Original Article

Ultra-light and compressible 3D BiOCl/ RGO aerogel with enriched synergistic effect of adsorption and photocatalytic degradation of oxytetracycline

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\textbf{A B S T R A C T}

An ultra-light and compressible three-dimensional bismuth oxychloride/reduced graphene oxide (BiOCl/RGO) aerogel is fabricated via a facile hydrothermal method and characterized by various techniques. Owing to the improved visible-light response, lower internal resistance and enhanced electron transfer ability, the BiOCl/RGO aerogel (BGA) displays outstanding synergistic effect of adsorption and photocatalytic degradation. This not only reduces the diffusion distance between pollutants and photocatalysts but also inhibits the recombination of electrons and holes, thereby augmenting the photocatalytic activity. The optimized 40% BGA harvests the highest removal rate of 93.3\% for 20 mg L\textsuperscript{-1} oxytetracycline (OTC), which is ca. 1.43 folds higher than that of the pure BiOCl. Holes has been proved to play a dominate role in the OTC degradation. Meanwhile, the antibacterial activity test shows that the biotoxicity of OTC toward Escherichia coli DH5a is largely eliminated after 40\% BGA treatment. In addition, the 40\% BGA presents superior stability and recyclability after 4 cycles. It is anticipated that the BGA has great potential in actual wastewater treatment.

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1. Introduction

As a broad-spectrum antibiotic, Oxytetracycline (OTC) is widely used in human therapy, animal husbandry and aquaculture fields \cite{1}. However, OTC is poorly metabolized by human or animals on account of the long half-life and stable naphthacene ring structure \cite{2,3}, which transfers into the environment in the form of unmodified parent compound or metabolites \cite{4}, and becomes a new environmental pollutant \cite{5}. Previous researches had reported the existence of OTC in soil, water, meat, milk and eggs with concentrations ranging from ppb to ppm \cite{6,7}. What’s more, the traditional treatment such as biodegradation \cite{8,9}, adsorption \cite{10–12}, photolysis...
Fenton oxidation [14] could not remove OTC effectively. Hence, appropriate techniques are needed for elimination of OTC.

Photocatalysis is regarded as a promising technology and extensively used for refractory wastewater purification due to its high degradation and mineralization efficiency [15–18]. As an efficient semiconductor photocatalyst, bismuth oxychloride (BiOCl) has evoked intensively attention due to its outstanding photoluminescence properties, high chemical stability and low toxicity [19]. Accordingly, BiOCl had been successfully used in environmental remediation and power source [20], Nevertheless, two fatal flaws, wide band gap energy ($E_g = 3.4$ eV) and high recombination rate of electron and holes, still limited the practical application of BiOCl [21]. By now, various strategies had been adopted to overcome those defects, such as doping [22], surface modification [23], incorporation [24,25] and morphology control [26,27]. Among all the methods, combining photocatalyst with the graphene to fabricate three dimensional structure aerogel has become a research hotspot in recent years due to the remarkable electrical conductivity, large specific surface area and unique mechanical properties of graphene aerogel [28–32], which not only enhanced the electron transfer and electron-hole separation, but also promoted the visible light adsorption and reusability [33]. These advantages are very beneficial to improve the photocatalytic performance of BiOCl. A few works had reported the application of graphene aerogel in wastewater treatment so far, such as methyl-orange, bisphenol A [34], rhodamine B [35], carbamazepine [36], methylene blue [37]. However, the combination of BiOCl with graphene to fabricate 3D aerogel for the treatment of OTC wastewater has been rare reported.

Herein, a novel 3D BiOCl/RGO aerogel (BGA) was successfully fabricated via a simple hydrothermal method. The synthesized samples were examined by a wide suite of characterization techniques. The photocatalytic activity of BGA composites with different ratios was detected by the degradation of oxytetracycline (OTC), rhodamine B (RhB), chloramphenicol (CAP) and sulfanamethoxine sodium (SMM), where the 40% BGA exhibited the advanced synergistic effect of pollutant adsorption and photocatalytic degradation. The stability and recyclability of BGA was also verified by batch experiments. The outstanding activity has great relation with the combination of BiOCl and RGO, which supplied plenty of channels for pollution adsorption and electron transfer, and promoted the separation of electrons and holes. More importantly, the antibacterial activity of OTC towards Escherichia coli DH5a has been largely eliminated after the BGA aerogel treatment. In addition, the BGA aerogel solved the problem of reusability, indicating its potential application in long-term utilization.

2. Experimental

2.1. Fabrication of BiOCl, GA and BGA

GO was prepared according to our previous report [38]. The BGA with different BiOCl concentrations were fabricated by a chemical reduction self-assembly method. Fig. 1 showed the preparation procedure of BGA. Typically, a specific amount of Bi(NO$_3$)$_3$·$5H_2O$ and KCl were dissolved in 20 mL of distilled water and stirred continuously for 30 min, then 30 mL of GO suspension (3 mg mL$^{-1}$) and 0.6 mL of hydrazine hydrate were added into the solution and stirred for another 30 min, the homogeneous mixture was quickly poured into a 100 mL of polytetrafluoroethylene reactor, and heated at 180 °C for 6 h under autogenous pressure. The as-formed hydrogel was washed three times with 1% alcohol/water solution, and then freeze at –20 °C for 24 h and vacuum freeze-dried for 48 h to obtain the ultra-light and compressible BGA (Fig. S1). The as synthesized composites with 20, 40, 60 wt% BiOCl concentrations were labeled as 20% BGA, 40% BGA and 60% BGA, respectively.

The BiOCl and graphene aerogel (GA) was synthesized by the same procedure without adding GO or Bi(NO$_3$)$_3$·$5H_2O$ and KCl.

2.2. Photocatalytic activity test

The photocatalytic activity of different BGA composites towards OTC (20 mg L$^{-1}$) was investigated according to our
previous method. Briefly, the 3D BGA was directly put into 100 mL OTC wastewater, it took 9 h for BGA to get their adsorption equilibrium, afterwards, the 300 W xenon lamp was turned on and 3 mL of solution was sampled every 30 min for further analysis. The concentration of OTC was detected by High performance liquid chromatography (HPLC Waters e2695) equipped with a 2489 UV/vis detector based on the previous reported method [39].

The cyclic stability of the 40% BGA was evaluated by refreshing OTC solutions (20 mg L⁻¹) under the same conditions. The effect of BGA on Rhodamine B (RhB, 20 mg L⁻¹), Chloramphenicol (CAP 10 mg L⁻¹) and Sulfamonomethoxine Sodium (SMM 10 mg L⁻¹) were also detected by the same method.

2.3. Antibacterial activity measurement

The antibacterial activity of OTC and its photocatalytic products toward Escherichia coli DH5a was evaluated. Three test groups were conducted: 1) the control group (5 mL LB medium and 5 mL aseptic water), 2) the photocatalytic effluent group (5 mL LB medium and 5 mL photocatalytic effluent), 3) OTC group (5 mL LB medium, 5 mL aseptic water and 20 mg L⁻¹ OTC). Two parallel experiments were performed in each group. Next, 1 mL DH5a strains in the exponential phase were inoculated into the above groups and incubated at 37 °C for 24 h. The optical density value of bacterial culture at 600 nm was measured by using UV–vis spectrophotometry (UV-1700, SHI-MADU).

2.4. Characterization

The detailed methods were supplied in supplementary information.

3. Results and discussion

3.1. Structure and composition of BGA

Fig. 2a showed the XRD patterns of GA, pure BiOCl and different BGA composites. The distinctive peaks at 11.9°, 25.9°, 32.5°, 33.4°, 36.5°, 40.9°, 46.6°, 49.7°, 54.1°, and 58.6° of BGA were perfectly consistent with (001), (101), (110), (102), (003), (112), (200), (113), (211), and (221) planes of the tetragonal phase of BiOCl (ICPDS 06-0249). In comparison with pure BiOCl, BGA composites exhibited wide and low peaks, indicative of smaller size and lower crystallinity [40]. With the increase of BiOCl, the peaks of the (102) plane shifts slightly to the higher 2θ value, indicating a decrease in the interplanar spacing according to the Bragg equation. Due to the higher peak intensity of BiOCl, the diffraction peaks of GA were not obvious in different BGA composites. What’s more, the peak intensity of BGA was directly proportional to the content of BiOCl, which indicated that the RGO had no effect on the growth orientation of BiOCl but did restrain the growth of BiOCl crystal in some degree [29].

Raman spectra were used to evaluate the chemical structure of BGA. As shown in Fig. 2b, GO exhibited two characteristic peaks at 1344 cm⁻¹ and 1590 cm⁻¹, which belonged to the D and G bands of graphene. The D and G bands reflect the structural defects and the crystallinity of graphene, respectively [41]. However, in the BGA composites, the D and G bands moved towards 1340 cm⁻¹ and 1584 cm⁻¹ on account of the chemical interaction between RGO and BiOCl. Moreover, as shown in Table S1, the ID/IG ratio of GO was 0.93, while the value ascended to 1.02, 1.17, 1.37 and 1.15 for GA, 20% BGA, 40% BGA and 60% BGA, respectively, which suggested more defects and disorders, as well as the remarkable disruption of symmetrical lattice were emerged for BGA composites.

X-ray photoelectron spectroscopy (XPS) was used to investigate the element and valence of BiOCl and 40% BGA composite. In the full survey scan spectrum (Fig. 3a), Bi 4f, O 1s, Cl 2p and Cl 2s were all observed in BiOCl and 40% BGA, and the C 1s existed in 40% BGA, which indicated that RGO had been successfully introduced into BGA. Bi 4f spectra of BiOCl and 40% BGA were shown in Fig. 3b, two characteristic peaks at 165.0 eV and 159.7 eV were ascribed to Bi 4f 5/2 and Bi 4f 7/2, indicated the existence of Bi³⁺ in the 40% BGA [42]. The peaks with a separation of 5.3 eV indicated the presence of Bi 3p in a normal state in BiOCl [43]. The high-resolution Cl 2p spectra were shown in Fig. 3c, two peaks with binding energy of 198.4 eV and 199.9 eV were ascribed to Cl 2p 1/2 and Cl 2p 3/2, indicating the existence of Cl⁻ in BGA. Fig. 3d showed the O 1s region of BiOCl and 40% BGA. Compared with BiOCl, more than one chemical state was observed from the O 1s spectrum in 40% BGA. The peaks at 530.6 eV and 532.2 eV were classed
as Bi–O and C–O, respectively, confirming the formation of new chemical bond in 40% BGA. Fig. 3e displayed the C 1s XPS spectra of 40% BGA, three notable peaks were found at 284.7 eV, 285.6 eV and 287.9 eV, which was ascribed to C–C, C–O and O–C=O bonds. Moreover, a weak peak at 279.5 eV appeared, which indicated the formation of Bi–C in 40% BGA [44], and provided direct evidence for the formation of chemical bonds between BiOCl and RGO.

Fourier transform infrared (FTIR) was employed to analyze the interaction between RGO and BiOCl. As shown in Fig. 3f, the precursors (GO and BiOCl) and BGA composites owned similar absorption bands at 3420 cm$^{-1}$ and 1628 cm$^{-1}$, which corresponded to the stretching vibration of O–H or water and C=O. The FTIR spectra of GO at 1724 cm$^{-1}$ was assigned to the stretching vibration of C=O which could either be the carboxyl group on the edge of GO or the conjugated carbonyl group, the peaks at 1226 cm$^{-1}$ and 1051 cm$^{-1}$ corresponded to C–O and C–O–C band. However, the distinctive peaks of GO at 1724 cm$^{-1}$, 1226 cm$^{-1}$ and 1051 cm$^{-1}$ were absent in the FTIR spectrum of GA and different BGA composites, which indicated the successful reduction of GO in hydrothermal process. The absorption peak at 523 cm$^{-1}$ belonged to Bi–O band, which could be observed both in BiOCl and BGA composites, the peak intensity was gradually enhanced with the raise of BiOCl contents, but the positions shifted slightly to higher frequency region, which indicated there had an interaction between RGO and BiOCl. In addition, the FTIR spectra of 60% BGA at 1116 cm$^{-1}$ was assigned to Bi–C band, which supplied direct evidence for the chemical interaction between RGO and BiOCl [45]. However, there were no obvious Bi–C peaks in 20% BGA or 40% BGA, which may be related to the less doping of BiOCl.

Combining the cross-check results of Raman, FTIR, and XPS, the fabrication of BGA was confirmed, and the combination of BiOCl and RGO could facilitate the electron transfer and enhanced the photocatalytic efficiency.
The morphology and microstructure of BGA were observed by SEM and TEM. As can be seen, BiOCl (Fig. 4a) showed typical flake structure, with the size of 1–5 μm in diameter and 50 nm in thickness, which was consistent with our previous result [19]. GA exhibited a multiporous network structure with super slim graphene sheets cross-linked together (Fig. 4b); this phenomenon could be further proved by TEM (shown in Fig. 5a). Fig. 4c–f displayed SEM images of 20% BGA, 40% BGA and 60% BGA. The BiOCl grew uniformly into the 3D network structure of GA (Fig. 4c), with the rise of BiOCl content, more and more BiOCl sheet was observed homogeneously on the surface and inside of graphene, which was consistent with the energy dispersive spectra (EDS) results in Fig. S2. The Bi, Cl, O and C elements were all evenly distributed in the 3D BGA. The unique structure endowed BGA with superior flexibility and mechanical property.

The detailed internal structure of 40% BGA was further surveyed by TEM (Fig. 5a–d), as shown, the BiOCl was typical flake structure and dispersed homogeneously in the wrinkly RGO sheet. Compared with pure BiOCl, the encapsulation of BiOCl with graphene facilitated electron transfer. The HRTEM result of BiOCl showed the lattice spacing of 0.27 nm ascribed to the (102) plane [26], which was consistent with XRD result. The Selective Area Electron Diffraction (SAED) pattern (inserted in Fig. 5d) had both continuous circles and bright spots, which verified the polycrystalline nature of the BGA, the result confirmed the effective formation of BGA [46].

The optical absorption properties of GA, BiOCl and BGA were analyzed by UV-vis diffuse reflectance spectroscopy (DRS). Compared with the narrow absorption ability of BiOCl in ultraviolet region with the light edge at 385 nm, BGA exhibited wider absorption ability in visible and ultraviolet regions (Fig. 6a), and the absorption ability was coinciding with the RGO contents, which implied that RGO played a dominant role in sunlight harvesting and electron capture under irradiation [47]. In Fig. 6b, the band gap energy of BiOCl, 20% BGA, 40% BGA and 60% BGA were 3.08 eV, 2.35 eV, 2.35 eV and 2.7 eV, respectively. The prepared BGA composite had lower band gap energy than pure BiOCl, indicated higher optical absorption ability in visible light region. This result could be attributed to the chemical interaction of Bi–C band between RGO and BiOCl, which accelerated the electron transfer [48], and enhanced photocatalytic performance consequently [41].

The BET specific surface area of the prepared 40% BGA, GA and BiOCl were analyzed by the nitrogen adsorption–desorption method. A typical IV adsorption isotherm with clear H3 hysteresis loop was found at a relative pressure between 0.45 and 1.0 (Fig. 6c), which implied the mesoporous structure of the aerogels. The GA and BiOCl isotherm exhibited relatively low nitrogen uptake compared to 40% BGA and thus the BET surface areas were 110.49 m²g⁻¹, 2.909 m²g⁻¹ versus 214.98 m²g⁻¹, respectively. According to Fig. 6d, the pores diameter of 40% BGA (3–5 nm) was smaller than GA (4–7 nm). The smaller pore diameter may arise from the interaction between BiOCl and RGO, which was coincide with the SEM and TEM results. What’s more, the 40% BGA showed narrow pore size distribution from micro to macro scale, which supplied more sites for pollution adsorption and become an ideal adsorption material [30]. The porous structure and high specific surface area are favorable for light harvest, charge migration and mass transfer, which are ultimately beneficial to enhancing the photocatalytic performance [49, 50].

3.2 Electrochemical properties

The electrochemical properties of GA and BGA composites were analyzed by CV (Fig. 7a). Compared with GA, the electrochemical surface activity of BGA composites was notably
improved. The 40% BGA possessed the largest longitudinal extension and spindle curve area to indicate the highest capacitance and response current, which may attribute to the additional faradaic capacitive effect related to BiOCl [51].

EIS was further used to gain insight into the properties of conductivity and charge carrier transfer in GA and BGA composites. Fig. 7b and c showed the corresponding EIS Nyquist plots of prepared samples. The Nyquist plots consisted of semicircles in the high frequency and straight lines in the low frequency regions. As shown, the $R_S$ and $R_{CT}$ of 40% BGA were 22.71 Ω and 4.96 Ω, substantially lower than those of GA (41.80 Ω and 113.24 Ω), 20% BGA (39.83 Ω and 53.23 Ω) and 60% BGA (36.36 Ω and 55.98 Ω), indicating the lowest charge transfer resistance and the highest conductivity. The decreased Warburg resistance value at low frequency could be attributed to the high surface area of the 40% BGA, which promoted rapid electrolyte ion transport to the active sites and surfaces of the 40% BGA.

The transient photocurrent responses of different BGA composites were exhibited in Fig. 7d. All synthesized samples presented excellent photocurrent intensity and kept stabilities during the cyclic experiments. 40% BGA showed dramatically increased photocurrent intensity (1.3 × 10⁻⁶ A), implying enhanced charge transfer and separation efficiency of photo-induced carries.

3.3. Photocatalytic activity

The adsorption capabilities of GA, BiOCl and BGA composites toward OTC (20 mg L⁻¹) were illustrated in Fig. 8a. Nine hours were needed before the BGA getting their adsorption equilibrium. The pure BiOCl could adsorb only 6.8% of OTC, while GA absorbed 75.6% of OTC within 9 h. The adsorption efficiency of 20% BGA, 40% BGA and 60% BGA samples reached to 61%, 63% and 56%, respectively, which was about 8.97, 9.26 and 8.23 times of the pure BiOCl. The results confirmed that the combination of BiOCl and RGO greatly improved the adsorption and enrichment ability of OTC and facilitated the photocatalytic degradation [33].

After getting their adsorption equilibrium, the photocatalytic activities of the as-synthesized composites was assessed by degradation of 20 mg L⁻¹ OTC. As shown in Fig. 8b, the removal efficiency of pure BiOCl attained 65.1% in 12 h, while the BGA composites remarkably heightened the removal rate. The 40% BGA displayed the highest degradation efficiency of 93.3%, which was about 1.43 times of the pure BiOCl. The HPLC spectrums of OTC degraded by 40% BGA was shown in Fig. 8a. The characteristic peak of OTC was located at 2.96 min, and the peak areas decreased significantly with the extension of illumination time. This result indicated that the addition of GA not only improved the adsorption capacity but also
Fig. 6 – (a) UV-Vis diffusion reflectance spectra and (b) the relationship between $(A\nu)^{1/2}$ and the photon energy $(\nu)$ of as-prepared samples. (c) Nitrogen adsorption-desorption isotherms and (d) Barret-Joyner-Halenda (BJH) desorption pore size distribution profiles of prepared samples (Insets are the corresponding enlarged drawing of the pore size ranged from 0 to 20 nm).

Fig. 7 – (a) CV; (b,c) EIS and (d) transient photocurrent response of BGA.
enhanced the photocatalytic performance of BGA composites, realizing the synergistic effect of adsorption-enrichment and photocatalytic degradation. The stability of 40% BGA was further verified by batch experiments. As shown in Fig. 8c, the synergistic efficiency of adsorption and photocatalysis reduced slightly after 4 cycles, indicating the reusability of 40% BGA.

The excellent synergistic effect of adsorption and photocatalysis of 40% BGA was further investigated to degrade three different dye or antibiotic wastewater, including Rhodamine B (Rhb, 20 mg·L⁻¹), chloramphenicol (CAP, 10 mg·L⁻¹) and Sulfamonomethoxine Sodium (SMM, 10 mg·L⁻¹). As illustrated in Fig. S3, the degradation rate was commonly found to be in the order of Rhb (92.9%) > SMM (87.8%) > CAP (79.1%).

To demonstrate the advanced photocatalytic properties of our composite material, the degradation efficiency of similar 3D graphene aerogel in other literatures was compared in Table S2 (Supplementary Information), and the novel 3D BGA exhibited wide application prospects in actual wastewater treatment.

It is meaningful to clarify the main active species in photocatalytic process. The trapping experiment was conducted to discover the main active species in this work. Methyl alcohol (MA), ammonium oxalate (AO) and isopropanol (IPA) were used to detect the active species such as •O₂⁻, h⁺ and •OH, respectively [52]. As shown in Fig. 8d, the photodegradation efficiency was suppressed slightly by the use of MA and IPA, implying that •O₂⁻ and •OH played weak roles in this process. In contrast, the photocatalytic performance of 40% BGA was significantly inhibited with the addition of AO, suggesting h⁺
was the major active species, and the degradation of OTC was dominated by the direct hole oxidation.

3.4. Antibacterial activity of OTC degradation products

Although OTC was effectively adsorbed and degraded by the BGA aerogel, its degradation products and residual trace oxytetracycline may possess potential environmental risk. Therefore, the antibacterial activity of photocatalytic degraded water to model microorganism E. coli DH5a was investigated. As illustrated in Fig. 9b, OTC (20 mg L\(^{-1}\)) significantly inhibited growth of E. coli DH5a compared to the control group. However, It is gratifying to note that the antibacterial activity of photocatalytic degraded effluent towards E. coli DH5a decreased dramatically, the antibacterial activity was found to be in the order of BiOCl > 60% BGA > 20% BGA > 40% BGA, which was consistent with the photocatalytic performance. It appeared that the antibacterial activity of OTC had been largely eliminated after the synergistic adsorption-enrichment and photocatalysis treatment, which exhibited remarkable environmental friendliness.

3.5. Mechanism of photocatalytic activity enhancement

Based on all above discussion, the proposed mechanism for BGA composite under visible light irradiation was illustrated in Fig. 10. Firstly, the BiOCl and GA were successfully combined via facile hydrothermal method. Based on the unique mechanical properties such as large specific surface area, porous structure and low density, the 3D GA supplied plenty of channels for pollution absorption and electron transfer, and worked as adsorbent to adsorb OTC to the surface of BGA, which not only reduced the diffusion distance between OTC and photocatalysts but also improved the photocatalytic degradation rate. In addition, BGA exhibited wider absorption ability in sunlight harvesting. The central catalytic component BiOCl was inspired and generated electrons(e\(^{-}\)) and holes(h\(^{+}\)) under visible light irradiation [53]. The electrons quickly flowed into the GA sheet and avoided the recombination of electrons and holes on account of the excellent conductivity of RGO (Eq. (2)) [54]. The electrons could be captured by O\(_2\) to form superoxide radicals (O\(_2\)•\(^{-}\)) for further reaction (Eq. (3)). The holes on the VB possessed higher oxidizing ability and was proved to be the major active species in this degrading process, which partly reacted with water molecules to form •OH radical (Eq. (4)) [49,55]. Then both the holes and •OH radicals might oxidize the OTC absorbed on the surface of BGA into H\(_2\)O and CO\(_2\) directly (Eq. (5)) [56]. In this regard, the 3D BGA composite play a crucial synergetic role in pollutant adsorption-enrichment and photocatalytic degradation. In addition to it, the BGA composite possessed excellent recyclability and reusability, indicating its potential application in long-term utilization.

\[
\text{BiOCl} + h^+ \rightarrow h^+_{\text{VB}} + e^-_{\text{CB}} \quad (1)
\]
\[
\text{BiOCl}(h^+_{\text{VB}} + e^-_{\text{CB}}) \rightarrow \text{recombinationsupressed} \quad (2)
\]
\[
e^-_{\text{CB}} + O_2 \rightarrow \text{OH}_2^- \quad (3)
\]
\[
h^+_{\text{VB}} + H_2O \rightarrow \text{•OH} \quad (4)
\]
\[
\text{OTC} + h^+_{\text{VB}} / \text{•OH}/\text{O}_2^- \rightarrow \text{degradedproducts} \quad (5)
\]

4. Conclusion

In conclusion, 3D BiOCl/RGO aerogel was fabricated via a simple hydrothermal method. The BGA composite especially 40% BGA exhibited the highest synergetic effect of pollutants adsorption and photocatalytic degradation towards OTC. Firstly, the satisfactory adsorption ability of 40% BGA composite has great relation with porous structure, high specific surface area and the abundance of adsorption sites both resulting from RGO. Secondly, the enriched photocatalytic performance of 40% BGA would be ascribed to the enhanced visible-light response and efficient separation of electron and hole. In addition, the 40% BGA composites was much easier to separate than powder photocatalyst and kept superior reusability up to at least four cycles. What’s more, the antibacterial activity of OTC had been largely eliminated after the 40% BGA treatment. Hence, the novel 3D BGA possesses wide application prospects in actual wastewater treatment.

Conflicts of interest

The authors declare no conflicts of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2019.08.002.

The additional tables and graphics are shown in supplementary information.

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