Organics removal from shale gas wastewater by pre-oxidation combined with biologically active filtration

Organics Removal from Shale Gas Wastewater by Pre-oxidation Combined with Biologically Active Filtration

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ABSTRACT: Biological treatment technology is increasingly explored in shale gas wastewater (SGW) treatment owing to its cost effectiveness and requires efforts to improve its efficacy. In this work, ozone and ferrate(VI) oxidation pre-treatment were evaluated to enhance the performance of the subsequent biologically active filtration (BAF) in the removal of organic contaminants. The oxidation improve the SGW biodegradability and organic composition in the presence of high salinity (~20 g/L). Due to the degradation activity of microorganisms, the organics removal efficiency in the BAF system was observed to gradually improve and then reaching stability in long-term continuous-mode operation. The removal rate of dissolved organic carbon (DOC) of the ozone-BAF (O_3-BAF) and the ferrate(VI)-BAF (Fe(VI)-BAF) systems was 83.2% and 82.8%, respectively, higher than that of BAF alone (80.9%). This increase was attributed to higher activity and content of microorganisms in O_3-BAF and Fe(VI)-BAF systems. The presence of uncultured bacteria of genus *Rehaibacterium* with high abundance of 7.2-21.0% was significantly correlated with DOC removal. Also, uncultured bacteria of genus *Methyloversatilis* (2.24-22.31%) were significantly correlated with fluorescent organics removal. Results suggest that these two bacterial species have strong ability to degrade organics. More research is needed to understand whether the species were new and their specific function. This study provides valuable suggestions for extracting safe water from SGW with an efficient treatment train.

KEYWORDS: Shale gas wastewater; Biologically active filtration; Ozone; Ferrate

(VI); Microbial community

1. INTRODUCTION

With the fast development of the shale gas industry, associated shale gas wastewater (SGW) streams caused by hydraulic fracturing increasingly threaten water ecosystem and human health. In 2016, 6 million tons and 131 million tons of SGW were produced in the Sichuan Basin of China and in the United States, respectively.[1, 2] SGW contains high concentrations of salt, heavy metals, microorganisms, and refractory organics released from the shale formation or as chemical residue of compounds added to enhance hydraulic fracturing.[3, 4] Effectively managing SGW produced from shale gas extraction has become an urgent environmental and engineering issue.

Membrane technologies are usually considered as the most effective tertiary treatment for SGW, but they require significant energy and face serious fouling challenges.[4, 5] A limited number of studies has investigated hybrid systems that apply biological treatment to reduce membrane fouling, and found that biological treatment processes can efficiently control fouling in ultrafiltration and nanofiltration.[6] Furthermore, cost-effective biological treatment technology is regarded as a high-potential treatment technology for SGW, because the large amount of organics present in SGW is mostly biodegradable.[7, 8] In the past few years, activated sludge,[9] sequencing batch reactor,[10, 11] membrane bioreactor,[12-14] microbial mats,[15, 16] moving bed biofilm reactor,[17] biologically active filtration (BAF)[6, 18-21] and bioelectrochemical system[22-26] have been evaluated for SGW treatment.

BAF exploits the biofilm attached to filter media to degrade and adsorb organics from the wastewater.[3] Limited research has shown that BAF can remove organics (72-90% COD and 72-92% DOC) from six different SGW generated in basins of USA with varying salinity (10.5-31.2 g/L TDS) and organics content (85-6360 mg/L COD and 36-2170 mg/L DOC).[6, 19] The BAF efficiency under different operating conditions (aeration rate, temperature, empty bed contact time, and type of activated carbon) was systematically studied. [19-21] However, analysis of the microbial community composition and function in BAF is still scarce. Concurrently, the feasibility of BAF in treating SGW needs further evaluation and the mechanism of pollutant migration and transformation in BAF needs more detailed study.

At present, the combination of ozonation and BAF (O_3-BAF) has been widely used in water treatment, because ozone can degrade refractory pollutants and improve the performance of the subsequent biological process.[27, 28] Also, biological processes can effectively remove ozonation by-products. This system has never been tested for the treatment of shale gas wastewater and its feasibility is still unclear for this application. Ferrate(VI) or Fe(VI) has been also successfully used in water and wastewater treatment as a new type of green oxidant.[29] The redox potential of Fe(VI) is +0.7-+2.2 V.[29] The redox potential of ozone is slightly higher than that of Fe(VI) in solutions of basic pH.[29] SGW typically contains high concentrations of Cl^- and Br^-, which seriously weaken the oxidation ability and the safety of ozonation.[30] On the contrary, Fe(VI) has no known reactivity with halogens,[29] indicating that Fe(VI) might have a certain advantage in oxidizing shale gas wastewater. Similar to ozone, Fe(VI) can degrade refractory pollutants and improve their biodegradability. Nevertheless, there are only a few studies on the combination of Fe(VI) and biological processes.[31-33] Ma et al.[32] found that Fe(VI) (1 mg/L) pretreatment significantly increased the removal rate of COD_{Mn}, UV_{254}, NH_4 by BAF in treating river water. Besides, a simple comparison of Fe(VI)-BAF and O_3-BAF showed that the COD_{Mn} removal rate of Fe(VI)-BAF was slightly lower than that of O_3-BAF, and the NH_4^+ removal rate of Fe(VI)-BAF was much higher than that of O_3-BAF. In general, Fe(VI)-BAF has shown interesting potential, but a more systematic and comprehensive assessment of Fe(VI)-BAF is needed, especially in the treatment of SGW.

Therefore, the objectives of this study are to (i) evaluate the effect of Fe(VI) and O_3 pre-oxidation on organics removal; (ii) assess the effect of Fe(VI) and O_3 pre-oxidation on the performance of BAF systems; (iii) analyze the composition and evolution of microbial community in such hybrid systems, and explore the dominant and functional microorganisms; (iv) comprehensively analyze the feasibility of Fe(VI)-BAF in treating SGW compared with that of O_3-BAF.

2. EXPERIMENTAL SECTION

2.1. Water Samples and Water Quality Analysis. SGW samples were collected from the Changning shale gas play (Sichuan Basin, China). Due to the high turbidity (>

1000 NTU) of SGW, SGW was pre-treated with coagulation-sedimentation before the subsequent processing. Therefore, the raw water in the article referred to the SGW after coagulation. Aluminum sulfate was chosen as flocculant and the dose was 600 mg/L according to our previous work.[34] The coagulation step was divided into three stages: rapid mixing at 200 rpm for 1 minute, then slow mixing at 40 rpm for 20 min, and settling for 30 min.[34] The water quality parameters of SGW were summarized in Table S2 of the Supporting Information (SI). The methods for the quantification of dissolved organic carbon (DOC), turbidity, pH, chemical oxygen demands (COD), biochemical oxygen demand (BOD_5), UV absorbance at 254 nm (UV_{254}), total dissolved solid (TDS), and fluorescence excitation-emission matrix (EEM) can be found in our previous articles[30, 35] and in Text S1 of the SI.

2.2. Experimental Setups and Procedures of Pre-oxidation. Ferrate (VI) treatment was one of pre-oxidation method. The dosage of Fe(VI) was 40 mg/L. The recrystallization method was used in this study to increase the purity of potassium ferrate (K_2FeO_4) to >90%.[36-38] The Fe(VI) pre-oxidation experiment consisted of three stages: rapid mixing at 200 rpm for 2 min, then slow mixing at 40 rpm for 20 min, and settling for 30 min. The supernatant was used as feed water for the subsequent BAF process.

Ozonation was another pre-oxidation method. The dosage of ozone was 80 mg/L, according to our previous work.[30] Treatment of raw water by pre-ozonation was carried out in batch experiment. In each batch experiment, 1 L raw water was added into a reactor and oxidized by ozone produced form ozone generator (Beijing Tonglin Co., Ltd., China) at desired flow rate. Before the subsequent BAF treatment, the residual ozone in water was quenched by water bath heating with 30 min at 50 ℃.

2.3. Experimental Setup and Protocol of BAF Tests. In the BAF column acclimation process, microorganisms in shale gas wastewater were gradually enriched in activated carbon carrier through sequential batch influent and gradient dilution of raw water, thus forming biofilm on activated carbon. Operation parameters and steps of BAF column acclimation can be found in Table S1 (SI). A carbon source (sodium acetate anhydrous) was added to adjust the C:N ratio to 3.5:1 of the raw water, which was beneficial to the growth of microorganisms. BAF systems were operated in batch-mode at influent flow rate of 0.14 L/h and aerated at a rate of 50 mL/min. The volume of circulation feed tank was 0.55 L, and 0.5 L raw water was changed every two days. The inner diameter and height of the BAF reactor were 1.4 cm and 80 cm, respectively. The filling height of activated carbon (CPG LH 12×40, Calgon Carbon Co., Ltd., USA) was 45 cm, and the filling mass was about 30 g. The corresponding data and analysis during the acclimation stage are summarized in Figure S2 and Figure S3 (SI).

In the continuous-mode BAF systems, the raw water pre-oxidized by ozone or Fe(VI) was used as BAF influent to investigate the treatment effect of combined processes of ozone-BAF (O_3-BAF) and Fe(VI)-BAF. The raw water was also used as BAF influent for comparison. Three BAF systems were thus operated in continuous-mode at influent flow rate of 0.014 L/h and aerated at a rate of 10 mL/min. The backwashing frequency, backwashing flow rate, and backwashing time were 20 days, 0.14 L/h, and 10 min, respectively.

2.4. Analysis of Biofilm on GAC. At the end of BAF operation, a certain amount of granular activated carbon (GAC) samples were collected from each BAF column to evaluate the activity, relative concentration and growth of the biofilm on GAC through measurement of the oxygen uptake rate (OUR), extracellular polymeric substances (EPS), GAC static adsorption, and using scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS) analysis. GAC samples were collected from ~15 cm bed-depth (from the top).

A mass equivalent to 0.3 g GAC was placed into a 150 mL conical flask on a magnetic stirrer. The conical flask was then filled with raw water (about 8 mg/L dissolved oxygen). A rubber plug with a dissolved oxygen probe was installed on the conical flask to ensure that there were no bubbles. Then, the dissolved oxygen was measured as a function of time under stirring (400 rpm) at 20 °C. The final result was expressed in mg of dissolved oxygen consumed per g of activated carbon per hour ($mg_{O2}/(g_{GAC}\cdot h)$).

Extraction and detection of EPS, which was defined as the sum of polysaccharides and proteins, were conducted using the standard methods, while the specific detection of polysaccharides and proteins was undertaken using the anthrone/H_2SO_4 and Bradford methods, respectively.

Static adsorption experiments were performed on new GAC, used GAC, and used GAC after sterilization to distinguish the adsorption and microbial degradation in each BAF systems. A high pressure steam sterilizer was used to sterilize the used GAC. The operating temperature was 125 ℃ and the sterilization time was 20 min. In the static adsorption experiment at 20 ℃, the dosage of GAC was 2 g/L, the stirring speed was 400 rpm and the running time was 72 h. Reaction mixtures were withdrawn at specific time intervals to measure the variation of DOC and UV_{254}.

GAC samples were analyzed using SEM (FE-SEM, Regulug-8230, Hitachi, Japan) and EDS (X-MAX Extreme, Oxford-Instruments, UK) to detect physical and chemical changes on the GAC surface and observe the morphology of biofilm. GAC was prepared for SEM imaging by fixation with 2% glutaraldehyde, dehydration in 20–100% ethanol, and drying in a freeze vacuum dryer. EDS was applied in tandem with SEM to map and evaluate the deposition of elemental content on the GAC surface throughout BAF treatment.

2.5. Microbial diversity analysis. Through the microbial diversity sequencing of the raw water, the GAC at the end of BAF column acclimation, and the GAC at different times of continuous-mode BAF systems, the temporal and spatial variation of the microbial community and the dominant functional microorganisms were analyzed. Details about microbial diversity sequencing and analysis are presented in Text S2 of the SI and in our previous study.[35, 39] Note that the same amount of GAC was filled into the reactor after sampling.

3. RESULTS AND DISCUSSION

3.1. Effect of Pre-oxidation on Water Quality. Pre-oxidation had a negligible effect on the DOC parameter, shown in Figure 1a. The DOC change upon Fe(VI) treatment was −2.1%, while that upon O_3 treatment was +4.1%, caused by the competing effect of organic matter mineralization and solubilization. More explicitly, pre-oxidation only partly mineralizes the organic content, which would translate into a decrease of DOC values. However, this reaction simultaneously increases the solubility of suspended organic matter and promotes the release of intracellular organic substances from sterilized bacteria, with the effect of increasing the DOC.[30] The effect of oxidation was instead directly associated with the reduction of other parameters related to organic composition. The UV_{254} removal rates by O_3 and Fe(VI) were 13% and 23%, respectively (Figure 1b). As shown in Figure 1c, O_3 and Fe(VI) removed part of the COD (9.2%-11.8%) and, most importantly, increased the concentration of BOD_5 (33.2%-22.7%), as well as the value of BOD_5/COD (47.2%-39.6%), suggesting that pre-oxidation significantly improved the biodegradability of SGW. The composition and relative content of fluorescent organic matters in SGW were obtained through fluorescence EEM spectra and FRI analysis method (Figure S4 and Figure 1d).[40] The soluble microbial by-product-like matters (region IV) and humic acid-like matters (region V) were the dominant fluorescent organic components in SGW. O_3 had excellent removal effect on all kids of fluorescent organic matters (74.5%), while Fe(VI) only slightly removed fluorescent organic matters (9.4%), mainly acting on soluble microbial by-product-like matters and humic acid-like matters. In summary, the mineralization of organic matters by O_3 or Fe(VI) was limited, while pre-oxidation mainly changed the properties of organic matters.

Some interesting phenomena were found in GAC static adsorption experiments of pre-oxidized SGW. In the first 24 h of adsorption, the adsorption rate of DOC in pre-oxidized SGW was practically the same of that measured in raw SGW, as shown in Figure 1f. The same trend was observed for UV_{254} before and after ozonation (Figure 1g). On the contrary, the adsorption rate and equilibrium adsorption capacity of GAC for UV_{254} in SGW treated by Fe(VI) was lower than that assessed in raw SGW. The value of UV_{254} mainly represents the content of low molecular weight aromatic compounds.[41, 42] This result might indicate that, as this fraction of organic matter was removed more efficiently by Fe(VI) than O_3 (Figure 1b), the affinity or the kinetics of adsorption for other fractions was higher upon oxidation with ferrate. In general, these tests suggested a complex effect of pre-oxidation on organic content and composition. Also, the data evidently indicate that pre-oxidation would not translate into better water quality if followed by simple GAC adsorption in the absence of microorganisms. However, the analysis of organic matter biodegradability upon oxidation suggests that the performance of BAF systems may be improved compared to a raw water not subjected to this pre-treatment step, and this effect is discussed below.

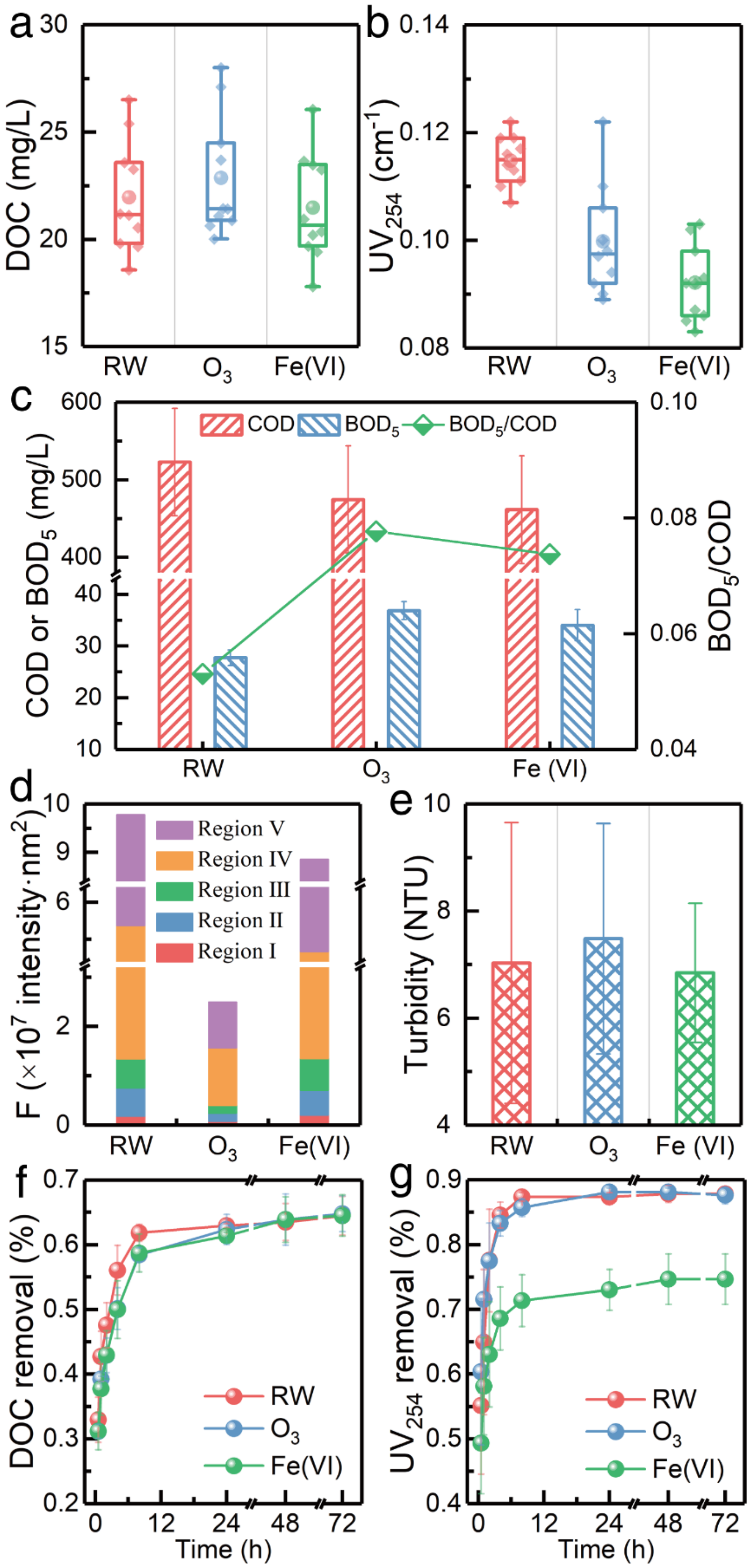

Figure 1. Effect of preoxidation on (a-e) water quality, (f) DOC adsorption on GAC, and (g) UV_{254} adsorption on GAC. The dosages of O_3 and Fe(VI) were 80 mg/L and

40 mg/L, respectively. The GAC dosage was 2 g/L.

3.2. Performance of BAF, O_3-BAF, and Fe(VI)-BAF. The variation of DOC and UV_{254} in three BAF systems effluent measured during 60 days of continuous operation is shown in Figure 2a and Figure 2b. In the first 18 days of continuous operation, the DOC removal rate of the three BAF systems was somewhat erratic with the water pre-treated by Fe(VI) oxidation showing the highest value. With the operation and related strengthening of microbial activity, the removal rate of DOC in all three systems increased and reached stability at values around 80%, specifically with rates that decreased in the order O_3-BAF > Fe(VI)-BAF > BAF. Similarly, the removal rate of UV_{254} by three BAF systems was more inconsistent during the initial stage of BAF experiments and reached stability toward the end. Generally, the UV_{254} removal rate of BAF was the highest, while that of Fe(VI)-BAF was the lowest, consistent with what reported in Figure 1g for static adsorption tests. However, the efficiency of UV_{254} removal by Fe (VI)-BAF was gradually improved during operation, which may be attributed to the continuous enrichment of microorganisms.

Overall, the BAF systems had high COD removal rates (90.7%-91.4%) (Figure 2c). In particular, the COD content in effluent from BAF, O_3-BAF, and Fe(VI)-BAF was 48.8, 42.0, and 39.5 mg/L, respectively. The turbidity (0.42-0.49 NTU) of the effluents was also low (Figure 2d). The composition and relative content of fluorescent organic compounds were measured in the effluents of the three BAF systems on the 20th day, 40th day, and 60th day of operation, and the results are shown in Figure 2e and Figure S4. BAF systems efficiently removed fluorescent organic compounds, and the removal rate increased gradually with the operation. The soluble microbial by-product-like matters (region IV) and humic acid-like matters (region V) were the dominant fluorescent organic components in the effluents.

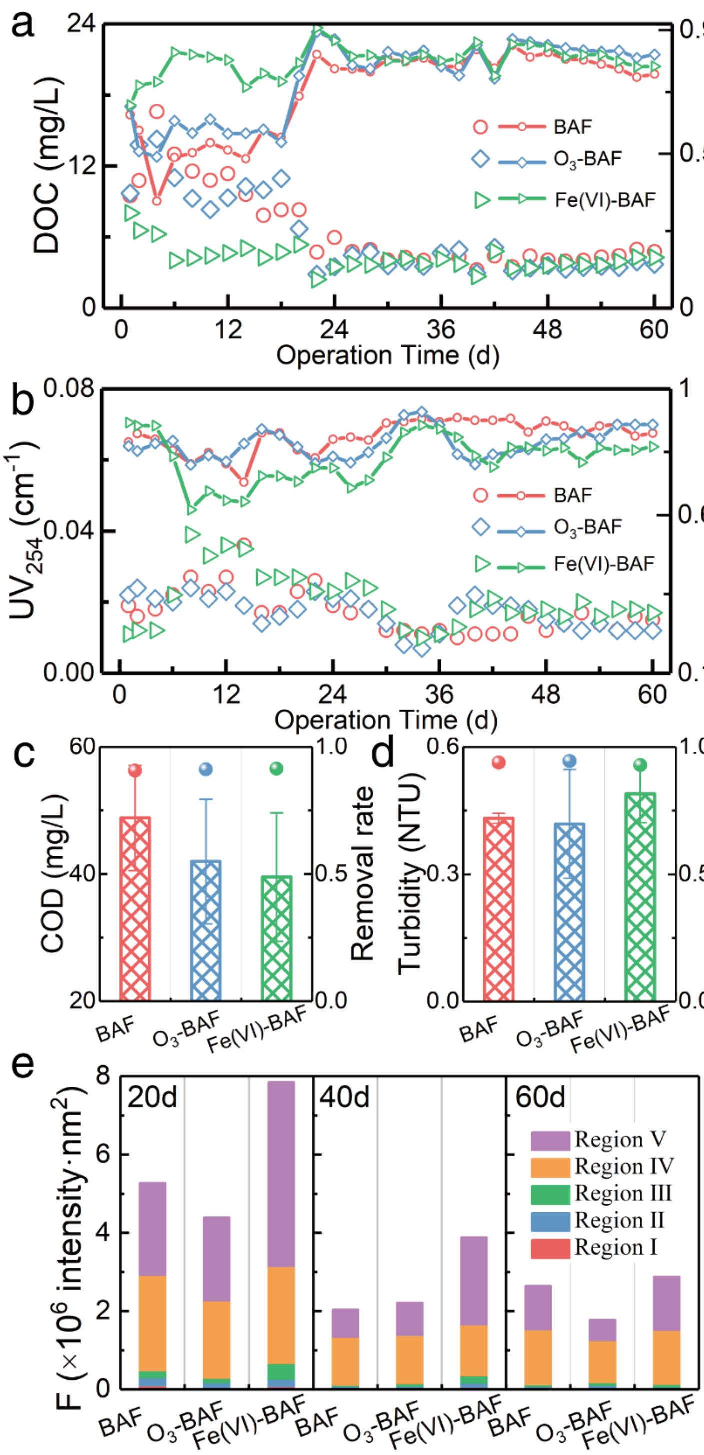

Figure 2. Quality of the effluents from the BAF systems. (**a-b**) DOC and UV254 parameters as a function of time during operation: here the larger data points refer to the concentrations (left axis) and the small data points connected by lines to the removal rate (right axis). **(c-d)** COD and turbidity values of the effluent: here, the bars refer to the value of each parameter (left axis) and the circles to the average removal rate (right axis). **(e)** Fluorescent organic components at three moments of the BAF operation.

3.3. Biofilm Morphology and Microbial Activity. The results in Figure 3a and Figure S6 indicate the presence of a large amount of microorganisms and of some microbial micelleons on the GAC surface from the three BAF systems. The microorganisms were mainly bacilli, cocci, and filamentous bacteria. Clearly, the microorganisms observed in samples from O_3-BAF and Fe(VI)-BAF reactors were far more than those observed in the BAF reactor. As shown in Figure 3b and Figure 3c, the OUR of microorganisms and the concentration of EPS decreased in the order Fe(VI)-BAF > O_3-BAF > BAF, corroborating that the activity of the microorganism in BAF systems was higher upon pre-oxidation.[43, 44]

The adsorption performance of GAC after long-term operation in BAF systems was always lower than that of the new GAC, as presented in Figure 3d. This result is rationalized with the larger density of available sites for adsorption on pristine GAC. In real operation, the lower adsorption of biologically-enhanced GAC would be compensated by the concurrent degradation of organic matter, which is the main target of this treatment. Interestingly, sterilization of the GAC used in the BAF system without pre-oxidation did not change its DOC removal performance compared to the material analyzed after use and without sterilization. On the contrary, both the adsorption rate and the equilibrium adsorption capacity of sterilized used GAC for DOC were significantly lower than that of used GAC from O_3-BAF and Fe(VI)-BAF systems. This analysis, combined with the observations from Figure 3a-d, suggests that microorganisms in O_3-BAF and Fe(VI)-BAF systems were highly functional and played an important role in the removal of organic matter. This result is attributed to the better biodegradability of pre-oxidized SGW, which helped sustaining a healthier and more active microbial community in the BAF systems.

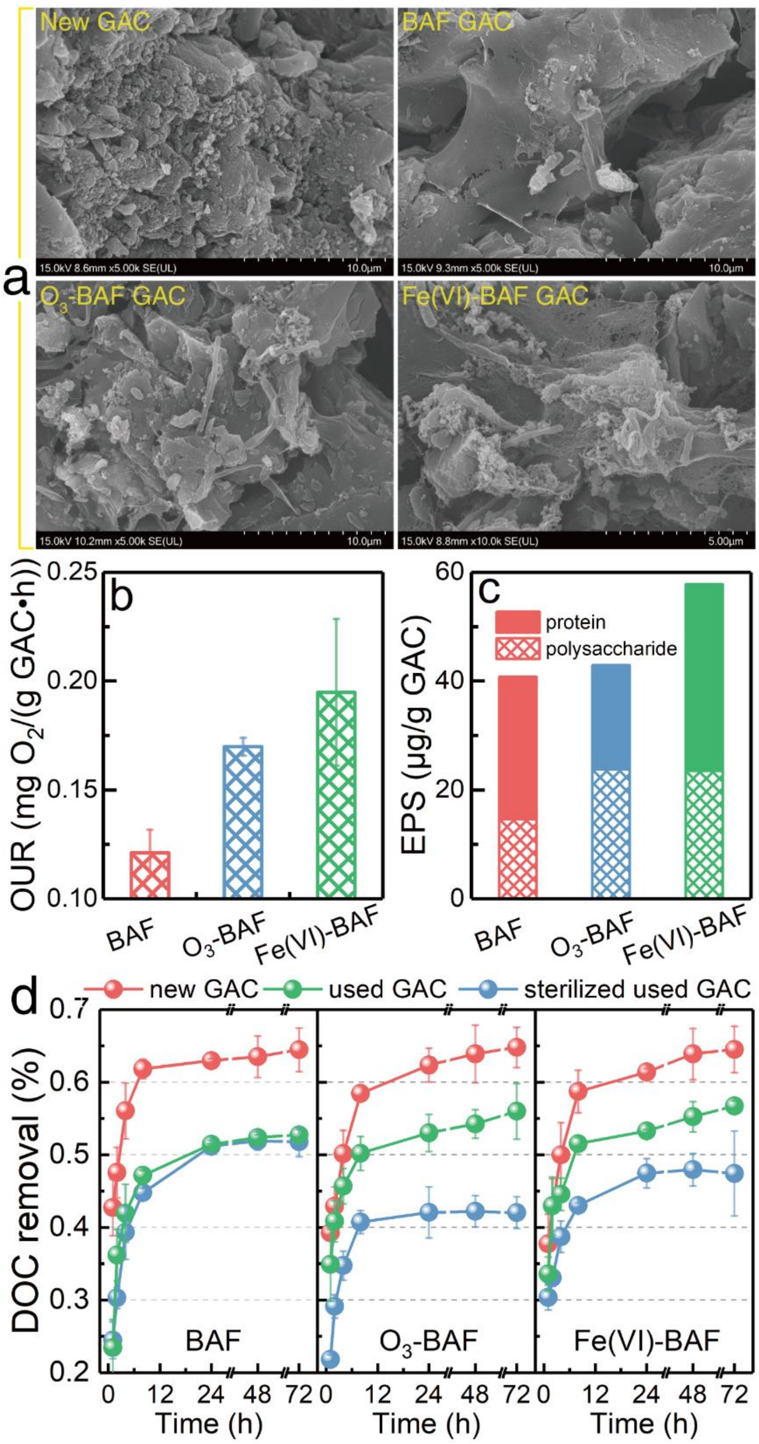

Figure 3. (**a**) Surface micrographs of new GAC and used GAC from three BAF systems. (**b**) OUR of microorganisms and (**c**) EPS concentration in the used GAC biofilm. (**d**) Variation of DOC removal in static adsorption experiment with new GAC, used GAC, and sterilized used GAC as adsorbents. The used GAC was collected on

the 60th day of continuous operation of the three BAF systems. The magnification of surface micrographs is 5k × or 10k ×. In static adsorption experiment, the GAC dosage was 2 g/L.

3.4. Microbial Community Analysis. The number of effective sequences, OUTs, alpha diversity indexes, and rarefaction curves for microbial communities in raw water and three BAF systems at different operation times are presented in Table S4 and Figure S8. The richness and diversity of microbial communities in raw water were higher than those in the three BAF reactors. The coverage values and rarefaction curves suggested the sequencing depth were sufficient.[45, 46] Through principal component analysis (PCA) at OUT level (Figure S9), the affinity relationships of microbial community between raw water and three BAF reactors, as well as among the three BAF reactors are revealed. The microbial community in the raw water was vastly different from that in the BAF reactor at 0 day after acclimation process, indicating new dominant microorganisms had been formed in BAF reactors. Also, the microbial communities in the same reactor at different times were similar, and O_3 seemed to have an effect in affecting more pronounced changes of the microbial community compared to ferrate pre-treatment.

Figure 4a and Figure 4b show in details the microbial community composition at the phylum and genus level, respectively. *Proteobacteria* (30.4%), *Actinobacteriota* (18.1%), *Bacteroidota* (14.7%), *Firmicutes* (12.3%), *Desulfobacterota* (9.5%), and

Synergistota (7.0%) were the major phyla and constituted 92% of bacteria in raw water. Through acclimation, *Proteobacteria* (98.1%) became the absolute dominant microbial phylum in BAF reactors. Similarly, the major genera in raw water, which also were widely detected in SGW from shale gas wells,[46-48] were *norank_f_Coriobacteriaceae* (18.0%), *Marinobacterium* (8.7%), *Lentimicrobium* (6.0%), *Roseovarius* (5.0%), and *Desulfovibrio* (4.6%). Family *Coriobacteriaceae* is an anaerobic fermentative bacteria within phylum *Actinobacteriota*.[23] *Marinobacterium* is a strict aerobe microorganism capable of utilizing a wide range of carbon sources.[49, 50] *Lentimicrobium* is a strictly anaerobic bacterium with the function of hydrolyzing organics.[51, 52] Almaraz et al.[18] reported *Roseovarius* as an iodine oxidation bacterium, which can promote the formation of large amounts of iodinated organic compounds that would cause serious negative implications to the water environment . *Desulfovibrio* as a sulfate-reducing bacterium is widely detected in shale gas wastewater, and is associated with the risk of corrosion to shale gas production facilities.[47, 53, 54]

A large amount of relatively low abundance microorganisms were enriched upon acclimation, with the major genus components being *Methyloversatilis* (39.1%), *Rhizobium* (20.0%), *Rehaibacterium* (10.4%), *Acinetobacter* (6.3%), *Pseudomonas* (4.5%), and *Acidovorax* (2.9%). During the BAF tests, the communities adapted differently based on the presence and type of oxidation pre-treatment. Consistent with PCA analysis, the microbial communities in the same BAF reactor at different operation times were similar. Although there were some differences in the microbial community structure of the three BAF systems, the core microorganisms were similar. These were *Rehaibacterium*, *Methyloversatilis*, *Pseudomonas*, *Rhizobium*, *Porphyrobacter*, *Acinetobacter*, *Bosea*, *Roseovarius*, *Acidovorax* and *Xanthobacter*. *Methyloversatilis* is a salinity tolerant bacterium with the ability of denitrification and organics degradation.[55, 56] *Rhizobium* are typical denitrifying bacteria, which widely exists in activated sludge, soil, and wastewater.[35, 57, 58] Genus *Acinetobacter* is related rich functions, such as degradation of organics, denitrification, phosphorus removal, and oxidation of heavy metals.[59-62] Members of *Pseudomonas* can degrade organics like toluene and chloroform.[63] Some research shows that members of *Acidovorax* could conduct heterotrophic denitrification.[64, 65] In general, SGW contains a large number of microorganisms with ability of degrading organic matter, removing nitrogen, and oxidizing heavy metals. Efficiently taking advantage of these microorganisms for biological treatment has great prospects in SGW management. Furthermore, a large number of anaerobes were eliminated during BAF acclimation process, and new dominant microorganisms were formed with the variation of environmental factors (aeration, variation of TDS, and the addition of sodium acetate).

In order to determine the microorganisms with significant abundance differences between the three BAF systems, we performed biomarker analysis using the linear discriminant analysis effect size (LEfSe) method. As shown in Figure S10**,** 9 bacterial clades presented statistically significant differences with an LDA threshold of 3.4. Each reactor had its own characteristic microorganisms whose abundance was higher than that of other reactors. Specifically, *norank_o_Bacteroideres_VC2_1_Bac22* and *norank_f_Vermiphilaceae* were enriched in the BAF reactor without pre-oxidation. *Norank_f_Rhodospirillaceae*, *Gemmobacter*, and *Rhizobium* were enriched in O_3-BAF reactor. Instead, *Dietzia*, *Roseovarius*, *norank_o_ Gammaproteobacteria_Incertae_Sedis*, and *norank_f_Rhodobacteraceae* were enriched in the Fe(VI)-BAF reactor.

The correlation analysis between microbial community at genus level (top 50) and environmental variables (organic matter removal rate) is shown in Figure 4c**.** It was found that *Rehaibacterium* with the high abundance of 3.0-21.1% was significantly correlated with DOC removal rate ($P < 0.01$). In a previous study, *Rehaibacterium terrae*, a thermotolerant and strictly aerobic bacterium was found in geothermally heated soil of Rehai National Park, China.[66] *Rehaibacterium terrae* can survive under the conditions of 0-30 g/L NaCl solution and 30-55 °C and degrade some organics.[66] One species in the genus *Rehaibacterium* was detected in our study but could not be defined: the base pair fragments were different from those of *Rehaibacterium terrae*. This result might indicate that a new species of genus *Rehaibacterium* was present with the strong ability of degrading DOC. Of course, more research is needed to study this hypothesis and to understand the new functions of this putative species. *Mesorhizobium* (0.01-0.20%) were correlated with UV_{254}

removal rate ($P < 0.05$). Research studies reported that *Mesorhizobium* members are halotolerant potential denitrifying bacteria and organics degrading bacteria.[67, 68] In addition, *Labrenzia* (0.01-1.29%), *Magnetospira* (0.01-3.04%), and *SM1A02* (0.01-2.42%) were correlated with COD removal rate ($P < 0.05$). *Bosea* (0.75-3.58%) and *unclassified_f_Rhodobacteraceae* (0.02-1.25%) were correlated with EEM removal rate ($P < 0.05$). *Methyloversatilis* (2.24-22.31%) was significantly correlated with EEM removal rate ($P < 0.01$).

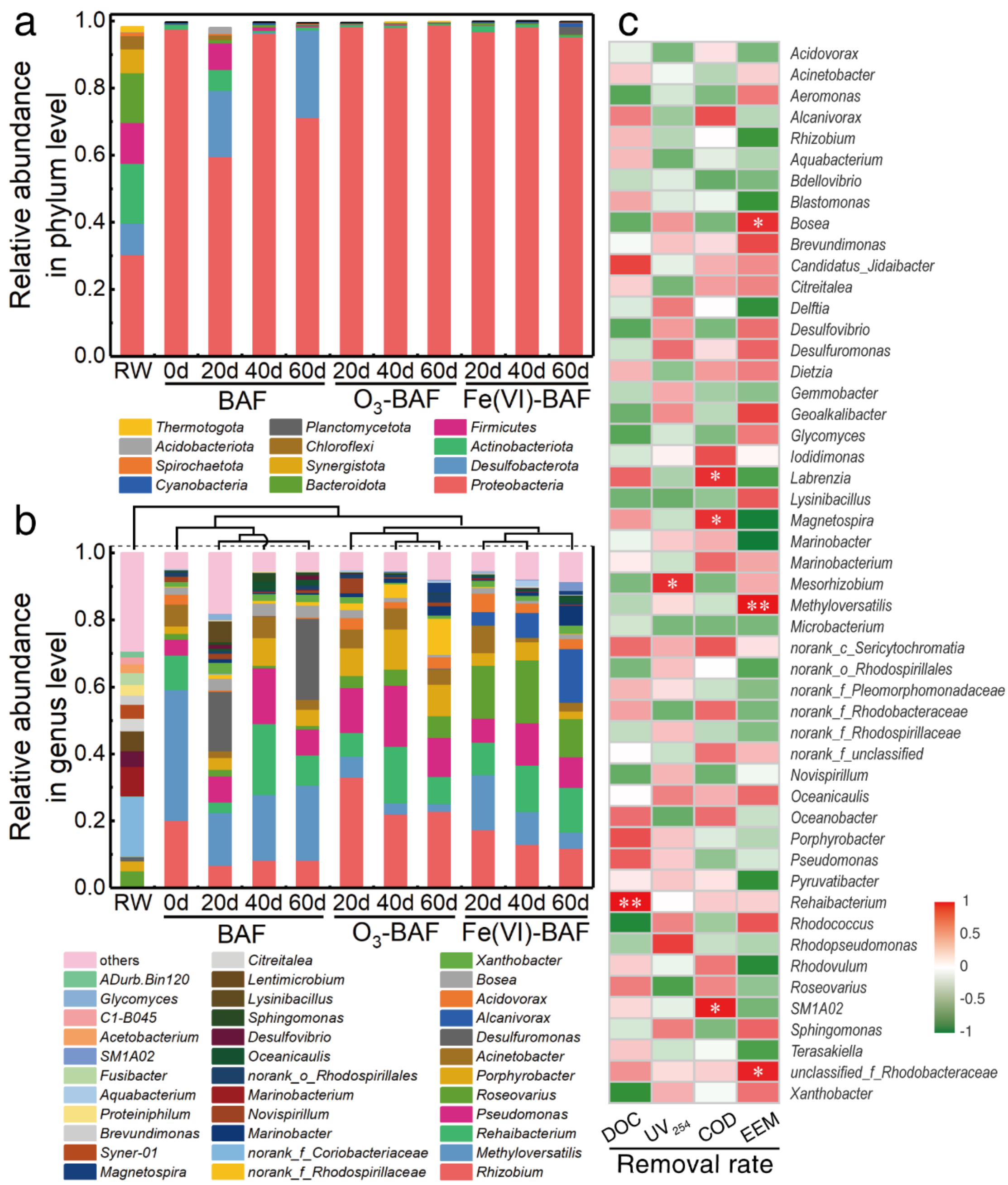

Figure 4. Bacterial community compositions at (**a**) the phylum (> 1%) and (**b**) the genus level (> 1.5%) in raw water and the three BAF systems at different operation times. (**c**) Correlation analysis between microbial community at genus level (top 50) and environmental variables (organic matter removal rate). Here, "⁎" represents a value of $p < 0.05$ and "⁎⁎" represents a value of $p < 0.01$.

Implications. O_3 and Fe(VI) pre-oxidation can effectively improve the removal efficiency of organics in BAF, which is attributed to higher activity and content of microorganisms in O_3-BAF and Fe(VI)-BAF systems compared with BAF. In our experiments, the removal rate of organic matters by BAF systems gradually increased and stabilized, owing to the enhancement of the microbial degradation function, with the enrichment of a large number of microorganisms with specific functions, such as organic matter degradation, nitrogen removal, heavy metals oxidation. For example, *Rehaibacterium* is significantly correlated with DOC removal rate ($P < 0.01$). Besides, *Methyloversatilis* is significantly correlated with fluorescent organics removal ($P < 0.01$).

The oxidation behavior of O_3 is different from that of Fe(VI), but both processes can effectively improve the biodegradability of wastewater. However, the mineralization rate and the improvement of organic quality in the effluent of systems upon pre-oxidation with O_3 and Fe(VI) were still limited. Combination with other oxidants (such as H_2O_2) or with electrooxidation may further improve the oxidation efficiency and the efficiency of the BAF process. Ozonation has feasibility and application value in the treatment of SGW, already at this stage of its technological development. Compared with pre-ozonation, Fe(VI) pre-oxidation has the potential advantages of easy operation and maintenance, but its application is still under development and should be optimized.[32] The in-situ Fe(VI) synthesis in wastewater treatment plant through wet chemical or electrochemical method is expected to further reduce the chemical cost.[69] It should be noted that the results presented here were obtained at the lab scale, while further studies are needed to evaluate the relevant systems at the pilot and full scales in long-term operation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interest.

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