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# One-pot synthesis of sulfur doped activated carbon as a superior metal-free catalyst for adsorption and catalytic oxidation of aqueous organics

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Synthesis of S-doped activated carbon with well developed porous structure and enhanced catalytic activity has been extensively investigated for their great potential application in various fields. Here, we report a facile one-pot thermal process for preparation of in-situ S-doped activated carbon by using a potential waste material (Poly(phenylene sulphide) (PPS)) as precursor, and KOH as activator for adsorptive and oxidative removal of aqueous organics. Experiment results demonstrated that the as-prepared sample treated at 800 °C (S-AC-800) exhibited both strong adsorption ability and enhanced persulfate (PS) activity for phenols removal. The effect of adsorption on oxidation was illustrated by investigating the removal of different phenols organics in their individual solution and mixture solution. It was suggested that a higher adsorption capacity led to a more rapid degradation process. In the process, the adsorbed organics were preferentially in-situ degraded, which in turn accelerated the adsorption, then the adsorption and oxidation synergistically promoted the efficient organics removal. Quenching experiments demonstrated that the activation of PS mainly proceeded through both surface-bounded radicals and non-radical pathway. The effects of several operate parameters as well as the influences of various inorganic anions, and background organic matters in water on organic removal were investigated in detail. In addition, the stability of S-AC-800 and its deactivation reason were also studied. It is expected that this work could not only provides a promising way to utilize PPS waste, but also provides a facile, economical and effective method for future development of more efficient sulfur-doped activated carbons for wastewater treatment.

# 1. Introduction

Organic pollutants in wastewater with the features of high toxicity and bad biodegradability have been a big issue in environmental remediation, which pose great threat to aquatic ecosystems and to human beings even at low exposure levels. Although diverse technologies, such as adsorption, microbial degradation, membrane processes, and advanced oxidation processes (AOPs) (ultrasonic degradation, chemical oxidation, photocatalytic oxidation, plasma process),<sup>1</sup> have been proposed to remove the hazardous compounds, the most economical and easiest one is adsorption.<sup>2</sup> Moreover, the adsorbents can be reused with an appropriate aftertreatment. However, it just move contaminants from one phase to another phase without destroying them. In terms of destruction, AOPs are widely acknowledged to be the most efficient method, since it can degrade organics to harmless compounds, CO2 and H<sub>2</sub>O.<sup>3</sup> As well known, porous carbonaceous material is the most commonly used adsorbent<sup>4-6</sup> when compared with other designed

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adsorbents such as zeolites,<sup>7</sup> metal-organic frameworks (MOFs),<sup>8</sup> and mesoporous silica<sup>9</sup> because of its low cost, porous structure, and high special surface area. Also, it is an excellent potential alternative to the metal-based catalysts for organic catalytic oxidation due to its non-toxicity, good thermal stability, and easy tunability.<sup>10-15</sup> Thus, we suppose that if a porous carbon exhibits both strong adsorption ability as well as excellent catalytic activity, it would be an efficient solution to degrade the adsorbed organics and regenerate the material in-situ, which would be much efficient and mild for aqueous organics removal in wastewater. Unfortunately, the generally used carbon materials, such as activated carbon (AC), carbon nanotubes (CNTs), reduced graphene oxide (rGO), and nanodiamond (ND) show a weak adsorption ability and moderate catalytic performance for organic oxidation.<sup>16-18</sup> It was suggested that physical structure can be easily modified by physical and/or chemical activation.<sup>3, 19</sup> Therefore, exploring preeminent methods for preparing of carbonaceous materials with high activity is the key for environmental remediation.

Recently, both theoretical calculations and experiments have proven that tailoring the electron states and creating active sites within the carbonaceous matrix by heteroatoms (N, B, P, S) doping could be an excellent strategy for producing significantly improved materials for numerous applications.<sup>20-22</sup> In terms of environmental remediation, many investigations have demonstrated that N atom is a prominent exotic specie for improving the catalytic activity of

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rGO (or CNTs, GO, ND) toward persulfate (PS)/peroxymonosulfate (PMS) activation for aqueous organics oxidation,<sup>17, 18, 23</sup> which is an AOP based on sulfate radical (SO4<sup>--</sup>) generated from PS/PMS activation. In addition, S atom, as another important heteroatom, has also attracted researchers' much interest. Because the incorporation of sulfur-containing functional groups into the carbon matrix would give rise to materials with unique physicochemical properties (i.e. good electrical conductivity, excellent catalytic activity and superior chemical stability)<sup>24</sup>, which has been applied in the storage of hydrogen and carbon dioxide,<sup>25</sup> anode materials in lithium batteries,<sup>26</sup> metal-free electrocatalyst for oxygen reduction reaction in fuel cells,<sup>27</sup> and adsorbents for heavy metals<sup>28</sup> as well as toxic contaminants.<sup>29</sup> However, much less attention has been focused on S-based catalyst for the heterogeneous catalytic oxidation of refractory organics in wastewater. Wang et al. reported that sulfur could act as a promising co-dopant to further improve the performance of nitrogen doped graphene toward PMS activation,<sup>30</sup> but using of only S-doped as the catalyst for organic oxidation is rarely reported.

In previous studies, we first discovered that in-situ S-doped activated carbons prepared by chemical activation of polythiophene derived from 2-thiophenemethanol and thiophene exhibited outstanding performance in persulfate (PS) activation for catalytic oxidation of aqueous organic contaminants.<sup>31-33</sup> Compared with post-treatment method that sun et al. applied for N-doping,<sup>34</sup> in-situ process could make sulfur groups homogeneously be distributed throughout the matrix and permanently fused into the backbone of the carbon framework. Nevertheless, the catalyst preparation process involves multiple steps, harsh treatment (such as using FeCl<sub>3</sub>) and high toxicity as well as high cost of starting materials. For widespread applications, economical, less toxic reagents involving and simple synthesis would make sulfur doped activated carbon more attractive.

Poly(phenylene sulphide) (PPS), as one of the sulfur-containing polymers, has been extensively investigated in technological applications such as molding resins, fibers, and matrices for thermoplastic composites due to its good mechanical properties, thermal stability, excellent chemical resistance and electrical properties.<sup>35</sup> Note that the widespread use of PPS would result in a lot of PPS waste owing to its non-biodegradable property, we suppose that the conversion of PPS waste into high value-added carbon materials would be a potential promising way to utilize PPS waste.

Herein, a facile one-pot thermal process for preparation of in-situ S-doped activated carbon (S-AC) by using PPS as precursor, and KOH as activator was proposed. Results show that the obtained material annealed at 800 °C (S-AC-800) exhibits high performance for adsorptive and oxidative removal of phenols organics. The effect of adsorption on organics degradation and the mechanism of PS activation were studied. Moreover, the effects of several operational parameters as well as the influences of various inorganic anions, and background organic matters in water on organic degradation in S-AC with PS were investigated in detail. In addition, the stability of S-AC-800 and its deactivation reason were also studied. The strong adsorption ability, excellent PS activity, wide pH usable range, as well as resistant to various anions made us believe that this work is beneficial since it not only provides a promising way to utilize PPS waste, but also provides a new method for future development of more efficient sulfur-doped activated carbons for green remediation, even for applications in other fields.

## 2. Materials and methods

#### 2.1. Chemicals and reagents

Polyphenylene sulfide (PPS), phenol (PE,  $\geq$ 99.0%), p-chlorophenol (PCP,  $\geq$ 99.0%), 2,4-dichlorophenol (DCP,  $\geq$ 99.0%) and potassium persulfate (PS) were obtained from Sigma-Aldrich Inc. (St. Louis, MO, USA). Methanol (for HPLC analysis) were of HPLC grade and bought from Aladdin Chemistry Co., Ltd. Other reagents used in this study were provided by Taiyuan Chemicals Co. (Taiyuan, China). All chemicals were of analytical grade or higher and used as received without further purification. Milli-Q water was employed throughout the experiments.

#### 2.2. Catalyst preparation

Chemical activation method using KOH as activating agent was used to synthesize in-situ S-doped activated carbon (S-AC) from PPS precursor (Scheme S1). In a typical synthesis, 2 g of PPS and 4 g of KOH were fully dissolved into 50 mL of mixture solution with 70% water and 30% ethanol (V:V). After drying in an oven at 110 °C for 12 h, the mixture was ground and then transferred into a porcelain crucible for annealing under nitrogen atmosphere at different temperature for 2 h with a heating rate of 5 °C min<sup>-1</sup>. The S-AC samples were obtained after being washed with 10 wt.% HCl solution twice (remove any impurities), ultrapure water several times (until neutral pH), and dried in an oven at 110 °C overnight. The as-prepared carbons are labeled as S-AC-x, where x refers to the annealing temperature. For comparison, a S-AC-800-free sample was prepared similarly by using PPS as precursor without adding KOH. In addition, for demonstrating the role of sulphur dopant, a Sfree activated carbon (AC-800) was also synthesized by chemical activation of polyphenylether (PPO) with KOH as activator at 800 °C.

#### 2.3. Characterization

X-ray diffraction (XRD) patterns were obtained on a Bruker D8-Advanced diffractometer system using Cu-K $\alpha$  radiation ( $\lambda$  = 1.5418 Å). Thermogravimetric analysis (TGA) was conducted in a Netzsch thermal analyzer with a heating rate of 5 °C min<sup>-1</sup> in air. Surface morphologies of the as-prepared S-AC were observed on a scanning electron microscope (SEM, JSM-7001F, JEOL, Japan) combined with an energy dispersive X-ray spec-troscopy (EDX) for element mapping. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) equation from nitrogen sorption isotherms at 77 K using a Micromeritics TriStar II 3020 apparatus. Prior to measurement, the samples were degassed at 80 °C for 8 h under vacuum condition. The total pore volume (V<sub>t</sub>) was calculated from the volume adsorbed at a relative pressure of 0.99. The micropore surface area and micropore volume were determined by Dubinin-Astakhov equation adapted for micro-pore carbon. The pore size distribution (PSD) was determined by Original Density Functional Theory (ODFT). All samples were coated with a thin gold film under vacuum before microscopy. Raman spectra were acquired on a

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Horiba (LabRAM HR800) dispersive Raman spectrometer using a 514 nm argon ion laser. The elemental contents of the carbon samples were determined using a Vario EL CUBE elemental analyzer with the oxygen content calculated by mass difference. X-ray photoelectron spectroscopy (XPS) was performed on a specs spectrometer (AXIS ULTRA DLD) using Al Ka X-ray source (1486.6 eV). The binding energies of the XPS spectra were calibrated by setting C 1s to 284.8 eV. Fourier transform infrared spectra (FTIR) were recorded on a Bruker Tensor 27 FTIR spectrometer fitted with a transmission attachment. The pHpzc (point of zero charge) of the samples were evaluated by dispersing 250 mg of carbon samples into 4 ml of CO<sub>2</sub>-free water at 25 °C.<sup>36</sup>

## 2.4. Adsorption experiments

The typical adsorption experiment was carried out in a 250 mL conical flask containing 200 mL of reaction solution with predetermined concentration of phenols (20-60 mg L<sup>-1</sup>) and 0.05 g L<sup>-1</sup> of as-prepared catalyst. The flask was shaken in a constant temperature shaker (TENSUC Instrument, TS-200B, China) with 280 rad min<sup>-1</sup> at 25 °C. At regular time intervals, 1 mL of the solution was sampled and filtered into a HPLC vial through 0.22  $\mu$ m PES syringe filter. The concentration of residual phenols was detected immediately by high performance liquid chromatography (HPLC). All the experiments were performed in duplicates, and the results showed that the relative errors were less than ±5%.

## 2.5. Catalytic oxidation experiments

The batch catalytic oxidation experiment was conducted in a 250 mL conical flask containing 200 mL of a 80 mg  $L^{-1}$  phenols solution. The flask was shaken in a constant temperature shaker with 280 rad  $\min^{-1}$  at 25 °C. For testing the effect of adsorption on phenols degradation, pre-adsorption or not pre-adsorption methods were put in the degradation experiments. In the pre-adsorption experiment, unless otherwise specified, 0.1 g  $L^{-1}$  of S-AC was first dispersed in the reaction solution and shaken for 60 min to fully achieve the adsorption/desorption equilibrium, followed by adding 15 mM of PS into the solution to initiate the degradation. In the not pre-adsorption experiment, S-AC and PS were added to the reaction solution simultaneously. At given time intervals, 1 mL of sample was withdrawn and filtered by 0.22 µm PES syringe filter into a HPLC vial for analysis. After completion of the reaction, the catalysts were separated and washed with water and ethanol several times, followed by drying in an oven at 110 °C overnight for reuse tests.

# 2.6. Analytic methods

The concentration of residual phenols was determined by using an U3000 HPLC system (Thermo Fisher, USA) equipped with a SunFire<sup>TM</sup> C<sub>18</sub> column (4.6 × 150 mm, 5.0  $\mu$ m) and a photodiode array detector (PDA) set at 270 nm for PE, 280 nm for PCP and 288 nm for DCP. The mobile phase was a binary mixture of 70% methanol and 30% water at a flow rate of 1 mL min<sup>-1</sup>. Chemical oxygen demand (COD) test was carried out according to the Chinese national standard method (HJ/T 399-2007) on a COD analyzer (5B-3A, Lian-hua Tech. Co., Ltd., Lanzhou, China). Biochemical oxygen demand after 5 days (BOD<sub>5</sub>) was determined according to the Hach DOI: 10.1039/C7TA09814F

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# 3. Results and discussion

#### 3.1. Characterization of S-AC

Fig. S1 shows the XRD patterns of the as-made S-AC samples. The broad diffraction peaks located at about 23.1° (002) and 43.6° (101) indicated the existence of hexagonal graphitic structure in the S-AC samples.<sup>37</sup> Thermogravimetric analysis (TGA) shows that the carbon samples exhibit high thermal stability (Fig. S2), further demonstrating the existence of graphitic structure. SEM images of S-AC are shown in Fig. S3. It can be found that, the surface of the activated carbon obtained at lower temperature was relatively flat and intact with less porous structures. As the activation temperature increased, a large amount of pores were generated originated from thermal cracking and corrosive effect of KOH. Remarkably, partially aggregated and crinkled structures can be observed on S-AC-900 due to the excessive enlargement of porous structures. As a result, the S-AC samples can be tailored with well developed porous structures and high amount of defective edges. In addition, the elemental mapping of S-AC-800 suggested that the distribution of S in the carbon matrix was relatively uniform (Fig. S4a-d), which further illustrated that in-situ process could make sulfur groups homogeneously distributed throughout the matrix.

To deeply investigate the textural properties of S-AC, N<sub>2</sub> sorption isotherms were carried out. The corresponding results are concluded in Table 1 and Fig. 1. It can be seen that annealing temperature strongly influenced the formation and the development of pore structures during carbonization. With the thermal treatment at 600-800 °C, the specific surface area (S<sub>BFT</sub>) and total pore volumes (V<sub>p</sub>) of S-AC presented a growing trend. At 800 °C, a sharp and significant orifices extension occurred as revealed by the increased  $S_{BFT}$  from 1628 m<sup>2</sup> g<sup>-1</sup> for S-AC-700 to 2777 m<sup>2</sup> g<sup>-1</sup> for S-AC-800. It indicates that the alkali metal compounds (KOH and/or K<sub>2</sub>CO<sub>3</sub>), as chemical activators, strongly modified the carbonization behavior of PPS at 800 °C (Fig. S5), leading to the significant release of volatile matters and the development of micro- and mesopore structure. While further increasing of the annealing temperature to 900 °C would slightly decrease the specific surface area and pore volume attributing to the combination of pores derived from the excess enlargement.<sup>38</sup> According to Fig. 1a, it can be seen that depending on the annealing temperature, the S-AC samples treated at 600-800 °C were predominantly microporous with typical type I isotherm. While the sample treated at 900 °C belonged to type IV with a hysteresis loop above  $P/P_0 = 0.4$ , demonstrating the copresence of micropores and mesopores.<sup>39</sup> This can be further supported by the pore size distribution results (Fig. 1b). It should be noted that for the cases of S-AC-600, -700, and -800, all of the pores fell into the size less than 5 nm, and the average pore size was calculated to be 1.93, 2.01, and 2.09 nm, respectively. While the thermal treatment at 900 °C imposed a significant enlargement of the pore size to (~ 8 nm) and resulted in an average pore size of 2.74 nm.

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 Table 1
 Textural properties of the carbon samples

Sample	S <sub>BET</sub> /m <sup>2</sup> g <sup>-1</sup>	$S_{micro}/m^2 g^{-1}$	$V_p/cm^3 g^{-1}$	V <sub>micro</sub> /cm <sup>3</sup> g <sup>-1</sup>	Average pore size (nm)
S-AC-600	1585	1131	0.77	0.46	1.93
S-AC-700	1628	1126	0.82	0.46	2.01
S-AC-800	2777	1816	1.45	0.76	2.09
S-AC-900	1912	1292	1.31	0.55	2.74



Fig. 1 (a)  $N_2$  sorption isotherms, and (b) pore size distributions of the S-AC samples.

Raman spectroscopy has been proved to be a powerful, structural probe for carbonaceous materials.<sup>40</sup> Hence, Raman spectroscopic investigation was further conducted as shown in Fig. 2. It can be seen that the Raman spectra of the samples contained a G band at 1594 cm<sup>-1</sup> related to in-plane vibrations of sp2 carbon in S-AC, and a D band at 1341 cm<sup>-1</sup> arised from disorder (structurally disordered carbon, defects, and edges).<sup>13</sup> The intensity ratio of D band versus G band ( $I_D/I_G$ ) could reflect the defect and disorder level of the samples. A notable observation is that the  $I_D/I_G$  ratio gradually increased from 1.01 to 1.21 as the annealing temperature increased from 600 to 900 °C, suggesting that an increased amount of defect sites was obtained at an elevated temperature. This may be originated from the severe etch of alkali metal compounds at higher temperature, as characterized by SEM combined with N<sub>2</sub> sorption isotherms. In addition, it was suggested that the removal

of superabundant oxygen/sulfur-containing groups would also release the defect edges occupied by the excess oxygen/sulfur groups.  $^{10}$ 

To detect the elemental composition and the surface chemistry of the as-prepared samples, FTIR spectra (Fig. S6) and XPS spectroscopic technique was performed. As shown in the XPS survey spectra for the S-AC samples (Fig. 3a), characteristic peaks of C 1s, O 1s, and S 2p were observed at ~285, ~532, and ~164 eV, respectively. According to the XPS data, it can be noted that the S content was gradually decreased with an increase in the annealing temperature, and then underwent a slight increase at 900 °C. In view of this, elemental analysis was also performed and a similar trend of 10.85, 7.57, 4.05, and 5.31 wt.% was obtained for S-AC-600, -700, -800, and -900, respectively (Table S1). This may be attributed to the more intense reaction between carbon matrix and KOH at 900 °C, leading to a reduction of carbon content, and then the sulfur and oxygen contents were relatively increased.

The high resolution XPS C 1s spectra was shown in Fig. S7. It can be found that the C 1s spectra can be deconvoluted into five components. The main peak at 284.5 eV is assigned to carbon atoms with sp<sup>2</sup> hybridization, suggesting that most of the C atoms were in the conjugated honeycomb lattice.<sup>30</sup> The asymmetric and broadened C 1s peak of sp2 carbon toward the high binding energy side indicated that the samples contained a relatively high amount of functional groups.<sup>41</sup> The three broad peaks located at 285.8, 287.2, and 289.2 eV could be attributed to sp<sup>2</sup> carbon bonded with heteroatoms such as C–O and/or C–S, C=O species (carbonyl or quinine), and O=C–O (carboxyl or ester), respectively, which are consist with the FTIR results.<sup>30</sup> The band on the high binding energy side located at



Fig. 2 Raman spectra of the carbon samples.

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291.2 eV is possibly assigned to the  $\pi\text{-}\pi^*$  transition due to conjugation.  $^{42}$ 

The high resolution XPS S 2p spectra (Fig. 3c) can be decomposed into four components. The two peaks centered at 164.0 eV and 165.2 eV are corresponded to the S  $2p_{3/2}$  and S  $2p_{1/2}$  of thiophene sulfur (-C-S-C-) and/or -C-S-C- sulphide bridges, and the other two peaks located at 168.7 eV and 169.9 eV can be attributed to oxygen-containing S groups (-C-SO<sub>x</sub>-C-, x=2, 3, 4).<sup>43, 44</sup> It is worth noting that with the increase of annealing temperature, the thiophene sulfur species became dominant as shown in Fig. 3b. Remarkably, the percentage of -C-S-C- in overall S dopants can reach 65.3% for the sample treated at 800 °C, indicating that a better reductive degree was obtained on S-AC-800. This point can also be confirmed by the fact that the sample was characterized as a weak acidic material with the highest pH<sub>PZC</sub> of 4.6 (Table S1). This may be favorable because activated carbon with basic character is presumed to be beneficial for the catalytic oxidation process.<sup>45</sup>

#### 3.2. Adsorption kinetics and isotherms of phenols on S-AC

The roles of KOH activation and sulfur doping in the adsorption performance of carbon samples are shown in Fig. S8. It can be found that almost no PCP was adsorbed by S-AC-800-free with a small  $S_{BET}$  of 6.8 m<sup>2</sup>g<sup>-1</sup> (Fig. S9). While both S-AC-800 and AC-800 show an excellent adsorption performance, suggesting that KOH could strongly modify the carbonization behavior of PPS and lead to the significant development of pore structures, hereby endowing the carbon samples with strong adsorption ability. However, it is worthy noting that AC-800 shows a superior adsorption ability (50.9%) with a lower  $S_{BET}$  (2182 m<sup>2</sup>g<sup>-1</sup>, Fig. S9) when compared with S-AC-800 (46.0%). It indicates that sulfur doping is detrimental for the adsorption capacity enhancement, since the oxidized sulfur groups with acid character were not beneficial for the adsorption of acidic PCP molecules.

To evaluate the effect of carbonization temperature on the adsorption performance of S-AC, the adsorption behavior of several phenols on S-AC was investigated in detail. Fig. 4 shows the isothermal adsorption of PCP on S-AC. It can be seen that the adsorption process was quite rapid initially, then slowly increased until attaining adsorption/desorption equilibrium at about 20 min. Based on the experimental data, the adsorption kinetics of S-AC samples were evaluated. Results show that the data were well fitted with the pseudo-second-order model (Fig. S10), suggesting that the adsorption of PCP onto S-AC was dominated by chemical adsorption.<sup>46, 47</sup>

Three important isothermal models, including Langmuir, Freundlich, and Temkin isotherms, were applied to analyze the adsorption isotherms of PCP on S-AC. The experiment results and the parameters of isothermal models are shown in Fig. S11 and in Table S2, respectively. It can be seen that the adsorption data were well fitted with the Langmuir model, indicating that the adsorption of PCP on S-AC was a monolayer adsorption process. From the Langmuir parameters summarized in Table S2, we can find that the maximum monolayer adsorption capacities ( $q_m$ , mg  $g^{-1}$ ) of PCP on S-AC-600, -700, -800, and -900 were estimated as 292, 385, 526, and



**Fig. 3** (a) XPS survey spectra for the S-AC samples, (b) contents of different sulfur species, and (c) the high resolution XPS S 2p spectra of the S-AC samples.

417 mg  $g^{-1}$ , respectively. From the obtained results, we can conclude that the adsorptive performance of S-AC was significantly improved by increasing annealing temperature and then declined upon treatment at 900 °C. Associated with the BET analysis of S-AC samples, it is noted that the adsorption capacities were closely related with their  $S_{\text{BET}}$  order. In addition, the removal of oxidized sulfur groups at elevated temperature would also enhance the adsorption performance of S-AC. Compared with commercial activated carbon AC ( $q_m = 88 \text{ mg g}^{-1}$ ), and our previously prepared sulfur doped activated carbon ACS-800 ( $q_m = 481 \text{ mg g}^{-1}$ ) and SDAC-800 ( $q_m = 394 \text{ mg g}^{-1}$ ) (Fig. S12-14 and Table S2), S-AC-800 sample presented extremely high adsorption ability, which may be attributed to the ultrahigh SBET of S-AC-800. It was well established that the following aspects including  $\pi$ - $\pi$  interaction, hydrogen bonding, covalent and electrostatic attraction may contribute to the adsorption of organics on carbonaceous materials surface.<sup>48, 49</sup> Since S-AC-800 possessed the largest  $S_{BET}$ , more reaction space and active sites can be exposed for PCP contact, hereby enhancing the aforementioned interactions and resulting in a high adsorption capacity.

Furthermore, PE and DCP were also employed as model pollutants to investigate the role of -Cl substitution in the adsorption of phenols on S-AC-800, considering that chlorophenols (CPs) are common pollutants in both surface and ground waters.<sup>50, 51</sup> Their adsorption kinetics and isotherms were discussed similarly. Results (Fig. S15-16) show that the adsorption behaviour of PE and DCP on S-AC-800 is similar to PCP. It can be seen from Table S3 that the maximum monolayer adsorption capacities were evaluated to be 295, and 813 mg g<sup>-1</sup> for PE and DCP, respectively. It indicates that the adsorption capacities significantly increased with increasing the number of -Cl substitutions on phenols. Two possible solute-sorbent interactions may be responsible for the enhancement: (1) hydrophobic effect (their hydrophobicity increased sharply from PE

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**Fig. 4** The kinetic data for PCP adsorption on S-AC at different PCP concentration. Reaction conditions:  $[PCP]_0 = 20, 30, 40, 50, 60 \text{ mg } \text{L}^{-1}$ , catalyst = 0.05 g L<sup>-1</sup>, and temperature = 25 °C.

to PCP and then to DCP, since –Cl is a hydrophobic group);<sup>52</sup> (2) –Cl substitution enhanced  $\pi$ - $\pi$  interactions between the phenols and the S-AC surface.<sup>49</sup>

## 3.3. Adsorption and catalytic oxidation of phenols on S-AC

The catalytic activity of the as-prepared S-AC samples toward PS activation was initially evaluated by degrading PCP with PS. No PCP degradation was attained at the control test with PS alone (Fig. 5). In the pre-adsorption experiments, before the time of zero, around 29.4%, 34.0%, 46.0%, and 35.5% of PCP was removed attributing to adsorption on S-AC-600, -700, -800, and -900, respectively. After PS was rapidly introduced into the above systems, the PCP degradation process was significantly enhanced for all the S-AC/PS systems. To be specific, about 69.7% and 76.7% of PCP was removed on S-AC-600 and S-AC-700 in 170 min, respectively. Remarkably, S-AC-800 presented the best performance with 100% PCP removal within 45 min, and the residual PCP in solution can be fully degraded by S-AC-900/PS within 170 min.

The toxicity of initial PCP and its oxidation products produced after a 170 min reaction (Fig. S17) in S-AC/PS systems was evaluated by measuring the biodegradability index (the ratio of  $BOD_5$  versus COD). To eliminate the toxicity of PS to microorganism, the reaction solution was initially treated with excessive  $Na_2SO_3$  to convert all the residual PS to innocuous sulfate ions.<sup>53</sup> It is reported that the ratio less than 0.2 means a toxic aqua and greater than 0.4 means a good biocompatibility aqua. Results show that the values of  $BOD_5/COD$  sharply increased from 0.06 of initial PCP solution to 0.30, 0.52, 0.87, and 0.85 after treated by S-AC-600, -700, -800, and -900 with PS for 170 min, respectively. It indicates that the biodegradability of PCP can be significantly improved by the S-AC/PS systems, which might be applied as the pretreatment approach for the biological treatment of phenolic wastewater.

To test the role of adsorption on the catalytic oxidation process, the degradation experiments without pre-adsorption were also carried out as shown in Fig. 6. It can be seen that, compared with the pre-adsorption experiments, 6.9% and 4.1% decline in the total



**Fig. 5** The removal of PCP on S-AC samples with PS in preadsorption system. Reaction conditions:  $[PCP]_0 = 80 \text{ mg L}^{-1}$ , catalyst = 0.1 g L<sup>-1</sup>, [PS] = 15 mM, and temperature = 25 °C.

PCP removal were observed in the cases of S-AC-600, and S-AC-700 in 170 min, respectively. It indicates that pre-adsorption was beneficial for the PCP degradation enhancement, which can be also confirmed by the fact that PCP cannot be adsorbed by S-AC-800-free, and accordingly cannot be degraded (Fig. S18). As for the S-AC-800 and S-AC-900 samples, no decrease of PCP removal was observed, which may be attributed to the high catalytic activity of the two samples.

Although experiments confirmed that pre-adsorption played an positive role in PCP degradation process, the definite relationship between the adsorption and the oxidative degradation was still unclear.

Here, we designed a set of experiments following the method previously reported<sup>2</sup> to make clear the effect of adsorption on the degradation processes. In the tests, PE, PCP and DCP were employed as probes since sorption affinity of these compounds by S-AC-800 was obviously different as demonstrated in section 3.2. Fig. 7a shows that the adsorption capacity ( $q_{es}$ , mg g<sup>-1</sup>) on S-AC-800



**Fig. 6** The comparison of PCP removal on S-AC samples with PS in pre-adsorption and non pre-adsorption systems. Reaction conditions:  $[PCP]_0 = 80 \text{ mg L}^{-1}$ , catalyst = 0.1 g L<sup>-1</sup>, [PS] = 15 mM, and temperature = 25 °C.

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**Fig. 7** (a) The removal of phenols on S-AC-800 with PS in single-pollutant systems; (b) fitting of pseudo-first-order kinetic model for phenols degradation, and the correlation between the adsorption capacity ( $q_{es}$ ) and the apparent degradation rate constant ( $k_s$ ) for phenols in their individual single-pollutant solution (inset). (c) The removal of phenols on S-AC-800 with PS in mixture-pollutant system; and (d) fitting of pseudo-first-order kinetic model for phenols degradation in the first 5 min, and the correlation between the adsorption capacity ( $q_{em}$ ) and the apparent degradation rate constant ( $k_m$ ) for phenols in the mixture-pollutant solution (inset). Reaction conditions: [PE]<sub>0</sub>, [PCP]<sub>0</sub>, and [DCP]<sub>0</sub> = 80 mg L<sup>-1</sup>, catalyst = 0.1 g L<sup>-1</sup>, [PS] = 15 mM, and temperature = 25 °C.

was 589 mg  $g^{-1}$  for DCP, being about 1.54 times that of PCP (368, mg  $g^{-1}$ ), and 2.98 times that of PE (197, mg  $g^{-1}$ ). After PS was rapidly added, all the phenols could achieve a complete removal with an apparent rate constant ( $k_s$ ) of 0.31 min<sup>-1</sup> for DCP, 0.12 min<sup>-1</sup> for PCP, and 0.04 min<sup>-1</sup> for PE (Fig. 7b). In  $q_{es}$  and  $k_s$ , the subscript s represents the single solution. By plotting  $k_s$  against  $q_{es}$ , we found that the two parameters showed a good linear relationship (inset in Fig. 7b), indicating that a higher adsorption capacity leads to a more rapid degradation process. In the mixture of DCP, PCP, and PE, their adsorption capacities and degradation efficiencies were both decreased due to the competitive effect among the coexisting phenols. As shown in Fig. 7c, the adsorption capacities  $(q_{em}, mg g^{-1})$ of DCP, PCP, and PE were declined to 438, 187, and 34 mg  $g^{-1}$ , respectively. After PS was introduced, their corresponding apparent rate constants  $(k_m)$  in the first 5 min were estimated as 0.09, 0.04, and 0.01 min<sup>-1</sup> (Fig. 7d). Here, the subscript m represents the

mixture solution. By plotting  $k_m$  against  $q_{em}$ , a good linear relationship was also observed in the mixture solution (inset in Fig.7d). Accordingly, from the results we have obtained, one can speculate that the adsorbed phenols molecules may be in-situ preferentially degraded by the reactive species derived from the activation of PS, which in turn results in more adsorption of phenols on the S-AC-800 surface. Then, the adsorption and degradation facilitated on each other, synergistically promoted the efficient phenols removal. Interestingly, the AC-800 sample possessed a higher adsorption ability (50.9%), but showed an inferior catalytic performance with 86.5% of PCP removal in 45 min when compared with S-AC-800 (100%) (Fig. S18), suggesting that sulfur doping plays an important role in improving the catalytic activity of S-AC-800.

Based on the obtained results, we suppose that the excellent catalytic activity of S-AC-800 can be explained in several aspects. Firstly, its large adsorption capacity originated from its high  $S_{BET}$  is

Entry	Catalysts (g L <sup>-1</sup> )		Organics (mg $L^{-1}$ )		PS	Т	t	Efficiency	Def
	Species	Loading	Species	Concentration	(mM)	(°C)	(min)	(%)	Rel.
1	Co <sup>2+</sup>	0.1	РСР	80	15	25	170	1.8%	_
2	ZVI	0.1	РСР	80	15	25	60	90	_
3	$Ag^+$	0.1	РСР	80	15	25	10	100	_
4	SDBC	1	РСР	5	1.85	25	100	92.3	54
5	ACS-800	0.1	РСР	80	15	25	130	100	31
6	SDAC-800	0.1	РСР	80	15	25	90	100	33
7	S-AC-800	0.1	РСР	80	3	25	45	100	This work
8	Pre-Fe <sup>0</sup>	0.056	DCP	4	1	25	15	100	55
9	0.5%~Fe/S-CNTs	0.1	DCP	5	0.031	25	30	94.8	56
10	SDAC-800	0.1	DCP	80	15	25	60	100	33
11	S-AC-800	0.1	DCP	80	15	25	15	100	This work
12	AND-1000	0.2	PE	20	6.5	25	45	100	57
13	S-AC-800	0.1	PE	80	15	25	120	100	This work

Table 2 The removal of phenols over different catalysts with PS

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enable to expedite the in-situ degradation process. Also, its high  $S_{BFT}$  enable more active sites to be exposed for PS activation and organic oxidation. The other aspects are concerned with the surface chemistry of the catalyst, especially the species and concentration of sulfur-containing groups, which can be investigated by the XPS analysis (Table S4). To begin with, its high concentration of sp2 hybridized structure, O=C groups, and defect sites (that are widely accepted to be the active sites for PS/PMS activation) would endow S-AC-800 with high catalytic activity toward PS activation. In addition, the significant removal of oxidized sulfur groups is able to increase the reductive degree of S-AC-800 and promote the electron transport from carbon to PS. More importantly, the incorporation of sulfur atom into carbon framework would redistribute the spin density of carbon atoms and create more active sites, and hereby disrupting the chemical inertness of carbon and facilitating electron transfer. In conclusion, the synergistic effect exerted by the aforementioned aspects contributed to the best catalytic activity of S-AC-800 toward PS activation.

In addition, we also investigated the removal of PCP in the classical homogeneous Co<sup>2+</sup>/PS, Ag<sup>+</sup>/PS, and zero-valent iron (ZVI)/PS systems, and found that Co<sup>2+</sup> showed negligible degradation. In the other two systems, 100% and 90% of PCP removal can be achieved on  $Ag^{+}$  and ZVI within 10 min and 60 min, respectively. It indicates that the S-AC-800 samples can be comparable or superior to the most popular transition metal catalysis without involving any metal ions to the water body. Moreover, the catalytic performance of S-AC-800 was also compared with the advanced catalysts developed in recent years for the removal of phenols with PS. As listed in Table 2, complete PCP and DCP removal can be achieved in S-AC-800/PS system with less catalyst dosage and higher contaminant concentration in a shorter time when compared with advanced metal-free catalyst such as SDBC derived from sludge, and metal-based catalysts such as Pre-magnetized Fe0 (Pre-Fe<sup>0</sup>) and Fe/S modified carbon nanotubes (Fe/S-CNTs). Most importantly, compared with our previously prepared S-doped activated carbons derived from 2thiophenemethanol (ACS-800) and thiophene (SDAC-800), the time for PCP completely removal can be shorten from 130 min for ACS-800 to 90 min for SDAC-800 and to 45 min for S-AC-800 under the

same reaction condition. It indicates that PPS could act as an excellent and efficient sulfur precursor for preparation of S-doped porous carbons through a more facile process.

### 3.4. Catalytic mechanism of PS activation on S-AC

Based on the achievements above, we speculated that the degradation of PCP is mainly occurred on the catalyst surface, where the adsorbed PCP would be in-situ degraded by the activated PS. To further shed light on this point, the removal of PCP in the S-AC-800/PS system was conducted in the presence of radical scavengers. Halide (Br-: in the form of KBr) was applied as the scavenger for  $SO_4^{-}_{free}$  and  $HO_{free}^{+}$  produced in aqueous solution,<sup>58</sup> and I-histidine was used as singlet-oxygen (<sup>1</sup>O<sub>2</sub>) scavenger.<sup>11</sup> Fig. 8a shows that, the introduction of minor amount of Br would decrease the PCP degradation rate from 0.12 (0 mM Br<sup>-</sup>) to 0.11 (5 mM  $Br^{-}$ ) and to 0.10 min<sup>-1</sup> (10 mM  $Br^{-}$ ). Then the value gradually increased to 0.21 min<sup>-1</sup> when 30 mM Br<sup>-</sup> was presented. This is because that the hydrophilic Br can react with the free radicals produced in aqueous solution to form less reactive and more selective halogen radicals (Br and Br2 -, that are more prone to reacting with electron-rich target pollutant) (Eqs 1-3).<sup>59</sup> Thus, the presence of low level Br<sup>-</sup> would shield the highly reactive radicals, and then slow down the reaction rate. While the generation of excess Br<sup>•</sup> and Br<sub>2</sub><sup>•-</sup> from high concentration of Br<sup>-</sup> could facilitate the mineralization of electron-rich PCP and its intermediates such as benzoquinone and 4-chlororesorcinol, hereby improving the PCP degradation rate. Nevertheless, the slight effect of halide on PCP removal allows us to conclude that only a minimal amount of  $SO_4^{\bullet-}$  and  $HO_{free}^{\bullet}$  was generated in solution. Fig. 8b shows that the introduction of excess amount of I-histidine (30 and 60 mM) was able to compete the adsorptive sites with PCP, resulting in a decrease in the PCP adsorption efficiency, which in turn presented a minor inhibitory effect on PCP degradation. The quenching experiments by using I-histidine as scavenger suggested that  ${}^{1}O_{2}$  is not the major reactive species responsible for PCP degradation. From the obtained results, one can conclude that the particlesurface interaction plays a dominant role in PS activation and PCP oxidation.

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**Fig. 8** Effects of (a) Br<sup>-</sup>, (b) I-histidine, and (c) ethanol on PCP degradation in S-AC-800/PS system; and (d) the comparison of PCP degradation on S-AC-800/PS in initial pH 10.7 and in ethanol/PS of 100 systems. Reaction conditions:  $[PCP]_0 = 80 \text{ mg L}^{-1}$ , catalyst = 0.1 g L<sup>-1</sup>, [PS] = 15 mM, and temperature = 25 °C.

$$SO_4^- + Br^- \to Br \cdot + SO_4^{2-}, k_{SO_4^- + Br^-} = 3.5 \times 10^9 M^{-1} s^{-1}$$
 (1)

$$HO \cdot +Br^{-} \rightarrow BrOH^{-}, k_{HO \cdot +Br^{-}} = 1.1 \times 10^{10} M^{-1} s^{-1}$$
 (2)

$$BrOH^{-} + Br^{-} \rightarrow Br_{2}^{-} + OH^{-}$$
(3)

It was well established that, in terms of particle-surface interaction, two additional mechanisms including surface-bounded radical pathway and non-radical pathway were proposed for PS activation.<sup>57, 60</sup> Thus, to deeply investigate the PS activation process on S-AC-800, ethanol was used as a probe to shield the total radicals generated in the PS activation process ( $k_{ethanol/SO4}$  = (1.6-7.8) ×  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{ethanol/HO*}$  = (1.2-2.8) ×  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>60</sup> Fig. 8c shows that ethanol had a significant inhibiting effect on PCP adsorption and total removal in S-AC-800/PS system. We suppose that the high solubility of PCP in organic solvent led to the decrease in PCP adsorption. Remarkably, when the molar ratio of ethanol : PS elevated to 1000 : 1, only 3.5% of PCP was adsorbed. As discussed above, a higher adsorption capacity leads to a more rapid degradation process. Thus the decline in PCP adsorption originated from the addition of ethanol would in turn decrease the PCP degradation efficiency. In addition, if large amount of surfacebounded radicals were generated in the S-AC-800/PS system, the PCP degradation rate would also slow down in the presence of ethanol. Therefore, it is difficult to clearly differentiate the negative effects of the two aspects on PCP oxidation. Here we qualitatively analyze them in virtue of the effect of pH on PCP removal. As shown in Fig. 8d, the PCP adsorption efficiency in the system of initial solution pH 10.7 was comparable to the system with a certain amount of ethanol (ethanol : PS = 100 : 1). In addition, the system of pH 10.7 with PS alone suggested that the degradation of PCP attributed to base activation was not significant in the initial stage. Accordingly, if no surface-bounded radicals were generated in the S-AC-800/PS system, the degradation of PCP in the two systems were almost the same. However, Fig. 8d shows that after a 5 min reaction, PCP removal decreased from 65.3% with initial pH 10.7 to 51.1% with the presence of ethanol in the S-AC-800/PS system, demonstrating the generation of surface-bounded radicals. Moreover, it is worth noting that even though a large amount of ethanol (ethanol : PS = 1000 : 1) was added, 35.3% of PCP could still be removed in 170 min, unlike the classic radical-based oxidation process originated from PS activation on zero-valent iron (ZVI) (Fig.

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S19), suggesting that not only surface-bounded radicals but also non-radical oxidation process played an important role in PCP degradation in S-AC-800/PS system.

# 3.5. Effects of several parameters on PCP removal

Since S-AC-800 exhibited the best catalytic activity among all of the as-prepared S-AC samples, it was chosen for the subsequent studies. The effects of catalyst dosage and initial PCP concentration on PCP adsorption and oxidation were shown in Fig. S20 and S21. Fig. 9 depicted the influence of PS concentration on PCP degradation with different dosage of S-AC-800. It can be seen that the increase of PS concentration shows a marginal effect on PCP removal with a higher (0.1 g  $L^{-1}$ ) or a lower (0.025 g  $L^{-1}$ ) S-AC-800 loading. While at catalyst dosage of 0.05 g L<sup>-1</sup>, the removal of PCP increased as the PS concentration increased from 3 to 13 mM and then declined with the continuous increase of PS concentration. As discussed above, the PS activation and PCP oxidation is a surface phenomenon, in which the formation of reactive species from PS activation as well as the adsorption-desorption of PCP and its intermediates are diffusion- and equilibrium-driven processes.<sup>53</sup> We suppose that under higher catalyst dosage, larger surface area and more active sites were served for PCP adsorption and PS activation, where a relative large amount of intermediates can be produced instantly. In this case, the desorption of intermediates was the rate



**Fig. 9** Effect of PS concentration on PCP degradation with (a) 0.1 g  $L^{-1}$ , (b) 0.05 g  $L^{-1}$ , and (c) 0.025 g  $L^{-1}$  of S-AC-800. Reaction conditions: [PCP]<sub>0</sub> = 80 mg  $L^{-1}$ , [PS] = 3, 6, 13, 26 mM, and temperature = 25 °C.



**Fig. 10** Effect of initial pH on PCP degradation in S-AC-800/PS system. Reaction conditions:  $[PCP]_0 = 80 \text{ mg L}^{-1}$ , catalyst = 0.1 g L<sup>-1</sup>, [PS] = 15 mM, initial pH = 2.6, 4.2, 6.8, 8.6, 10.7, and 11.3, and temperature = 25 °C.

controlling step, leading to the insignificant role of PS concentration. Whereas under lower catalyst dosage, the limited reactive site was not available to active overdose PS. At this point, the activation of PS became the bottleneck, and the degradation of PCP was little influenced by the PS concentration. When an appropriate amount of catalyst was added, the two steps synergistically contributed to the PCP degradation.

The effect of initial pH (pH 2.6-11.3) on PCP removal was also investigated by adding 0.1 mol  $L^{-1}$  of  $H_2SO_4$  or 0.1 mol  $L^{-1}$  of NaOH. Fig. 10 shows that for the pH investigation range, both the adsorption and the oxidation efficiencies of PCP on S-AC-800 were little influenced by solution pH except for pH 10.7 and pH 11.3. The pHpzc of the S-AC-800 sample was estimated as pH 4.6 (Table S1), suggesting that the surface charge of the carbon was dominated by the negatively charged sites under a highly basic condition (pH 11.3). The p $K_a$  of PCP is 9.38, which implies that when pH > p $K_a$  (pH 10.7-11.3), the PCP species was mainly in its anionic forms. Thus, the electrostatic repulsion between the two aspects results in the decrease in PCP adsorption, and consequently decreases the PCP oxidation efficiency. In addition, the generation of hydroxyl radical (HO<sup>•</sup>) under strong alkaline conditions from  $SO_4^{\bullet-}$  (Eq 4),<sup>61</sup> with a lower redox potential (1.8 V) compared to  $SO_4^{\bullet-}$  (2.5–3.1 V),<sup>62</sup> could also reduce the PCP oxidation efficiency. These results suggest that S-AC-800 exhibits a high catalytic activity within a wide pH range, which can be applied in various aqueous environments since most of real wastewater matrix are usually not strong alkaline solution.

$$SO_4^- + OH^- \rightarrow SO_4^{2-} + HO; k = (6.5 \pm 1.0) \times 10^7 M^{-1} s^{-1}$$
 (4)

Further kinetic studies were performed to investigate the effect of reaction temperature on PCP oxidation over S-AC-800 (Fig. S22). Results show that the degradation of PCP with S-AC-800/PS obeyed pseudo-first-order kinetics and the reaction rate constant was estimated as 0.12, 0.14, and 0.16 min<sup>-1</sup> at the reaction temperature of 25, 45, and 55 °C, respectively. Based on the Arrhenius equation, the apparent activation energy was estimated to be 13.16 kJ mol<sup>-1</sup>, which was much lower than that on the reduced graphene oxide

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**Fig. 11** The influences of (a)  $HCO_3^{-}$ , (b)  $HPO_4^{2^-}$ , (c)  $CO_3^{2^-}$ , and (d) HA on PCP removal in S-AC-800/PS system. Reaction conditions:  $[PCP]_0 = 80 \text{ mg L}^{-1}$ , catalyst = 0.1 g L<sup>-1</sup>, [PS] = 15 mM, and temperature = 25 °C.

(rGO) (33.40 kJ mol<sup>-1</sup>), AC (65.69 kJ mol<sup>-1</sup>), and our previously prepared ACS-800 (22.53 kJ mol<sup>-1</sup>), and SDAC-800 (13.53 kJ mol<sup>-1</sup>) (Fig. S23), indicating the excellent catalytic activity of S-AC-800.

### 3.7. Effects of anions and natural organic matters on PCP removal

As well known, even trace amount of ions and natural organic matters (NOMs) existed in real wastewater matrix would have potential influences on AOPs. Especially when  $SO_4^{\bullet-}$  is the dominant reactive radical responsible for the organics oxidation. The anions such as Cl<sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>, as well as the NOMs could react with  $SO_4^{\bullet-}$  through Eqs. 5-9 to form less reactive radicals,<sup>63, 64</sup> resulting in the decrease of contaminants degradation efficiency. Besides, some anions have significant effects on the acidic/basic of wastewater, and hereby influencing the AOPs.

$$SO_4^{-} + Cl^- \rightarrow Cl^{-} + SO_4^{2-}, k_{SO_4^{2-} + Cl^-} = 3.0 \times 10^8 M^{-1} s^{-1}$$
 (5)

$$SO_4^{-} + HPO_4^{2-} \rightarrow HPO_4^{-} + SO_4^{2-},$$
  
 $k_{SO_4^{-} + HPO_4^{2-}} = 1.2 \times 10^6 M^{-1} s^{-1}$  (6)

$$SO_4^- + HCO_3^- \to HCO_3^- + SO_4^{2-},$$
  
 $k_{SO_4^- + HCO_3^-} = 2.8 - 9.1 \times 10^6 M^{-1} s^{-1}$  (7)

$$SO_4^{-} + CO_3^{2-} \rightarrow CO_3^{-} + SO_4^{2-}$$
,  
 $k_{SO_4^{-} + CO_3^{2-}} = 6.1 - 410 \times 10^6 M^{-1} s^{-1}$  (8)

NOM + SO<sub>4</sub><sup>--</sup>  $\rightarrow$  products,  $k_{SO_4^{--}+NOM} = 2.35 \times 10^7 M_C^{-1} s^{-1}$  (9)

Herein, the influences of several anions were taken into account in the PCP removal in S-AC-800 with PS. It is indicated from Fig. 11a that the presence of  $HCO_3^-$  at concentrations ranging from 10-30 mM exhibited a negligible effect on PCP adsorption but decreased its oxidation efficiency. A similar trend was also observed in the presence of  $HPO_4^{2^-}$  (Fig. 11b). The reason for these may be that the quenching effects of  $HCO_3^-$  and  $HPO_4^{2^-}$  on the surface-bounded radicals interfered with the catalytic oxidation process, leading to the decrease of PCP degradation. However, it should be noted that a steady and consistent PCP removal was observed with the increased  $HPO_4^{2^-}$  concentration. As  $Na_2HPO_4$  is a well-known alkaline agent, which would change the solution pH from 6.8 to 9.2 when 30 mM of  $HPO_4^{2^-}$  was presented in the PCP solution. We speculate that the basic environment facilitated the activation of

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PS, which could be further confirmed by the fact that  $HPO_4^{2^-}$  (30 mM) with PS alone contributed to 13.5% PCP removal. The influence of  $CO_3^{2^-}$  is depicted in Fig. 11c. As observed, the introduction of alkaline  $CO_3^{2^-}$  significantly decreased the PCP adsorption efficiency from 47.8% (0 mM  $CO_3^{2^-}$ ) to 18.5% due to the strong electrostatic repulsion under highly basic environment (pH = 11.1, 11.3, and 11.4 at a  $CO_3^{2^-}$  concentration of 10, 20, 30 mM, respectively), as revealed by the effect of initial pH on PCP removal (Fig. 10). As such, it is noted that, the presence of a minor amount of  $CO_3^{2^-}$  amount could facilitate the catalytic oxidation process attributed to base activation (48.8% PCP removal was obtained in PS with 30 mM  $CO_3^{2^-}$ ). In addition, Ma et al.<sup>59</sup> reported that the cO<sub>3</sub><sup>--</sup> was more selective, which may be also contributed to the enhanced PCP degradation.

The influence of humic acid (HA), a typical natural organic matter, is depicted in Fig. 11d. It was suggested that the presence of HA would decrease the removal efficiency toward target contaminant in AOPs via the competitive adsorption on catalyst surface and the competitive reaction with reactive species.<sup>10</sup> However, in the S-AC-800/PS system, HA at a concentration of 10-30 mg L<sup>-1</sup> presented a negligible effect on both PCP adsorption and oxidation. We suppose that the predominant micro-pore characteristic of S-AC-800 limited the adsorption of HA macromolecular structure, giving rise to the negligible influence on PCP adsorption, and hereby leading to a minor effect on PCP degradation.

#### 3.8. Stability and reusability of the S-AC-800 sample

The stability and reusability of the S-AC-800 sample was examined through three successive runs. Results show that both the adsorption and the oxidation efficiencies of PCP were significantly reduced over three cycles (Fig. S24). Characterization results indicated that the deactivation of catalyst can be attributed two aspects: 1) the change of porous structure due to the adsorption of PCP and PCP oxidation products, as confirmed by the  $N_{\rm 2}$  sorption isotherms that its  $S_{\rm BET}$  and pore volume significantly decreased after the first use (Table S5 and Fig. S25); and 2) the change of surface chemistry under the highly oxidative environment, as confirmed by the XPS S 2p spectra that the percentage of -C-SO<sub>x</sub>-C- in overall S dopants increased from 34.7% to 65.8% after the first use (Fig. S26), which was suggested to be detrimental for the electron transport from carbon to persulfate. However, it is worth noting that the adsorption performance and catalytic activity of S-AC-800 after 1<sup>st</sup> cycle can be greatly recovered after being annealed at 450 °C in N<sub>2</sub> for 2 h due to the partially removal of the adsorbed organics and recovery of the surface chemistry, as illustrated by the N<sub>2</sub> sorption isotherms (Table S5 and Fig. S25) and XPS analysis (Fig. S26). Nevertheless, further efforts should be made to enhance the stability of the carbon material in future studies.

# 4. Conclusions

In summary, in-situ sulfur doped activated carbon with both strong adsorption ability and enhanced PS activity was successfully synthesized through a one-pot thermal process by using a potential waste material (Poly(phenylene sulphide) (PPS)) as precursor, and KOH as activator. Experiments demonstrated that the obtained materials were extremely efficient for adsorptive and oxidative removal of phenols organics. The degradation of different phenols organics in their individual solution and mixture solution suggested that a higher adsorption capacity leads to a more rapid degradation process, which in turn accelerates the adsorption, then the adsorption and degradation synergistically promotes the efficient organics removal. Quenching experiments indicated that both surface-bounded radicals and non-radical pathway played a dominant role in PS activation. The high adsorption ability, excellent PS activity, wide pH usable range, as well as resistant to various anions and HA make it a promising candidate as an metal-free catalyst for wastewater purification and environmental remediation. The successfully fabrication of sulfur-doped activated carbons derived from PPS make us believe that this work not only provides a potential promising way to utilize PPS waste, but also opens a new way to synthesis other sulfur-doped activated carbon with both enhanced adsorption performance and catalytic activity via a facile, economical and efficient method for environmental remediation.

# **Conflicts of interest**

There are no conflicts to declare

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Sulfur doped activated carbon with strong adsorption ability and excellent catalytic activity is successfully synthesized through a one-pot process.