Floatable 3D sponge@SBC induced dual pathway activated persulfate for *Microcystis aeruginosa* inactivation

Lifei Deng [a,b,1], Yu Chen [a,b,1], Jiangfang Yu [a,b*], Jie Yuan [a,b], Qili Peng [a,b], Yuyang Yi [a,b]， Nile Wu [a,b,] Lin Tang [a,b*]

[a]College of Environmental Science and Engineering, Hunan University, Changsha 410082, China

[b]Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, Hunan, China[1]

[1]These authors contributed equally to this work

[*]Corresponding authors

E-mail: yujf@hnu.edu.cn, tanglin@hnu.edu.cn

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Text S1. Materials and regents

Sodium persulfate ($Na_2S_2O_8$; PS), hydrochloric acid (HCl), sodium hydroxide (NaOH), polyvinyl alcohol (PVA), methanol (MeOH), Tert-butyl-alcohol (TBA), 1, 4-benzoquinone (BQ), and furfuryl alcohol (FFA) were bought from Sinopharm Chemical Regent Co. Ltd (Shanghai, China). All agents used in this experiment were analytical grade. All solutions were prepared with ultrapure water 18.25 MΩ/cm) from a Milli-Q water purification system. The melamine sponge was obtained from Yancheng (Jiangsu Province, China).

Text S2. Preparation and characterization of the catalysts

Powdered biochar (SSBC) derived from shrimp shell was prepared by our previous work. In brief, after being washed, smashed and sieved, the shrimp shell was pyrolyzed in a tubular reactor (SK-G04123K, China) at 800 ℃ for 2 h under N_2 atmosphere. Then, the obtained powdered biochar was washed with 2 M HCl for 12 h, then dried and stored for later use.

With melamine sponge as 3D scaffold and PVA as crosslinking agent, the floatable sponge@SBC was prepared as follows. Firstly, melamine sponge blocks (1.0 cm × 1.0 cm × 0.5 cm) were cleaned with ultrapure water and ethanol for 3 times, respectively. Then, PVA was added in 100 mL ultrapure water and heated to dissolve. After that, different masses of SSBC powder were added into the PVA solution and sonicated for 15 min. Subsequently, two melamine sponge blocks were immersed in the above solution to obtain biochar coated melamine sponge blocks (floatable 3D sponge@SBC), which were dried in the oven with intermittent tumbling to prevent uneven sedimentation. At last, the dried floatable 3D sponge@SBC were activated in the tubular reactor at different temperatures (200 ℃, 300 ℃, and 400 ℃) and named as sponge@SBC_X-Y, where X represents the mass ratio of biochar to PVA and Y represents the activation temperature.

Text S3. Characterizations

Scanning electron microscope (SEM, Hitachi s-4800, Japan) was used to obtain the morphology and microstructure of catalysts. The specific area (SSA) and pore size distribution were acquired by nitrogen adsorption-desorption isotherms measured in a Quantachrome Nova Win (NOVA 2000e). The elemental composition and chemical states of prepared photocatalysts were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI spectrometer with Al Kα source). To

gain the chemical bonds or functional groups of catalyst, Fourier transform infrared (FTIR, Shimadzu IRAffinity-1) spectra was confirmed, in which KBr was used as reference. The total organic carbon (TOC) was measured by a Shimadzu TOC-VCPH analyzer.

Text S4. The detailed culture method of *M. aeruginosa*

M. aeruginosa (FACHB-913) was provided by the Freshwater Algae Culture Collection at the Institute of Hydrobiology (FACHB). The algal cells were cultivated in an incubator at 25 ℃ with 12 h light every day in BG11 medium. The conical flask was shaken three times a day to prevent cell sedimentation.

The BG11 medium contained $NaNO_3$ (1.5 g), K_2HPO_4 (0.04 g), $MgSO_4 \cdot 7H_2O$ (0.075 g), $CaCl_2 \cdot 2H_2O$ (0.036 g), citric acid (0.006 g), ferric ammonium citrate (0.006 g), $EDTANa_2$ (0.001 g), Na_2CO_3 (0.02 g) and 1 mL of A5 solution in 1 L distilled water. A5 solution contained H_3BO_4 (2.86 g), $MnCl_2 \cdot 4H_2O$ (1.86 g), $ZnSO_4 \cdot 7H_2O$ (0.22 g), $CuSO_4 \cdot 5H_2O$ (0.08 g), $Na_2MoO_4 \cdot 2H_2O$ (0.39 g), $Co(NO_3)_2 \cdot 6H_2O$ (0.05 g) in 1 L distilled water. The pH of the BG-11 medium was adjusted to pH 7.1 by adding either 1 M NaOH or 1 M HCl before autoclaving. Incubation temperature is 25 ℃ and light time: dark time is 12: 12.

Text S5. Method for determining the chlorophyll *a* content of *M. aeruginosa*

Chlorophyll a was determined by reference to "Water Quality-Determination of Chlorophyll A-Spectrophotometric Method" (HJ 897-2017) of the Ministry of Ecology and Environment of China and the Lichtenthaler method (Lichtenthaler and Wellburn, 1983). 4 mL samples were taken out every 1 h to measure the content of chlorophyll a. It was centrifuged at 8000 rpm for 5 min, then the supernatant was discarded. The precipitate was resuspended by adding 5 mL of 95% ethanol and placed in a 4℃ refrigerator for 24 h, protected from light. The suspension was then centrifuged again and the absorbance of the supernatant was measured at 750 nm, 664 nm, and 649 nm. The results obtained were calculated by the modified Lichtenthaler formula showed below.

$$Ca=13.95\times(A665-A750)-6.88 \times (A649- A750)$$

Ca——the concentration of chlorophyll a

A750, A665, A649——the absorbance at 750 nm, 665 nm, 649 nm, respectively.

Removal percentage was calculated by the Eq.1, where C_0 and C_t correspond to the chlorophyll *a* concentrations at initial state and degraded at time *t*, respectively.

$$R\ (\%)\ = \frac{C_0 - C_t}{C_0} \times 100 \text{ (Eq.1)}$$

Pseudo-first-order kinetic investigation of DCP degradation process were fitted by Langmuir-Hinshelwood model (Eq.3) shown as below, where the pseudo-first-order rate constant, k_{obs}, were calculated by the corresponding variable form (Eq.4).

$$-\frac{\mathrm{dC}}{\mathrm{dt}} = \mathrm{k}_{obs} C \text{ (Eq.2)}$$

$$\ln\left(\frac{\mathrm{C}_t}{\mathrm{C}_0}\right) = -\mathrm{k}_{obs} t \text{ (Eq.3)}$$

Text S6. Detailed descriptions of the analytical methods

Cellular morphologies observation and membrane permeability evaluation

To investigate the changes of cell membrane, the cellular morphologies were observed by SEM (Hitachi, S-4800, Japan), and the the leakage of intracellular non-electrolyte was indicated by the absorbance of the supernatant at 264 nm.

At the determined time intervals, 15 ml samples were collected and centrifuged 10 min under 4500 rad min^{-1}. Then the algae were fixed by 2 mL glutaraldehyde (2.5%). Secondly, the algae cells were washed with deionized water three times and dehydrated by gradient dehydration by various concentrations of ethanol (50%, 60%, 70%, 80%, 90%, 95%). Finally, the samples were observed using the SEM (Hitachi, S-4800, Japan).

At the determined time intervals, 5 ml samples were collected. The sample was centrifuged at 4 °C for 10 min at 8000 r min-1. Then, the optical density (OD) of UV-absorbing at 264 nm of the samples was acquired using the ultraviolet photometer, and the changes in OD264 were used to reflect the exudation of organic matter in the cells.

Extraction and determination of antioxidant enzymes

The effect on algal antioxidant enzymes system includes superoxide dismutase (SOD) and hydrogen peroxidase (CAT). The activity of SOD/CAT was determined by Kits from Nanjing Jiancheng Bioengineering Institute. For each sample, algae cells were harvested by centrifugation at

8000 r/min for 10 min and diluted in 1 mL PBS. After that, the suspension was ultrasound-treated by an ultrasonic cell disrupter (VCX130, Sonics & Materials Inc, USA). Subsequently, the supernatant was collected by centrifugation for the analysis of enzyme activity.

Cellular organics analysis

The extracellular organic matter (EOM) was determined by FL-7000 (Hitachi, Japan). At the scheduled time, 5 mL sample was taken and centrifuged at 8000 rpm for 10 min. The supernatant was filtered through 0.45 μm membrane and used to determine the EOM of algal cells in the reaction solution. The EOM scanning range of algae cells ranged from excitation wavelength Ex: 200–450 nm, emission wavelength Em: 200–550 nm, and the detection cell was a 1 cm quartz fluorescence sample cell. Meanwhile, the three-dimensional fluorescence spectra of ultrapure water were tested as blank correction results.

Text S7. Electrochemical test

Firstly, 1 mg of the prepared materials was dispersed into 0.5 mL of 5% naphthol and 0.5 mL ethanol solution for 3 h ultrasonic treatment. Then, certain volume of the mixture was added to glassy carbon electrode until natural drying. The obtained electrode was used as working electrode for the subsequent electrochemical testing. Pt electrode and Hg/Hg_2Cl_2 electrode (SCE) served as counter and reference electrode, respectively. Then LSV test was conducted with the potential ranging from 0 to 3 V vs SCE with the scan rate of 0.02 V/s and the sensitivity of 10^{-4} (A/V). The electrolyte was 30 mL 20 mM phosphate buffer (pH=7.4) with/without the addition of 0.2 g/L PDS and/or algae solution (OD_{680}=0.200). EIS were measured with the initial potential of 0.2 V (amplitude of 0.0005 V) and frequency ranging from 0.01 to 100000 Hz, in 5 mM $Fe(CN)_6^{3-/4-}$ solution with 0.1 M KCl. Similar, Chronoamperometry was carried out under the same condition as the LSV but the working electrode biased at an applied potential of +1 V.

Text S8. Detailed information of actual water sample

Actual water from Peach Lake (28°11′7.3″ N, 112°57′33.54″ E) and Xiangjiang River (28°11′6.35″ N, 112°57′39.33″ E) were selected for algae inactivation experiments. The Actual water was passed through a 0.45 μm filter membrane. The initial algal cell concentration was made consistent with the

experiment by inoculating the water samples with a high concentration of algal solution

Table S1. Porosity characterizations of the prepared materials.

Materials	S_{BET}[a] (m^2/g)	S_{mic}[b] (m^2/g)	S_{mes}[c] (m^2/g)	V_{total}[d] (cc/g)	V_{mic}[b] (cc/g)	Ave-pore radius (nm)
Sponge	150.9	-	150.9	0.17	-	2.30
sponge@SBC_1	94.28	56.61	37.67	0.19	0.028	3.97
sponge@SBC_1-300	264.6	-	264.6	0.43	-	3.27
SSBC	449.4	240	209.4	0.5	0.11	2.22

[a] S_{BET} is the specific surface area analyzed by BET method at $P/P_0 = 0.05$-0.3.

[b] S_{mic} (microporous surface area) and V_{mic} (microporous pore volume) are calculated by t-plot method at $P/P_0 = 0.4$-0.6.

[c] S_{mes} is the mesoporous surface area by the t-plot method external surface area ($S_{mes} = S_{BET} - S_{mic}$).

[d] V_{total} is the total volume acquired at $P/P_0 = 0.99$.

Table S2. Element content of sponge@SBC1-300 before reaction and after five repetitions by XPS

Materials	C1s (at%)	N1s (at%)	O1s (at%)
Fresh sponge@SBC_1-300	78.57	7.21	12.86
Used sponge@SBC_1-300	77.38	7.41	15.19

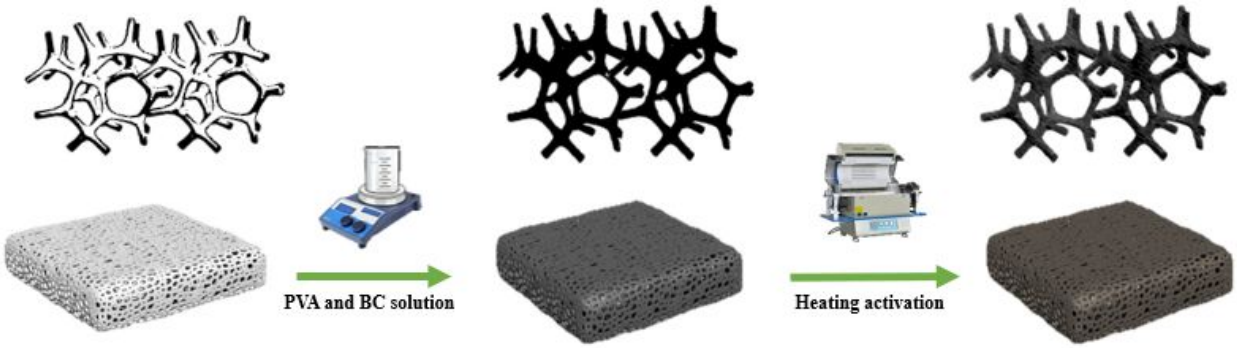


Fig. S1. The schematic diagram of synthesis of the sponge@SBC_1-300.

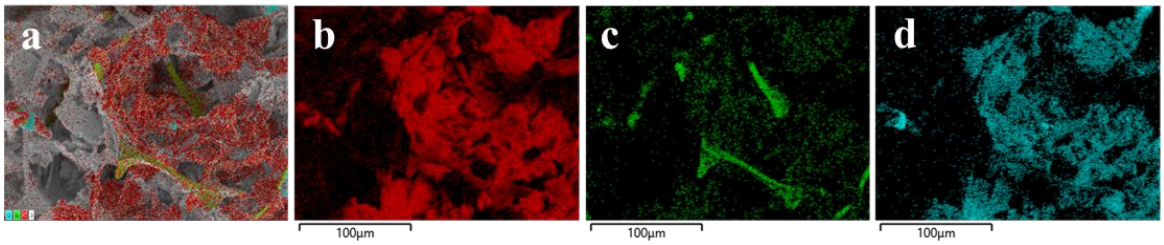


Fig. S2. The EDX mapping of sponge@SBC_1-300 (a), carbon (b), nitrogen (c), oxygen (d).

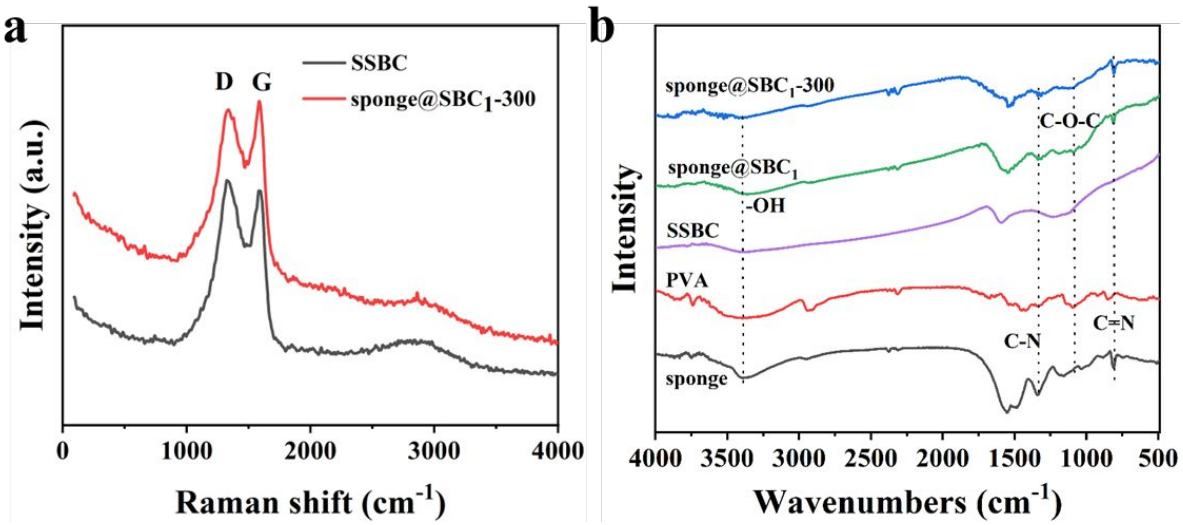


Fig. S3. Raman results of SSBC and sponge@SBC_1-300 (a), and FTIR spectra (b) of prepared catalysts.

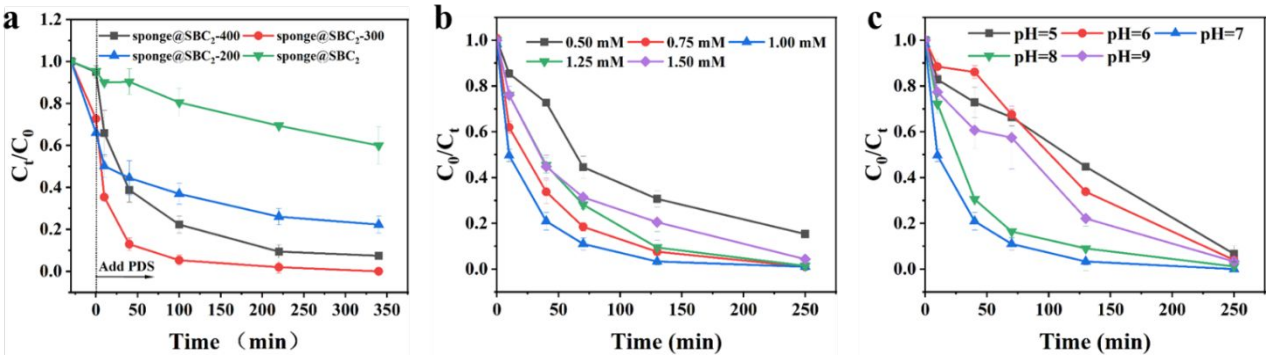
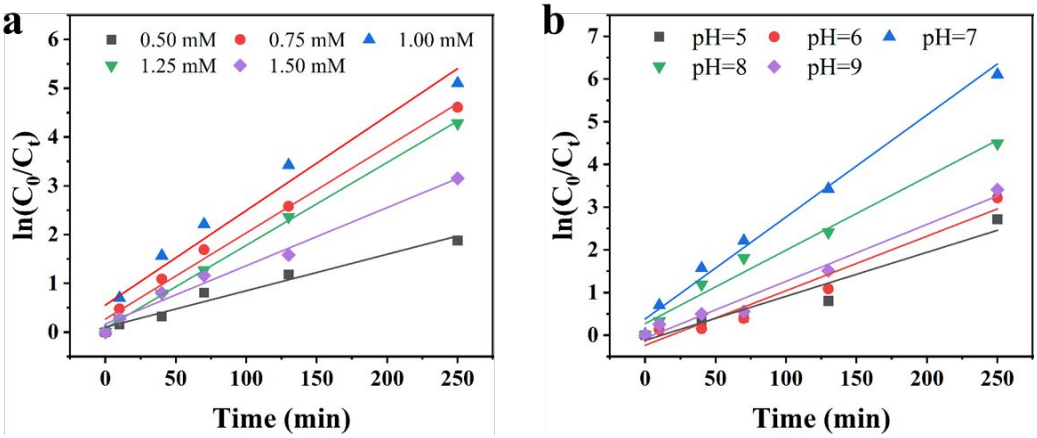


Fig. S4. The inactivation of *M. aeruginosa* by sponge@SBC activated at different temperatures (a); the effect of PS concentration (b), and initial pH (c) on algae inactivation.



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182 **Fig. S5.** The pseudo first-order reaction kinetic model fitting with different PS concentration (a), and

183 initial pH (b).

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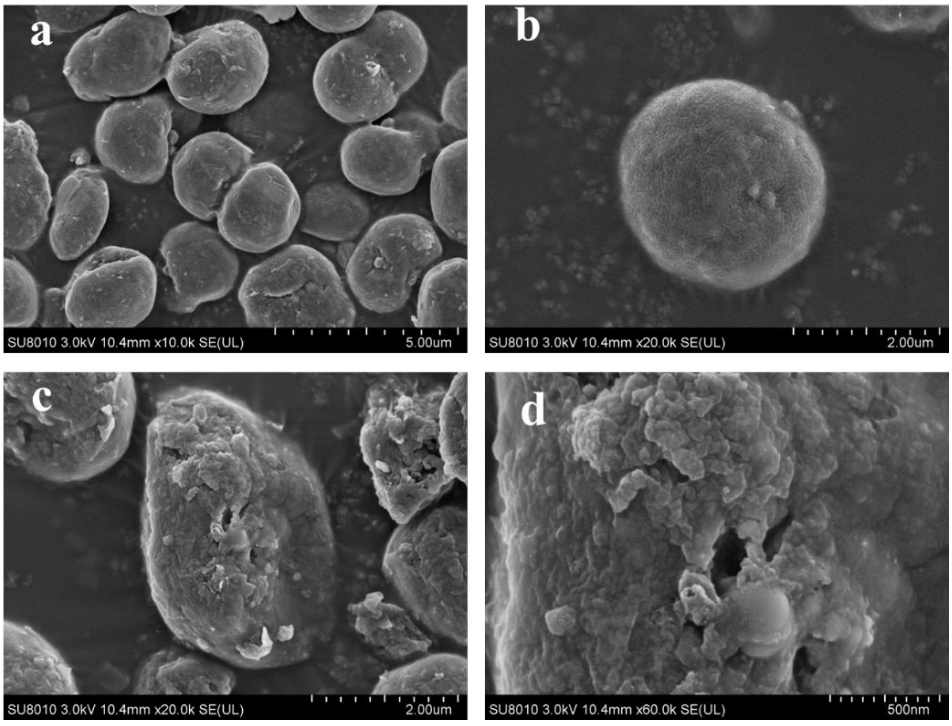

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186 **Fig. S6.** Scanning electron microscopy (SEM) images of *M. aeruginosa* cell morphology before

187 (a, b) and after 70 min reaction (c, d).

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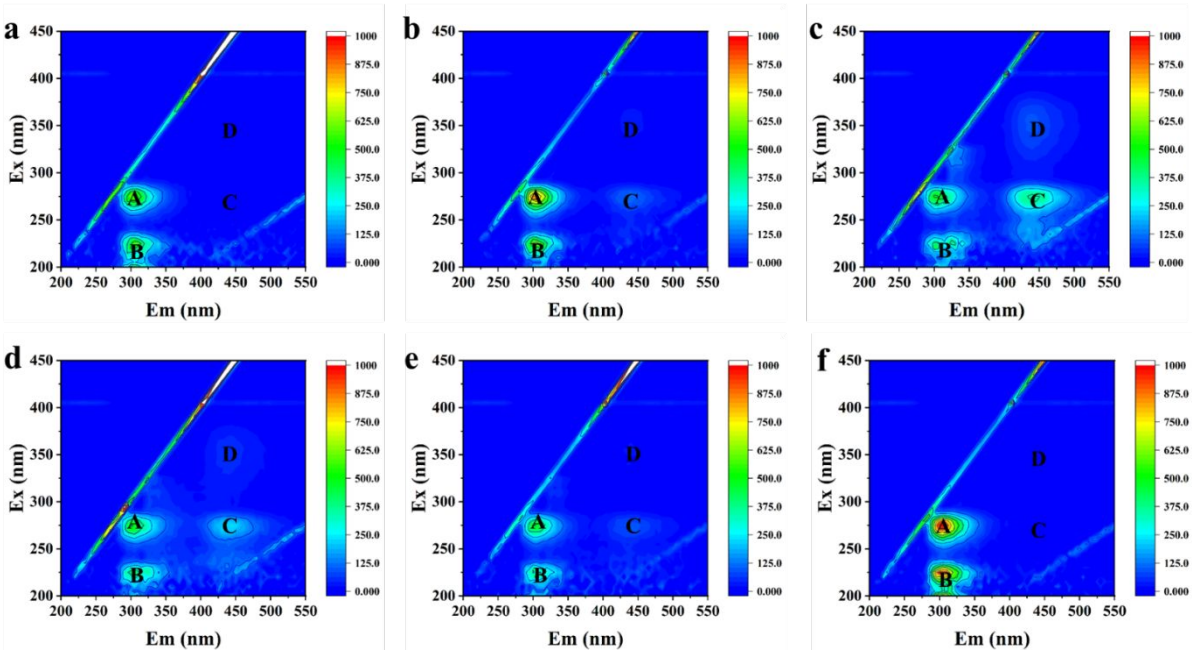

Fig. S7. Three-dimensional fluorescence spectrum of 0 min (a), 40 min (b), 70 min (c), 130 min (d), 250 min (e) after reaction and 250 min without treatment(f).

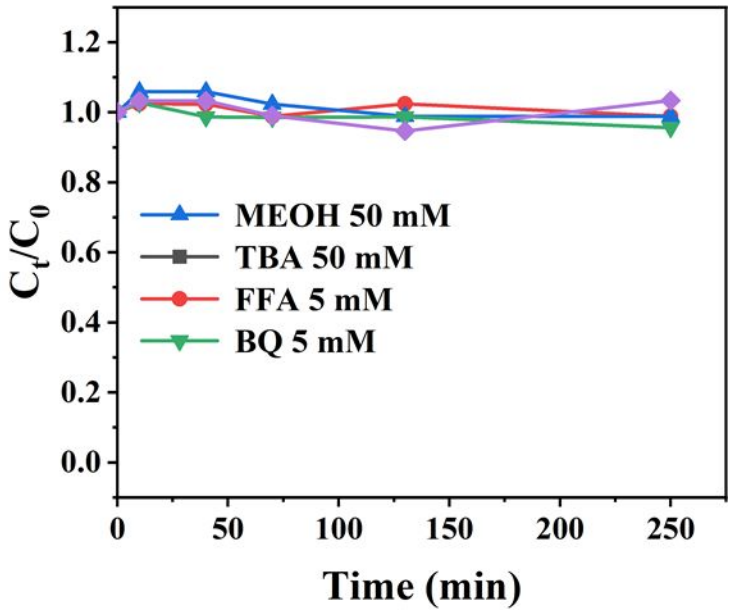

Fig. S8. Effects of different quenchers on chlorophyll *a* concentration.

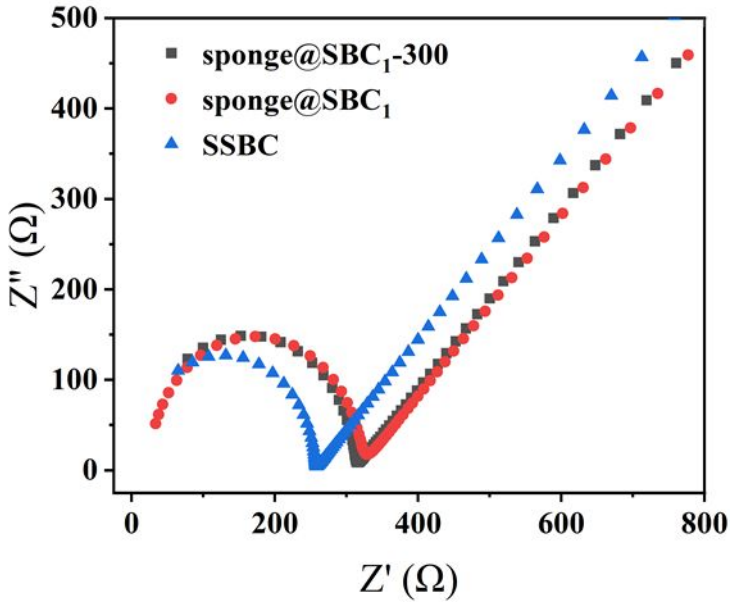

Fig. S9. The EIS analyst of different materials.

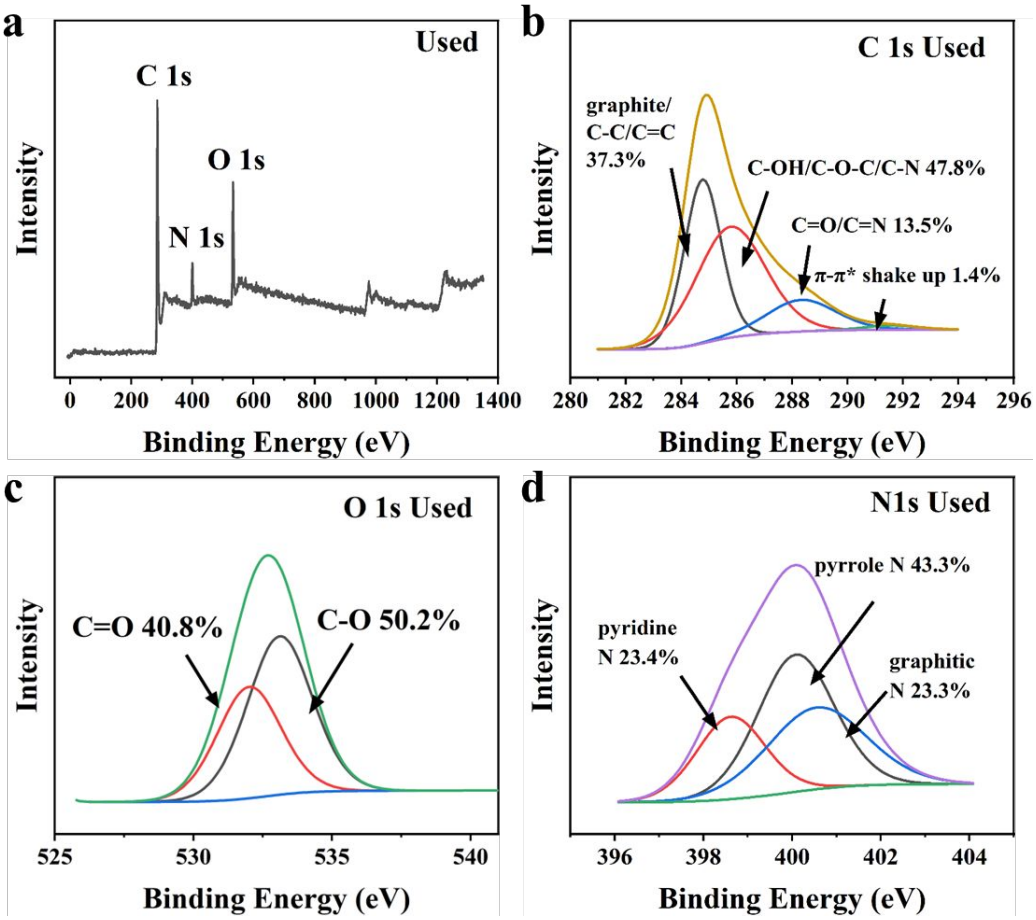

Fig. S10. XPS survey of sponge@SBC$_1$-300 after reaction (a), C1s (b), O1s (c) and N1s (d) high resolution scans after reaction.

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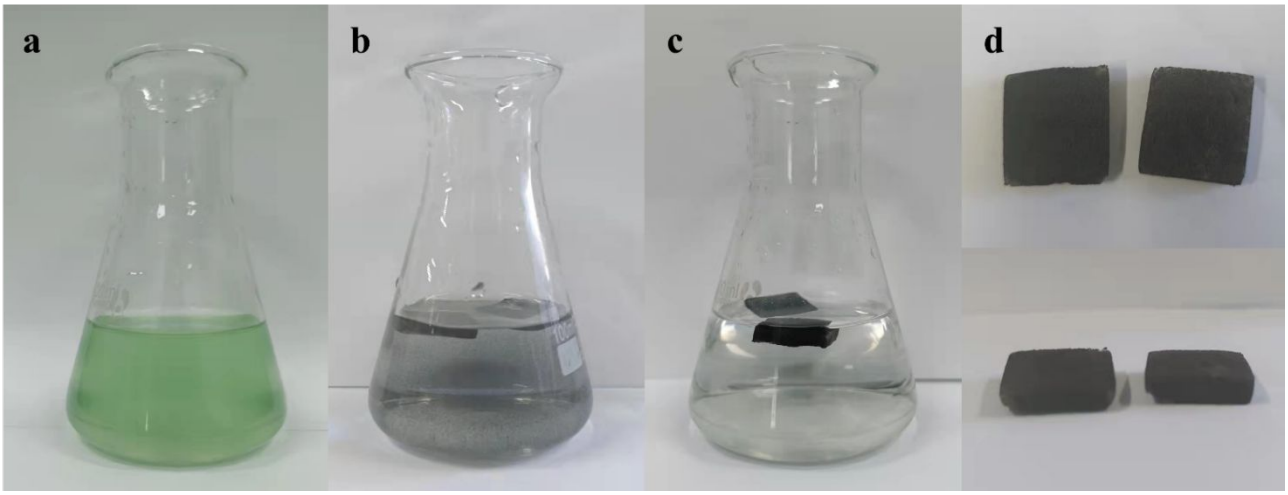

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214 **Fig. S11.** Photographs of the algae solution (a), treated by sponge@SBC_2-300 (b), sponge@SBC_1-
215 300 (c) and sponge@SBC_1-300 after four times reuse (d).

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