Original Research

Fabrication of AQ2S/GR composite photosensitizer for the simulated solar light-driven degradation of sulfapyridine

Shuang-Yang Zhao,a Cheng-Xin Chen,a Jie Ding,a,**, Shan-Shan Yang,a *, Ya-Ni Zang,a Xu-Dong Qin,b,c, Xin-Lei Gaob,c, Zhao Songd, Nan-Qi Ren,a

a State Key Laboratory of Urban Water Resource and Environment, School of Environment, Harbin Institute of Technology, Harbin, 150090, China
b Guangdong Institute of Technology National Engineering Research Center of Water Resources Co., Ltd., Harbin, 150090, China
c Guangdong Yuehai Water Investment Co., Ltd., Shenzhen, 518021, China
d UNSW Water Research Center, School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW, 2032, Australia

A R T I C L E  I N F O

Article history:
Received 19 May 2021
Received in revised form 28 July 2021
Accepted 28 July 2021

Keywords:
Photosensitizer
AQ2S
Visible-light-driven
Free radicals trapping
Reusability

A B S T R A C T

Chlorination has been intensively investigated for use in water disinfection and pollutant elimination due to its efficacy and convenience; however, the generation and transportation of chlorine and hypochlorite are energy-consuming and complicated. In this study, a novel binary photosensitizer consisting of anthraquinone-2-sulfonate (AQ2S) and graphene was synthesized via a π-π stack adsorption method; this compound could allow for the chlorination of organic pollutants using on-site chlorine generation. In this photosensitive degradation process, sulfapyridine (SPY) was selected as a model pollutant and was decomposed by the reactive species (Cl2−, ClO−, and ClO2) generated during the photosensitively oxidation of chloride. The synthesized AQ2S/graphene exhibited superior activity, and the degradation rate of SPY was over 90% after 12 h of visible light irradiation with a kinetic constant of 0.2034 h−1. Results show that 20 mg AQ2S/GR at a 21% weight percentage of AQ2S in a pH 7 SPY solution with 1 mol/L Cl− achieved the highest kinetics rate at 0.353 h−1. Free radical trapping experiments demonstrated that Cl2− and ClO− were the dominant species involved in SPY decomposition under solar light. The reusability and stability of this composite were verified by conducting a cycle experiment over five successive runs. The capacity of photodegradation still remained over 90% after these 5 runs. The current study provides an energy-efficient and simple-operational approach for water phase SPY control.

© 2021 Harbin Institute of Technology. Published by Elsevier B.V. on behalf of Chinese Society for Environmental Sciences, Harbin Institute of Technology, Chinese Research Academy of Environmental Sciences. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

With the growth of the chemical industry over the past few decades, plenty of chemosynthesis reagents with complex chemical structures and high chemical stability have been discharged into natural water systems [1]. These released compounds include sulfonamide antibiotics (SAs), which are broad-spectrum antibiotics widely used in animal husbandry, aquaculture, and health care. In aquaculture, only 20%–30% of the dosage of SAs can be absorbed by fish and shrimp, leaving large amounts of residue in water [2,3]. Due to their persistence and biotoxicity, SAs have low biodegradability and easily enter traditional biological sewage treatment processes, becoming threats to both human health and the environment [4,5]. Because of this, there is an urgent need to develop an efficient method to remove residual SAs in aqueous environments.

Many efforts have been carried out to deal with this issue, such as bacterial degradation, advanced oxidation process and adsorption method [6–9]. Among these attempts, advanced oxidation processes (AOPs) have been extensively applied for toxic, bio-refractory, and high pollutant concentration wastewater treatment [9,10]. During the AOPs, organic contaminants in wastewater are decomposed by free radicals with high oxidative activity [10,11]. Due to its strong oxidative properties and convenience of application, chlorination has drawn extensive attention and has been widely applied for the elimination of bacteria and the degradation of organic pollutants [12–14]. Cai et al. (2020) confirmed that...
S.-Y. Zhao, C.-X. Chen, J. Ding et al. Environmental Science and Ecotechnology 8 (2021) 100111

flunoxazolone could be efficiently removed from water by the UV/chlorine process with a removal rate of 90.6 % during 30 min of UV irradiation by a 100 μmol/L dosage of free available chlorine [13]. Zhang et al. (2020) investigated the kinetics and mechanism of ephephrine removal by chlorinated processes and found that ephephrine could be degraded by NaClO with a high reaction rate \([7.43 \times 10^2 \text{ (mol L}^{-1} \text{ )}^{-1} \text{ min}^{-1}]\) under ideal pH conditions [14]. Kong et al. removed atrazine and meprop at an 80 % and 30 % degradation rate, respectively, by applying a solar/chlorine process and determined the main active species (O₃ and ClO) for the degradation of these herbicides [15]. Despite these advantages, the generation of free chlorine (Cl₂) is an energy-intensive electrolytic process which demands electrical grid connectivity or high-voltage batteries [16]. In addition, although the transportation of hypochlorite seems to be relatively low cost, decomposition and leakage can occur during storage [17]. Therefore, an on-site chlorination generation method is ideal for organic pollutant chlorination in the water phase.

To deal with these issues, Michael Dodd from the University of Washington used the cyclic reaction of quinone compounds with chloride [18] to provide a reasonable option for on-site chlorination generation by solar photosensitized activation of Cl⁻. In their research, sodium anthraquinone-2-sulfonate (AQ2SNa) was applied as a photosensitizer to produce Cl₂ under solar light irradiation. The Cl₂ generated was sparged from the photoreactor and dissolved into a trap solution of 0.1 M NaOH. Because their research objectives were chlorine generation and collection, AQ2S was dissolved into the reaction solution with a pH of 0–2, which makes this method not ideal for the degradation of organic pollutants.

Recent studies have proved that loading photocatalysts or photosensitizers on graphene-related sheets are ideal for improving photoresponsiveness as well as providing numerous physicochemical properties that make it good support [19–21]. The addition of Graphene (GR) not only can provide a supporting platform to disperse and stabilize AQ2S, but can also improve the transportation of electrons, thus enhancing the efficiency of photoelectric conversion. Compared with pure AQ2S, the large surface area provided by GR gives the composite a high adsorptivity to organic pollutants, in creasing the probability of the encounter between organics and transient radicals [22,23].

In this study, GR was applied as a carrier for AQ2S in order to recover the photosensitizer and promote the photoresponsitiveness of the composite. Sulfapyridine (SPY) was selected as a model pollutant to test its ability to degrade organics. This study aimed to examine the feasibility of SPY chlorination via an on-site chlorine generation process, and to optimize the weight percentage of GR and AQ2S to provide the optimal performance for SPY degradation. The effects of various conditions on SPY degradation were also examined and the stability and resistance to photocorrosion of the obtained composite were examined.

2. Material and methods

2.1. Chemicals and reagents

Sodium anthraquinone-2-sulfonate (AQ2SNa), tert-butanol (TBA), and p-benzoquinone (p-BQ) were purchased from Shanghai Aladdin Corporation. NaCl, NaHCO₃, NaOH, and HCl were supplied by Tianjin Continental Chemical Reagent Factory. GR with a diameter of each sheet about 0.5–5 μm and thickness of 0.8–1.2 nm was obtained from Tangshan Jianhua Science Technology Co., Ltd. SPY was purchased from Shanghai Yuanye Biotechnology Co., Ltd. All reagents were analytical grade and were used without further purification. Deionized (DI) water was used throughout the experiment.

2.2. Synthesis of AQ2S/GR

The AQ2S/GR binary composite was synthesized using a π–π stack process (Fig. 1). 100 mg of GR was added into an AQ2SNa solution at different concentrations to form suspensions with different weight percentages of AQ2S and GR. These suspensions were then stirred for 12 h at room temperature. Centrifugation was then performed at 12,000 rpm for 0.5 h to draw the binary material out of the suspension. The synthesized composite was rinsed with DI water several times and then dried at 60 °C for 12 h.

2.3. Characterization

The morphologies and structures of the synthesized composites were determined via scanning electron microscopy (SEM, Merlin Compact, Zeiss, Germany) and transmission electron microscopy (TEM FEI Tecnai F20, USA). X-ray diffraction (XRD) patterns of samples were acquired using an X-ray diffractometer (X’Pert, Panalytical, Netherlands) with Cu Kα radiation in the 20 range from 10° to 90°. Raman spectra of the products were recorded on a Raman spectrometer (inVia-Reflex, Renishaw, UK) with a 532 nm laser. Fourier transform infrared (FT-IR) spectra were recorded on an infrared spectrometer (Nicolet is50, Thermo Fisher, USA) with KBr as a background over the range of 4000–400 cm⁻¹. The surface elemental compositions and the chemical states of each sample were investigated via X-ray photoelectron spectroscopy (XPS, PHI 5300, PerkinElmer, USA) with an Al Kα X-ray source. All of the binding energies were calibrated using the C1s peak at 284.8 eV. To evaluate the optical properties of the photosensitizers, the analysis of the UV–visible diffuse reflectance spectroscopy was carried out using a UV–vis spectrophotometer (UV–vis DRS, UV-2550, Shimazu, Japan) with barium sulfate (BaSO₄) as the background between wavelengths of 200 and 1000 nm. The specific surface area and pore size distribution of the composite were investigated using Quantachrome Autosorb IQ (USA).

2.4. Evaluation of SPY degradation

SPY degradation experiments were performed with a 300 W Xenon lamp (PLS-SXE 300UV, Beijing Perfectlight Co., Ltd.) as a light source and with an AM 1.5G filter (cutoff below 320 nm). An optical power meter was used, and the average incident light intensity at the surface of the reacting solution was determined to be
64 mW cm^{-2} (PL-MW2000, Beijing Perfectlight Co., Ltd.). In detail, 10 mg AQ2S/GR was added into a quartz cylinder (250 mL) containing 100 mL of 20 mg/L SPY solution. This suspension was then magnetically stirred in darkness for 30 min to build up an adsorption/desorption equilibrium between the prepared photosensitizer and SPY. Before illumination, 2.925 g of NaCl was dissolved into the suspension to act as a Cl^{-} acceptor. The mixed solution was then placed under the xenon lamp at a 10 cm distance. The concentration of SPY was quantitatively determined by Ultra High Performance Liquid Chromatography (UPLC) (Acquity, Waters, USA). The mobile phase contained water (0.1 % formic acid) and acetonitrile at a proportion of 85/15, and the flow rate was kept at 0.2 mL/min at a 308 K column temperature with a 10 μL injection volume. To optimize the degradation efficiency, control experiments were performed with various concentrations of Cl^{-}, different dosages of AQ2S/GR and various initial concentrations of SPY under the same conditions. After each run, the binary material was drawn out of the reaction solution by centrifugation at 12,000 rpm for 0.5 h and was dried for use in experiments to test its stability. The degradation of SPY was fitted using the pseudo-first-order kinetic model described by Eq. (1):

$$-\ln(C/C_0) = kt$$

where, $C_t$ is the concentration of the SPY solution (mg L^{-1}) at time $t$, $C_0$ is the initial concentration of SPY before solar light irradiation, and $k$ is the apparent reaction rate constant (min^{-1}).

To identify the dominant reactive species in the photosensitive reaction, quenching experiments were conducted. In these experiments, 50 mM tert-butanol (TBA), 100 mM HCO$_3$^{-}, and 1 mM benzoquinone (BQ) were applied as scavengers.

To consider the stability and reusability of AQ2S/GR, a consecutive 5-cycle test was carried out to assess the efficiency of SPY degradation under solar light irradiation for 12 h. After each run, the binary materials were recovered with centrifugation at 12,000 rpm for 0.5 h. The AQ2S/GR was rinsed with DI water several times and dried at 60 °C for 12 h. Each run was under the condition as below: 20 mg AQ2S/GR, 20 mg/L SPY, 0.5 mol/L Cl^{-}.

3. Results and discussion

3.1. Characterizations of the AQ2S/GR composites

The binary AQ2S/GR composite was prepared using a simple adsorption method. With the addition of GR into the AQ2SNa solution, AQ2S rapidly adhered to the surface of GR by π-π stacking. SEM and TEM images of the prepared samples are shown in Fig. 2. The SEM image exhibited a two-dimensional structure with a plicated surface of the GR (Fig. 2(a)). A similar image of AQ2S/GR showed that the loading of AQ2S leads to no obvious change to the structure and surface of GR (Fig. 2(b)). Compared with Fig. 2(c) and d, there are numerous small particles attached to the wrinkles of the GR surface. These particles might be formed by the aggregation of AQ2S molecules, which is indicative of the combination of AQ2S and GR. When the specific surface area of GR and the binary material was assessed by BET, as shown in Fig. 3(e) and (f), pure GR had a more distinct H2-type hysteresis loop and larger specific surface area (644.80m$^2$g^{-1}). The smaller specific surface area (119.08m$^2$g^{-1}) of the composite could be attributed to the occupation of the active adsorption site by AQ2S.

The interaction between AQ2S and GR was determined by UV−Vis spectrophotometry. AQ2S showed two adsorption peaks at 207 and 333 nm, which can be attributed to the short-wavelength n→π* transitions of the free electron pairs of the sulfonic group and the n→π* transitions of quinone group, respectively (Fig. 3(a)) [24]. The maximum absorption at 275 nm of GR corresponded to the π→π* transitions of the aromatic bond. For the binary composite, the presence of a 207 nm adsorption peak confirmed the successful combination of AQ2S and GR.

Raman spectra are widely used to reveal the lattice structure of composites. As shown in Fig. 3(b), peaks at 1350 cm$^{-1}$ and 1590 cm$^{-1}$ for GR corresponded to D and G bands, respectively. Compared with pure GR, both the D and G bands of the binary material were slightly blue-shifted. The intensity ratio I_D/I_G was inversely proportional to the average size of the sp$^2$ domains [25]. This ratio decreased from 1.14 to 1.07 after the addition of AQ2S, illustrating that the adsorption of AQ2S caused little damage to the conjugate structure of GR.

FT-IR spectroscopy was performed to further characterize the functional groups and carbon species of pure AQ2S, GR and AQ2S/GR (Fig. 3(d)). The characteristic absorption peaks of AQ2S were seen at 1047 cm$^{-1}$ and 1215 cm$^{-1}$, which can be attributed to the stretching vibration of −SO$_3$-. In addition, peaks of AQ2S at 701 cm$^{-1}$ and 612 cm$^{-1}$ were attributed to the bending vibration of the aromatic skeleton [26]. For the binary composite, slight shifting occurs with the bending vibration of the aromatic skeleton because of the π-π conjugate. The absorption peaks at 1675 cm$^{-1}$ and 1573 cm$^{-1}$ of AQ2S and AQ2S/GR corresponded to the vibration of C=O in quinon and C=C in aromatic rings, respectively [27].

X-ray photoelectron spectroscopy (XPS) was conducted to detect the surface composition and the chemical states of the elements in the AQ2S/GR composite material (Fig. 4). The XPS full survey spectrum indicated that the prepared composite material consisted of C, O, and S. As seen in Fig. 4(a), peaks at 284.67 eV, 531.44 eV, and 168.20 eV were present, which corresponded to C1s, O1s and S2p [25,27], respectively. Compared with pure GR, the presence of S2p is attributed to −SO$_3$-, which indicated the anchoring of AQ2S on graphene sheets. High-resolution spectra of the C1s and O1s region are shown in Fig. 4(c) and (d). The C1s spectra of GR deconvoluted into three characteristic peaks that were attributed to C=C (284.72 eV), C=O (286.80 eV), and O=C-O (289.00 eV) (Fig. 4(c)) [28]. For the binary material, the C=C band located at 533.2 eV could be caused by the loading of AQ2S.

Based on the aforementioned results, it is clear that AQ2S was successfully adsorbed on the surface of GR by π-π stacking. However, the sp$^2$ domains and the pore structure of GR were slightly destroyed by the presence of AQ2S, which may influence the adsorption capacity and conductivity of GR.

3.2. Degradation of SPY under different conditions

To examine the photosensitive performance of AQ2S/GR, degradation of SPY under various conditions irradiated by simulated solar light was tested. The degradation of SPY was monitored as changes in concentration (C_0/C_t) over time and was used to evaluate the photosensitivity of bare graphene, AQ2S, and AQ2S/GR (Fig. 5(a)). Here, C_0 and C_t represent the initial concentration of SPY and the concentration of SPY at the irradiation time t, respectively.
After 30 min of adsorption in the dark, an adsorption/desorption equilibrium was built up between SPY and the photosensitizer powders. Results show that after 12 h of irradiation, SPY had slightly decomposed (less than 10 %) with bare graphene and with a photolysis process, which indicates that GR had poor photosensitivity as well as the resistance of SPY under solar light irradiation. With the presence of pure AQ2S at a concentration of 26 mg/L, SPY was rapidly removed over 12 h with a degradation rate over 95 % and a kinetic constant of 0.3433 h\(^{-1}\)/C\(_0\). Although pure AQ2S showed excellent performance for SPY removal, the added AQ2S becomes dissolved in water and become a secondary pollutant, as was confirmed by the residual AQ2S concentration measurement after irradiation (25.2 mg/L). Therefore, fixing AQ2S on a conductive and stable support material with a higher specific surface like graphene is necessary to avoid secondary pollution. From the results, the degradation rate of SPY reacting with AQ2S/GR was over 90 % after 12 h irradiation with a kinetic constant of 0.2034 h\(^{-1}\)/C\(_0\). Compared with pure AQ2S, the decrease in the degradation rate and kinetic constant could be attributed to the shade of black graphene.

To determine the effect of the AQ2S proportion in the composite to the degradation performance, binary photosensitizers with 7 %, 11 %, 17 % and 21 % weight percentages of AQ2S were investigated under the same aforementioned conditions. The results shown in Fig. 5(b) indicated that the degradation rate of SPY increased with the increase in the AQ2S proportion. The maximum adsorption capacity of GR is theoretically 243.90 mg/g, which is calculated based on the Langmuir isothermal model, the weight percentage of AQ2S can not be improved by this π-π stack method. Therefore, a photosensitizer with 21 % AQ2S seems to be an ideal candidate for the photosensitized degradation of SPY.

From the results, the performance of the photosensitive degradation process is much better than the chlorination method with a degradation rate of around 65 % [10]. Moreover, compared with this degradation process, the adsorption removal of SPY by carbon nanotube-modified biochars can get a similar removal rate but in 18 h [4]. Peroxymonosulfate (PMS) activation shows a better degradation performance than this research; however, the dosage of the PMS is much higher at 1 g/L [5].

### 3.2.1. Effect of solution pH

The effect of solution pH on the removal of SPY is shown in Fig. 5(c). The kinetic constant of SPY degradation at pH 5 (0.0856 h\(^{-1}\)) was much lower than at pH 7 (0.2034 h\(^{-1}\)) and pH 9 (0.1718 h\(^{-1}\)). Since the components of SPY at pH 5–7 had little variation due to its pKa value (2.22 ± 0.03 to 8.58 ± 0.02) [29], the increase of the kinetic constant with the decrease of pH could be caused by the dissociation of HClO/ClO\(^{-}\)/C0. In addition, O\(_2\)/C15\(^{-}\) is going to be quenched by Cl\(_2\)/C15\(^{-}\) in a lower pH condition [30], which may also cause the suboptimal degradation performance at pH 5. With the pH value of the solution increased to 9, only one N atom appears on the substituent of SPY [4], leading to the decrease of its proton-donating ability, which enhances the stability of SPY and decreases the kinetic constant of degradation. As the inhibition of Cl\(^{-}\)/C15 increases with the rising pH [31], the degradation kinetics of SPY had no obvious decrease, which may indicate that Cl\(^{-}\)/C15 play no significant role during the degradation of SPY. The sunlight-induced decomposition of free chlorine also increases with the elevation of solution pH, thus also slowing down the removal of SPY.

### 3.2.2. Effects of Cl\(^{-}\) concentration

The kinetic constants of SPY degradation with various concentrations of chloride are shown in Fig. 5(d). The kinetic constant increased with increasing Cl\(^{-}\) concentration; with the absence of chloride, a low degradation rate (less than 40 %) and a 0.024 h\(^{-1}\) kinetic constant were observed after 12 h irradiation. As the chloride dosage increased from 0.1 mol/L to 1 mol/L, k values of SPY exhibited a significant increase from 0.0719 h\(^{-1}\) to 0.353 h\(^{-1}\), seemingly attributed to the generation of a larger amount of Cl\(^{\ast}\) and Cl\(^{\ast\ast}\) [14].
3.2.3. Effects of AQ2S/GR dosage

As shown in Fig. 5(e), when the AQ2S/GR dosage increased from 5 mg to 30 mg, the kinetic constant of SPY degradation changed from 0.1638 h⁻¹ with a dosage of 5 mg to 0.2034 h⁻¹ with a 10 mg dosage at its peak, before successively decreasing to 0.1692 h⁻¹ and 0.1359 h⁻¹ with a 20 mg and 30 mg dosage, respectively. Before a certain dosage, increasing amounts of photosensitizer accelerated the generation of RCS, which enhances the removal of SPY. Beyond a certain point, however, excess dosage blocks the light absorption of AQ2S due to the shading by black graphene. As a result, a 10 mg dosage of AQ2S/GR is the best option for photosensitized degradation of SPY.

3.3. Photosensitive mechanism analyses

The SPY photosensitive degradation process with AQ2S/GR reported in this study relied on the reactive species generated through photo-oxidation of chloride. This reaction requires an external photosensitizer, AQ2S, which exhibits excellent photochemical energy transferring ability due to its abundant conjugated double bonds. The theoretical basis of on-site chlorine generation and organic pollutant degradation utilizing AQ2S as a photosensitizer, as reported by Scharf and Weitz [18], could be summarized as the reaction cycle. Under irradiation with visible light, AQ2S transfers to an excited singlet state, and then proceeds through intersystem crossing to a lower-energy excited triplet state [32].
Several intermolecular reactions may occur from this excited triplet state, including self-quenching, hydrogen abstraction to yield a semi-quinone radical, or electron transfer [33]. In aqueous solution and with high concentrations of chloride present, this latter pathway may dominate, and an exciplex (i.e., an extremely short-lived charge transfer complex, in which one of the constituent molecules is in an excited state) between the excited quinone derivative and chloride forms. With additional chloride present, the halo-quinone exciplex accepts an electron from one of the chloride ions and a dichloro radical is formed within the exciplex [34]. This may subsequently diffuse into the solution to yield AQ2S/Cl\(^{-}\) and Cl2/Cl\(^{-}\), which may then interact with a second Cl2/Cl\(^{-}\) radical to yield a chlorine molecule and two chloride ions. The reduced radical form of AQ2S can then be oxidized back to its ground state by oxygen for continued cycling with the generation of superoxide (O2/Cl\(^{-}\)) as a byproduct [35]. Because of the very low yield of free available chlorine (FAC) (less than 0.02 mmol/L) detected in the reaction solution, FAC has little contribution to the degradation of SPY in this system. Based on the above, the oxidized species generated by the aforementioned reaction cycle (e.g., O2/Cl\(^{-}\), Cl\(^{-}\) and Cl2/Cl\(^{-}\)) have the potential to attack the organics.

To further identify the roles of the reactive species, a scavenger experiment was performed in which tert-butanol (TBA), HCO3\(^{-}\), or benzoquinone (BQ) was added into the reaction solutions. TBA is extensively used as a quencher for Cl\(^{-}\) and has a reaction rate constant of \(3.0 \times 10^{8} \text{ M}^{-1}\text{s}^{-1}\), HCO3\(^{-}\) has a high reaction rate of \(2.2 \times 10^{9} \text{ and } 8.0 \times 10^{7} \text{ with Cl}^{-} \text{ and Cl}^{2-}\), respectively [14]. BQ has been verified as an O2/Cl\(^{-}\) scavenger in plenty of photocatalytic studies [36]. According to these characteristics, if the degradation process of SPY is dominated by Cl\(^{-}\), the addition of TBA and HCO3\(^{-}\) will significantly decrease the reaction rate. Similarly, if O2/Cl\(^{-}\) is the dominant radical, the degradation of SPY will exhibit an obvious decrease with the addition of BQ. As shown in Fig. 5(f), the negligible inhibition of TBA amongst the scavengers indicates that Cl\(^{-}\) contributes least to the oxidation of SPY, which corresponds to the result provided by the effect of pH. With the reaction quenched by HCO3\(^{-}\), there was a significant decrease in the rate constant to 0.0515 h\(^{-1}\), indicating that Cl2/Cl\(^{-}\) could be considered the dominant radical. The low concentration of FAC also confirmed that most of the generated Cl2/Cl\(^{-}\) was captured by SPY but did not interact with a second Cl2/Cl\(^{-}\) to yield a chlorine molecule. The presence of BQ also had an obvious inhibitory effect on SPY degradation as the reaction rate decelerated from 0.2034 h\(^{-1}\) to 0.0646 h\(^{-1}\), illustrating that O2/Cl\(^{-}\) also plays an important role.

### 3.4. Cycle experiment

To determine the stability and reusability of the AQ2S/GR, a consecutive 5-cycle test was conducted to estimate the efficiency of SPY degradation under 12 h of solar light irradiation. From Fig. 6(a), it is clear that after five runs the degradation rate of SPY had minimal variation compared with the first run, indicating that the photosensitive activity of this AQ2S/GR decayed only slightly. A pH measurement was carried out after each run which were 6.8, 6.8, 6.9, 6.9 and 6.9. Compared with the original pH (pH7), there was no significant change during all 5 runs. The FT-IR spectra of the photosensitizer before and after five runs confirm these results. As shown in Fig. 6(b), there was no apparent discrepancy between the first and last run. The after-used AQ2S/GR were also characterized by SEM and XPS, results shown in Fig. 6(c) and (d) indicated that the morphology and component of the AQ2S/GR showed no obvious change. The calculated BET surface of the used material (Table 1)
decreased from 119.08 m²g⁻¹ to 24.01 m²g⁻¹, which may cause by the adsorption of SPY on the surface of GR. Based on the above, it can therefore be concluded that the obtained photosensitizer, AQ2S/GR, has acceptable stability and strong resistance to solar light irradiation.

4. Conclusions

In this study, a novel photosensitizer (AQ2S/GR) was obtained via a π-π stack adsorption method. A targeted pollutant, SPY, was decomposed with AQ2S/GR in saline water during 12 h visible light irradiation. The synthesized photosensitizer exhibited an excellent degradation efficiency for SPY using a low-energy-consumption process. This photosensitive degradation reaction was determined to be affected by pH, chloride concentration, and the photosensitizer dosage. The best SPY degradation performance was obtained by adding 20 mg of AQ2S/GR into a pH 7 solution with 1 M chloride, which was demonstrated to reach a degradation rate over 90% with a kinetic constant of 0.353 h⁻¹ within 12 h.

The active radical scavenging experiments demonstrated that Cl₂ and O₂ were the dominant species involved in the oxidation of SPY. The possible mechanism of photosensitive degradation of SPY by AQ2S/GR was depicted in Fig. 7. After five cycles of operation, the photosensitizer AQ2S/GR still maintained a high level of photosensitivity for SPY degradation, which confirms its stability, strong resistance under solar light irradiation, and recoverability. The present work suggests that the AQ2S/GR could be a promising candidate for removing recalcitrant contaminants in the water phase.

Declaration of competing interest

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.
Acknowledgements

This work was supported by the National Key Research and Development Program of China (2019YFD1100204); the National Nature Science Foundation of China (No. 51778175); the Research and Application of Treatment Technology for High Concentration and Refractory Wastewater (Printing and Dyeing, Pharmaceutical, Chemical) GJSZ2021030907-YF. We gratefully acknowledge supports from Heilongjiang Province touyan team.

References

[1] J. Zhong, H. Jiang, Z. Wang, Z. Yu, L. Wang, J.F. Mueller, J. Guo, Efficient photocatalytic destruction of recalcitrant micropollutants using graphitic carbon nitride under simulated sunlight irradiation, Environ. Sci. Ecotechnol. 5 (2021) 1–11.

[2] M. Elzinga, D. Liu, J.B.M. Klok, P. Roman, C.J.N. Buisman, A. Heijne, Microbial reduction of organosulfur compounds at cathodes in bioelectrochemical systems, Environ. Sci. Ecotechnol. 1 (2020) 1–6.

[3] W. Jansomboon, S.K. Boontanon, N. Boontanon, C.T. Da, Monitoring and determination of sulfonamide antibiotics (sulfamethoxydiazine, sulfamethazine, sulfamethoxazole and sulfadiazine) in imported pangasius catfish products in Thailand using liquid chromatography coupled with tandem mass spectrometry, Food Chem. 212 (2016) 635–640.

[4] M. Inyang, B. Gao, A. Zimmerman, Y. Zhou, X. Cao, Sorption and cosorption of lead and sulfapyridine on carbon nanotube-modified biochars, Environ. Sci. Pollut. Res. 22 (2015) 1868–1876.

[5] R.L. Yin, W.Q. Guo, H.Z. Wang, J.S. Du, X.J. Zhou, Q.L. Wu, H.S. Zheng, J.S. Chang, N.Q. Ren, Selective degradation of sulfonamide antibiotics by peroxymonosulfate alone: direct oxidation and nonradical mechanisms, Chem. Eng. J. (2017) 2539–2546.

[6] G. Sharma, V.K. Gupta, S. Agarwal, S. Bhogal, M. Naushad, A. Kumar, F.J. Stadler, Fabrication and characterization of trimetallic nano-photocatalyst for remediation of ampicillin antibiotic, J. Mol. Liq. (2018) 342–350.

[7] A. Kumar, A. Kumar, G. Sharma, A. Al-Muhtaseb, M. Naushad, A.A. Ghfar, F.J. Stadler, Quaternary magnetic Bio(OCl/CuO/CuO)/Fe3O4 nano-junction for visible light and solar powered degradation of sulfamethoxazole from aqueous environment, Chem. Eng. J. 334 (2018) 462–478.

[8] A. Kumar, G. Sharma, F.J. Stadler, C.T. Mola, A. Al-Muhtaseb, Bio-inspired and
biomaterials-based hybrid photocatalysts for environmental detoxification: a review, Chem. Eng. J. 382 (2020), 122397.

[9] N.S. Shah, X. He, H.M. Khan, J.A. Khan, K.E. O'Shea, D.L. Boccelli, D.D. Dionysiou, Efficient removal of endosulfan from aqueous solution by UV-C/peroxides: a comparative study, J. Hazard Mater. 263 (2013) 584–592.

[10] V.D. Gaffhey, V.V. Cardoso, M.J. Benoilet, C.M.M. Almeida, Chlorination and oxidation of sulfonamides by free chlorine: identification and behaviour of reaction products by uplc-ms/ms, Journal of Environmental Management, J. Environ. Manage. 166 (2016) 466–477.

[11] H. Dong, Y. Zuo, N. Song, S. Hong, M. Xiao, D. Zhu, J. Sun, G. Chen, C. Li, Bimetallic synergetic regulating effect on electronic structure in cobalt/vanadium co-doped carbon nitride for boosting photocatalytic performance, Appl. Catal. B Environ. (2021), 119954.

[12] W.K. Xiang, R.J. Qu, X.H. Wang, Z.Y. Wang, M.B. Jumah, A.A. Allam, F. Zhu, Z.L. Hued, Removal of 4-chlorophenol, bisphenol a and nonylphenol mixtures by aqueous chlorination and formation of coupling products, Chem. Eng. J. 402 (2020), 126140.

[13] W.W. Cai, T. Peng, B. Yang, C. Yu, Y.S. Liu, J.L. Zhao, F.L. Gu, G.G. Ying, Kinetics and mechanism of reactive radical mediated flunazine degradation by the uv/chlorine process: experimental and theoretical studies, Chem. Eng. J. 402 (2020), 126224.

[14] H. Zhang, C. Guo, J. Lv, S. Hou, Y. Zhang, J.F. Gao, J. Xu, Aquatic chlorination of ephedrine: kinetic, reaction mechanism and toxicity assessment, Sci. Total Environ. 740 (2020), 140146.

[15] X. Kong, L. Wang, Z. Wu, F. Zeng, H. Sun, K. Guo, Z. Hua, J. Fang, Solar irradiation combined with chlorine can detoxify herbicides, Water Res. 177 (2020), 115784.

[16] H. Nath, X. Wang, T.A. Langdon, A novel perforated electrode flow through cell design for chlorine generation, J. Appl. Electrochem. 41 (2011) 389–395.

[17] N.J. Scenna, A. Cruz, Road risk analysis due to the transportation of chlorine in road tankers, Environ. Sci. Technol. 35 (2001) 83–90.

[18] H.D. Scharf, J. Fleischhauer, H. Leismann, Criteria for the efficiency, stability, and capacity of abiotic photochemical solar energy storage systems, Angew Chem. Int. Ed. Engl. 18 (1979) 652–662.

[19] N. Yoshikawa, T. Tamaya, K. Tanaka, High-harmonic generation in graphene plasmonic, Science 357 (2017) 1562.

[20] J. Zhong, H. Jiang, Z. Wang, Z. Yu, L. Wang, J.F. Mueller, J. Guo, Efficient photocatalytic destruction of recalcitrant micropollutants using graphitic carbon nitride under simulated sunlight irradiation, Environ. Sci. Technol. 5 (2021), 100079.

[21] M.B. Lundeberg, Y. Gao, R. Asgari, C. Tan, B.V. Duppen, M. Autore, Tuning quantum nonlocal effects in graphene plasmonic, Science 357 (2017) 187–191.

[22] C. Yuan, G. Zhang, J. Chen, L. Fu, L. Xu, F. Yang, The electrochemical activities of anthraquinone monosulfonate adsorbed on the basal plane of reduced graphene oxide by $\pi$–$\pi$ stacking interaction, J. Solid State Electrochem. (2013) 2711–2719.

[23] S.B. Sertkol, B. Esat, A.A. Momchilov, An anthraquinone-functionalized reduced graphene oxide as electrode material for rechargeable batteries, Carbon 116 (2017) 154–166.

[24] K. Kalinathan, D.P. Desroches, X. Liu, P.G. Pickup, Anthraquinone modified carbon fabric supercapacitors with improved energy and power densities, J. Power Sources 181 (2008) 182–185.

[25] S. Stankovich, D.A. Dikin, R.D. Piner, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, Carbon 45 (2007) 1558–1565.

[26] J. Hitht, Charge transport in the inverted marcus region, Nat. Nanotechnol. 13 (2018).

[27] A.N. Diaz, Absorption and emission spectroscopy and photochemistry of 1,10-anthraquinone derivatives: a review, J. Photochem. Photobiol., A 53 (1990) 141–167.

[28] R.J. Waltman, J. Pacansky, C.W. Bates, X-ray photoelectron spectroscopic studies on organic photocatalysts: evaluation of atomic charges on chlorodiane blue and p-(diethylamino)benzaldehyde diphenylhydrazone, Chem. Mater. 5 (1993) 1799–1804.

[29] J.K. Chaliss, J.C. Carlson, K.J. Friesen, M.L. Hanson, C.S. Wong, Aquatic photochemistry of the sulfonamide antibiotic sulfapyridine, J. Photochem. Photobiol. Chem. 262 (2013) 14–21.

[30] J.E.Grebes, J.P. Pignatello, W.A. Mitch, Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters, Environ. Sci. Technol. 44 (17) (2010) 6822–6828.

[31] J. Fang, F. Yun, C. Shang, The roles of reactive species in micropollutant degradation in the UV/free chlorine system, Environ. Sci. Technol. 48 (3) (2014) 1859–1868.

[32] V.A. Kuzmin, A.K. Chibisov, One-electron photo-oxidation of inorganic anions by 9,10-anthraquinone-2,6-disulphonic acid in the triplet state, J. Chem. Soc., Chem. Commun. (1971) 1559–1560.

[33] G.O. Phillips, N.W. Worthington, J.F. Mckellar, One-electron photo-oxidation of inorganic anions by 9,10-anthraquinone-2,6-disulphonic acid in the triplet state, J. Chem. Soc., Chem. Commun. (1971) 1559–1560.

[34] A.N. Diaz, Critical evaluation of rate constants and equilibrium constants of one-electron photo-oxidation of inorganic anions by 9,10-anthraquinone-2,6-disulphonic acid in the triplet state, J. Chem. Soc., Inorg. Phys. Theor. 23 (1969) 1559–1560.

[35] A. Brenn, I. Loeff, J.K. Hurley, H. Linschitz, Charge-transfer interactions of excited molecules with inorganic anions: the role of spin-orbit coupling in controlling net electron transfer, Chem. Phys. Lett. 95 (1983) 333–338.

[36] X. Ying Yu, Critical evaluation of rate constants and equilibrium constants of hydrogen peroxide photolysis in acidic aqueous solutions containing chloride ions, Journal of Physical and Chemical Reference Data, J. Phys. Chem. Ref. Data 33 (2004) 747–763.

[37] R. Wang, M. Shi, F. Xu, Y. Qiu, P. Zhang, K. Shen, Q. Zhao, J. Yu, Y. Zhang, Graphene-modified TiO2 nanofibers with osteoinductive and enhanced photocatalytic antibacterial activities to prevent implant infection, Nat. Commun. 11 (2020), 4465.