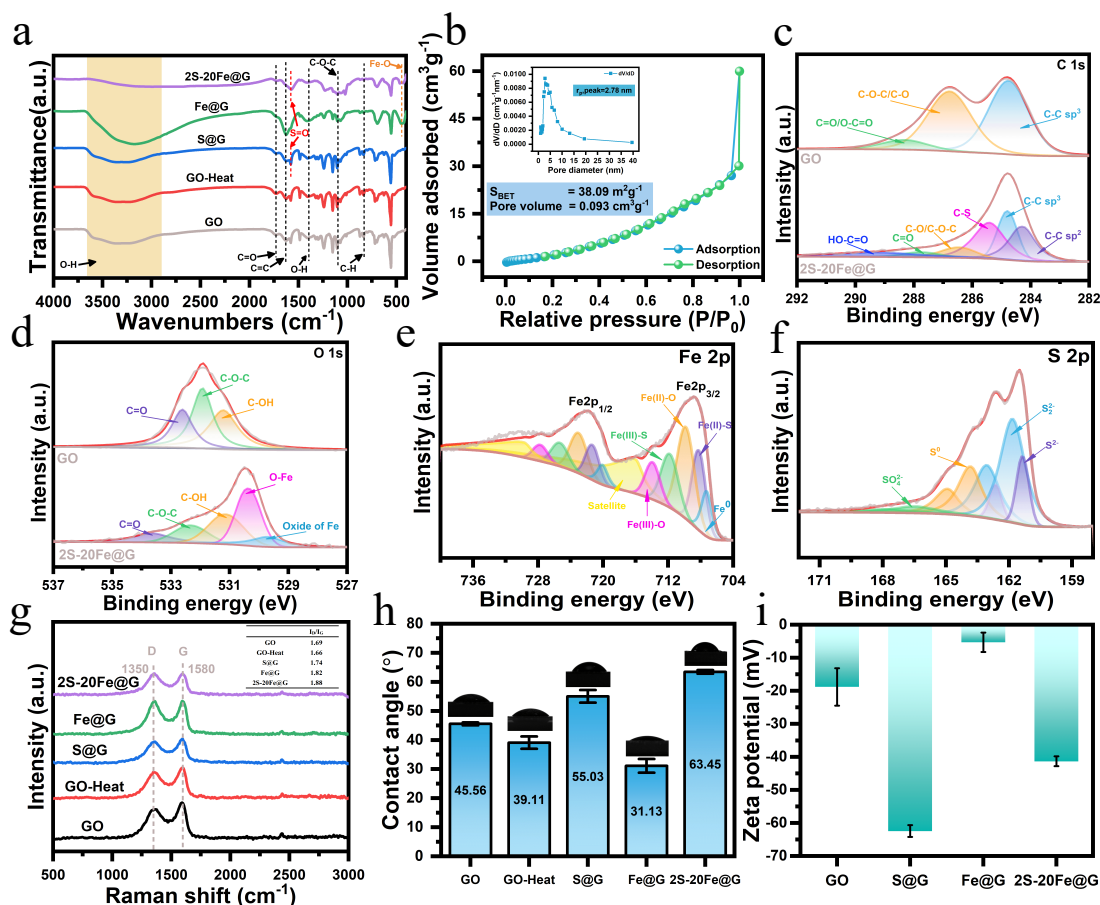


Figure 2. The FT-IR spectra (a) of the membranes; Nitrogen adsorption-desorption isotherm (b) and pore size distribution (Inset of b) of the 2S-20Fe@G membrane; C 1s (c) and O 1s (d) high-resolution XPS spectra of the GO membrane and the 2S-20Fe@G membrane; Fe 2p (e) and S 2p (f) high-resolution XPS spectra of the 2S-20Fe@G membrane; the Raman spectra (g), Initial contact angle values (h) and Zeta potential values (i) of the membranes.

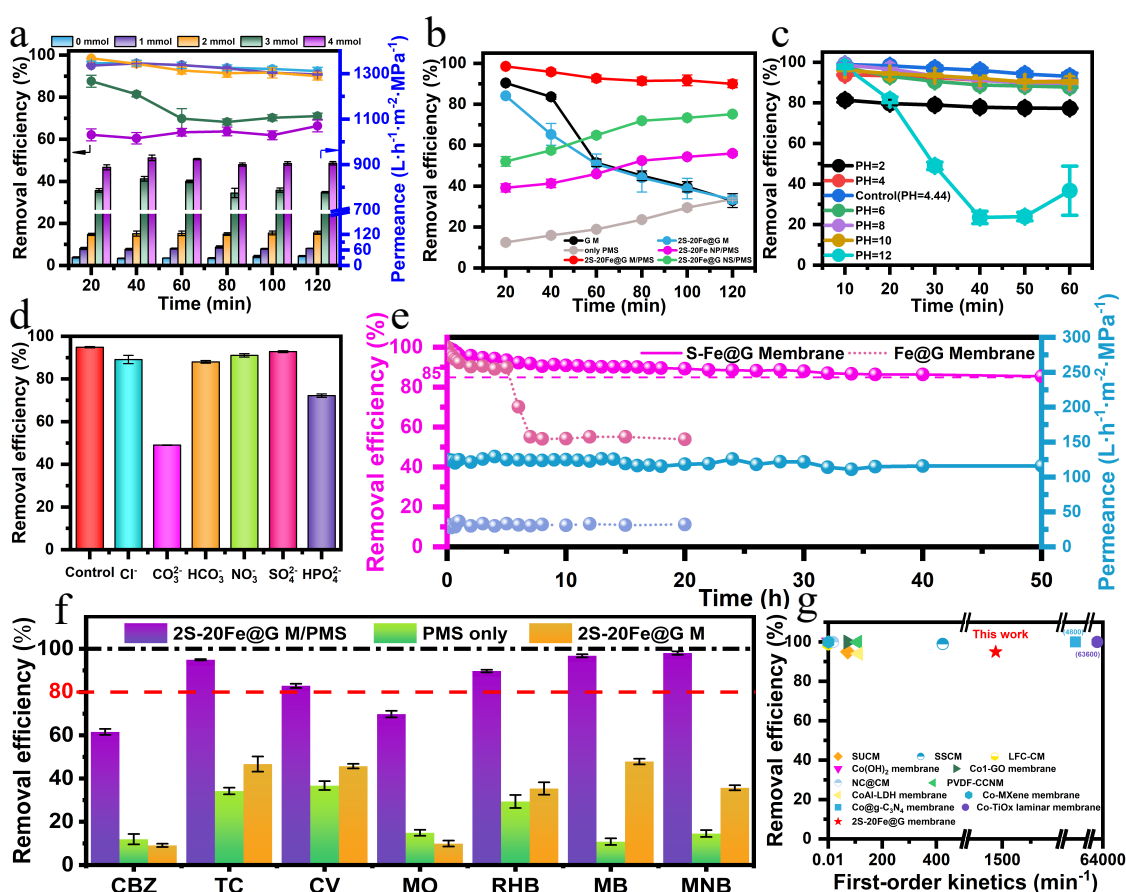


Figure 3. The catalytic performance for TC degradation and permeance of xS-20Fe@G (0-4 mmol $\text{Na}_2\text{S}_2\text{O}_3$ and 20 mL $\text{Fe}(\text{OH})_3$ colloid) membranes prepared with different $\text{Na}_2\text{S}_2\text{O}_3$ dosages (a); the catalytic performance for TC degradation by different catalytic systems (b); the effect of initial pH value on TC removal (c); the influence of Cl^- , CO_3^{2-} , HCO_3^- , NO_3^- , SO_4^{2-} and HPO_4^{2-} ($C_0 = 15\text{mM}$) on TC degradation in the 2S-20Fe@G membrane/PMS system (d); the variation of water permeance and TC removal efficiency of the composite membrane/PMS system with time (long-term operation) (e); the removal efficiencies of carbamazepine (CBZ), tetracycline hydrochloride (TC), crystal violet (CV), methyl orange (MO), rhodamine B (RhB), methyl blue (MB) and methylene blue (MNB) (conditions: $C_0 = 20\text{ mg}\cdot\text{L}^{-1}$, $[\text{PMS}] = 1\text{ mM}$, tested under 2S-20Fe@G membrane) (f); Comparison of the TC reaction times with other membrane-based catalytic processes (g).

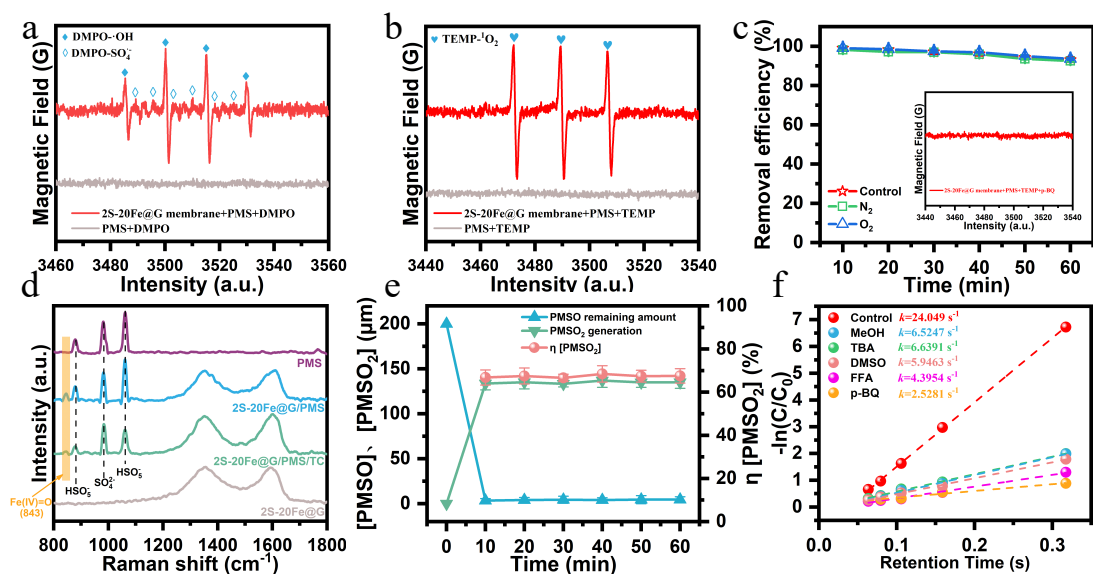


Figure 4. EPR spectra of the 2S-20Fe@G membrane/PMS system (a) and (b); TC removal in the 2S-20Fe@G membrane/PMS system under O₂ and N₂ saturated conditions (Inset: TEMP spin-trapping EPR spectra in 2S-20Fe@G membrane/PMS/p-BQ systems) (c); In situ Raman spectra of PMS activation and TC reaction on the surface of 2S-20Fe@G membrane (d); Residual PMSO and production of PMSO₂ in 2S-20Fe@G membrane/PMS system (e); First-order kinetics of TC under different quenching conditions in the 2S-20Fe@G membrane/PMS system (f). (Reaction conditions: [TC]₀ = 20 mg/L, [PMS] = 1 mM, (a) [DMPO] = 50 mM, (b) [TEMP] = 50 mM, (c) and (f) [MeOH] = [TBA] = [DMSO] = [FFA] = [p-BQ] = 20 mM, (d) [p-BQ] = 20 mM, (e) [PMSO] = 200 mM).

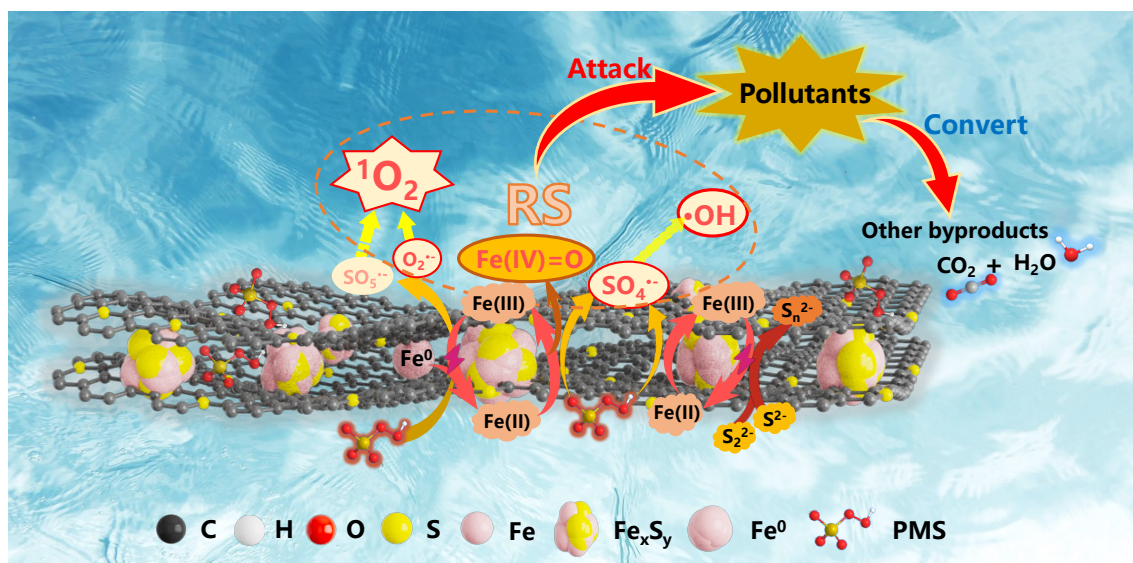


Figure 6. The possible mechanism of PMS activation and TC degradation in the 2S-20Fe@G membrane/PMS system.

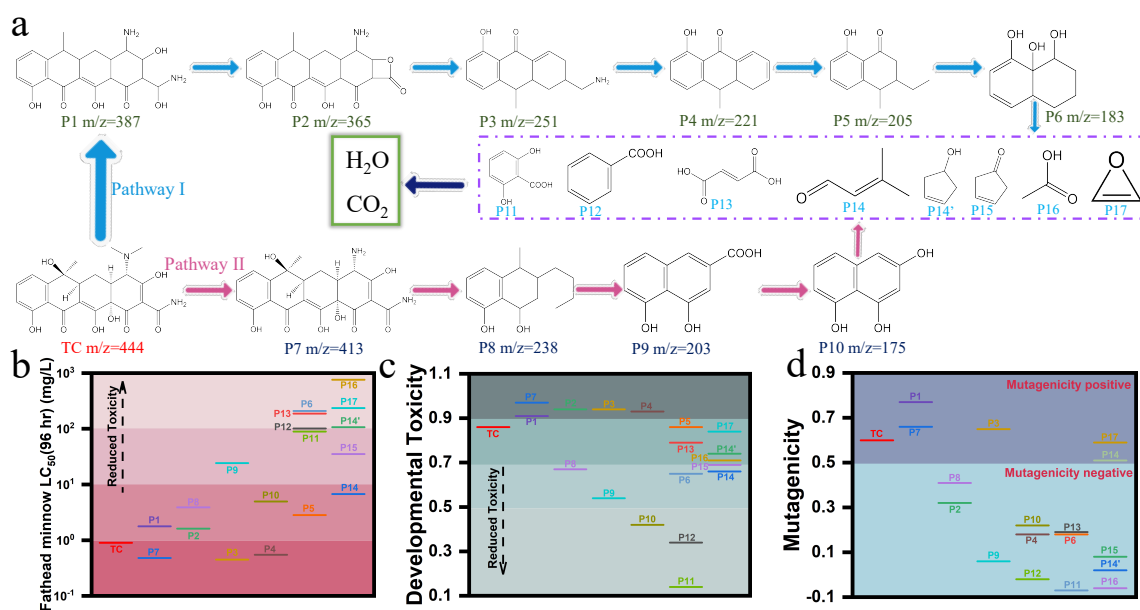


Figure 7. The proposed degradation pathways of TC in the 2S-20Fe@G membrane/PMS system (a); the Fathead minnow LC_{50} (96 h) (b), Developmental toxicity (c) and Mutagenicity (d) of TC and its intermediates.

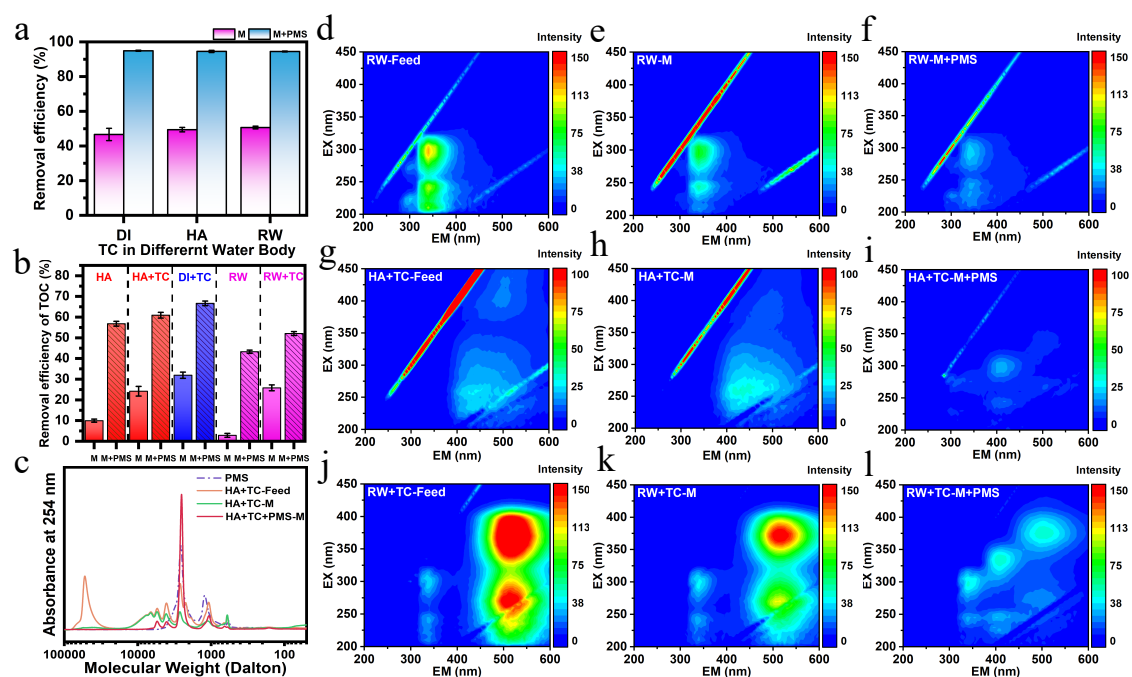


Figure 8. The removal efficiency of 2S-20Fe@G membrane for TC by retention (M) or degradation (M+PMS) in DI, simulated real water (HA, 20 mg/L) and RW (North Lake water), respectively (a), Mineralization efficiency of various contaminants by 2S-20Fe@G membrane under different conditions (b); MW distributions (SEC analysis) of contaminants (HA+TC) after degradation by 2S-20Fe@G membrane/PMS system (c); 3D EEM of spectra of various water samples (RW, HA+TC and RW+TC) under different treatment conditions (d-l).

Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Author Statement

Wenwa Weng: Conceptualization, Data curation, Formal analysis, Investigation, Methodology and Writing – original draft

Jiawei Hou: Conceptualization, Data curation, Investigation

Nigel J. D. Graham: Investigation, Supervision, Validation and Writing – review & editing

Xinyu Yu: Formal analysis, Investigation

Wenzheng Yu: Resources, Supervision, Validation and Writing – review & editing

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Ting Liu (Corresponding Author): Formal analysis, Funding acquisition, Project administration, Software, Supervision, Validation, Visualization and Writing – review & editing