Journal of Hazardous Materials 164 (2009) 726–732

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Developing sulfide-oxidizing biofilm on H_2S-exhausted carbon for sustainable bio-regeneration and biofiltration

Xia Jiang[a], Rong Yan[b,*], Joo Hwa Tay[a]

[a] Environmental Engineering Research Center, School of Civil and Environmental Engineering, Nanyang Technological University, Block N1-B3, 50 Nanyang Avenue, Singapore 639798, Singapore
[b] Institute of Environmental Science and Engineering, Nanyang Technological University, Innovation Center, Block 2, Unit 237, 18 Nanyang Drive, Singapore 637723, Singapore

ARTICLE INFO

Article history:
Received 21 May 2008
Received in revised form 19 August 2008
Accepted 20 August 2008
Available online 26 August 2008

Keywords:
Exhausted carbon
H_2S
Bio-regeneration
Sulfide-oxidizing bacteria
Biofiltration

ABSTRACT

The feasibility of developing biofilm on exhausted carbon using pre-deposited sulfur compounds as the sole energy source was studied, aiming to re-use them in odor biofiltration. The exhausted carbon with different properties, including surface pH, sulfur content and porosity, was used. A series of off-line trials were conducted to investigate the release of sulfur compounds from the exhausted carbon and the attachment of sulfide-oxidizing bacteria on the exhausted carbon. Without any pre-treatment, a few bacteria attachment on exhausted carbon was observed by SEM, due to possibly the limitation of reduced sulfur compounds release for bacterial growth. The biofilm development was much improved by adding NaOH solution to partially pre-desorb the deposited sulfur into liquid phase, which provided initial energy for bacterial growth. With the attached bacteria, the further significant release of the deposited sulfur was achieved through an additional driving force: biodegradation. The key issues for developing biofilm on exhausted carbon were concluded, which mainly concerned of desorption of pre-deposited reduced sulfur compounds and porosity of carbon. The sulfur-associated reactions occurring in developing biofilm on exhausted carbon was proposed. Bio-regeneration of exhausted carbon in the course of biofilm development was also preliminarily assessed.

1. Introduction

Biofiltration is a relatively new and exciting technology for controlling odors in an ecological and environmental-friendly way compared to physical and chemical methods. Selecting a proper packing material is an important step towards a successful biofiltration operation [1]. Recently, the use of activated carbon (AC) as packing material for odor biofiltration has been explored and proven to be greatly effective with such advantages as: shortening residence time and thus reducing the bioreactor size; higher removal efficiency due to combining adsorption and biodegradation; acting as a buffer during fluctuating loadings; and much extended lifetime [2–4]. And generally a low pressure drop was encountered for H_2S removal in a horizontal biotrickling filter [3]. Still, further studies are needed to shorten the start-up period and cut down the investment cost of using a large amount of AC, as a packing material in odor biofiltration [5].

Meanwhile, the exhausted carbon coming from the H_2S adsorption process is a big environmental problem in wastewater treatment plants (WWTPs) [6]. An idea of reusing exhausted carbon in odor biofiltration process is considered because of a combination of the following attractive benefits: renewing adsorption capacity of AC (i.e. bio-regeneration), reducing the start-up time of biofiltration (the pre-deposited sulfur compounds could possibly serve as energy source for bacterial growth), prolonging AC service life, and producing a much cheaper packing material, etc. So far, it is not clear yet if a sulfide-oxidizing biofilm can successfully be developed on exhausted carbon by utilizing the pre-deposited sulfur compounds as the sole energy source. Once it can be verified, it will be feasible to transfer the exhausted carbon into biological activated carbon (BAC) for a sustainable bio-regeneration and/or re-use in biofiltration. The primary technical challenge associated is to confirm that most of the pre-adsorbed sulfur compounds in exhausted carbon could be released in the presence of bacteria for two benefits: (1) to serve as energy for bacteria to develop biofilm, and (2) to re-generate the active space for further adsorption (i.e. bio-regeneration). Although the term "bio-regeneration" was ever mentioned in odor biofiltration using AC as packing material [3,4], there has been little attempt found to identify the optimal

* Corresponding author. Tel.: +65 67942344; fax: +65 67921291.
E-mail address: ryan@ntu.edu.sg (R. Yan).

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doi:10.1016/j.jhazmat.2008.08.060

conditions for the largest release of pre-adsorbed sulfur, and to understand lots of unknowns concerning microbial metabolisms and sulfur mass transfer on exhausted carbon.

Therefore, research efforts should be involved to find out the conditions for sulfide-oxidizing bacteria to access most of pre-deposited sulfur compounds on exhausted carbon. For this purpose, a successful biofilm development on exhausted carbon, based on the pre-adsorbed sulfur as the sole energy source, will be a direct confirmation. In this study, the work was carried out to evaluate the feasibility of biofilm development and bio-regeneration of various exhausted carbon that are purposely differentiated in surface pH, sulfur content and porosity. The focus of the study is to understand the condition suitable for exhausted carbon as packing material in odor biofiltration. If this idea can be verified, exhausted carbon is expected to have comparable and even superior performance over fresh carbon as packing material in odor biofiltration.

2. Materials and methods

2.1. Preparation of H_2S-exhausted carbon

Activated carbon with pellet-shaped in 4 mm of diameter, from Jacobi Group (AddSorb VA3, designated as "VA"), was selected. It is chemically impregnated carbon, and is currently the most widely used type of AC for H_2S removal. The H_2S-exhausted carbon was obtained from the breakthrough capacity test following the standard adsorption method (ASTM-D6646-03). Details of the test can be found in our previous work [7]. The exhausted carbon was collected from top, middle and bottom of the adsorption bed, and designated with additional letter "E", and termed as "1, 2, 3" for the top, middle and bottom carbon, respectively.

2.2. Biofilm development on exhausted carbon

10 g of exhausted carbon was added into 500 mL of flasks containing 200 mL of sterilized mineral salt medium (pH 7.0 ± 0.2) in the following composition (g/L): KH_2PO_4, 3.0; K_2HPO_4, 3.0; NH_4Cl, 0.4; $MgCl_2{\cdot}6H_2O$, 0.4. 1 mL of enriched microbial consortium containing 1.9×10^7 CFU/mL of autotrophic sulfide-oxidizing bacteria (SOB) was inoculated into the flasks. The detailed procedure for enriching the microbial consortium was given in our previous work [8]. Control experiments were also conducted under the same experimental conditions but without adding microbial inoculums. Both experimental and control flasks were covered with cotton stoppers and incubated on a rotary shaker at 150 rpm at room temperature. During the whole stage, no external sulfur source was added into the flasks except for the sulfur previously deposited on the exhausted carbon. The pH of liquid was measured using a Horiba F-53 pH meter, and the concentration of sulfate (the final oxidized product) was determined by the standard method [9].

Bacterial count for autotrophic SOB on carbon surface was determined using thiosulfate (TS) medium agar, which was prepared using autoclave-sterilized mineral salt agar (mineral salt medium with 15% Bacto agar) and filter-sterilized TS solution. The bacterial cells were de-attached from carbon and suspended in solution following the method as described by Chung et al. [4]. Triplicate plates were prepared to get the average count.

2.3. Carbon identification

A thorough analysis of AC (fresh, exhausted carbon and BAC) was conducted using various approaches. Three analyses for each sample were carried out for repeatability and precision of the measurement. For measurement of surface pH and sulfate content of AC, 1 g of sample was soaked in 50 mL of ultra-pure water and swirled in an auto-shaker for 24 h to reach equilibrium. The resulted solution was passed through a 0.2-μm membrane filter to remove particles. The pH and the sulfate concentration of the filtered solution were then determined by the methods above mentioned. The Micrometrics BET Analyzer model ASAP 2010 was used to measure the porosity of AC samples. Thermal analysis was conducted using a thermal gravimetric analyzer (TGA) (Netzsch STA 409) to identify the deposited sulfur species on AC. The combustible sulfur of AC was determined using a thermo-analytical analyzer (PE2400 series II CHNS/O analyzer, PerkinElmer Instruments). For the morphological observation of carbon surface and biofilm development, the carbon pellets were fixed, dried and viewed with a scanning electron microscope (SEM) (Stereoscan 420, Leica, Cambridge Instruments) as described previously [3].

2.4. Pre-treatment of exhausted carbon

Chemical pre-treatment was performed to enhance the release of sulfur compounds from exhausted carbon into liquid phase and ensure an efficient biofilm development. 50 mL of 1N NaOH solution was added into 10 g of exhausted carbon in a 500 mL of flask, shaking 24 h for a complete reaction. And then, pH was adjusted back to neutral and the solution containing sulfur compounds and AC was ready for biofilm development.

3. Results and discussion

3.1. Characteristics of H_2S-exhausted carbon

In breakthrough test, total capacity of H_2S adsorption was 8.3% (w/w) H_2S/AC for VA carbon. The exhausted carbon was characterized for the surface properties, such as sulfur content, pH and structural parameters, which compared with those of fresh carbon (Table 1), for the purpose of screening the optimum exhausted carbon to be re-used as packing material in biofiltration.

The pH values of exhausted carbon decreased from the top (VA-E1) to the bottom (VA-E3) of adsorption bed, while both the combustible sulfur and sulfate contents increased largely with the same change of carbon. The detail explanation associated with these changing tendencies can be found in our previous publication [7]. After the breakthrough of the bed, the bottom carbon was fully used, but the top carbon still remained similar as fresh carbon with only a few sulfur detected, due to little H_2S left in the gas stream

Table 1
Sulfur content, surface pH and structural parameters of carbon samples

Sample	Sulfur content (w/w%, S/AC)		pH	Structural parameters			
	S-combustible sulfur	S-sulfate		V_{mic} (cm^3/g)	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{ext} (m^2/g)
VA	0.26	–	9.9	0.18	910	400	510
VA-E1	2.85	0.18	8.9	0.167	845	378	466
VA-E2	5.73	0.56	5.3	0.142	776	322	454
VA-E3	10.19	1.27	4.2	0.075	641	178	463

–: non-detectable. V_{mic}: micropore volume; S_{BET}: BET surface area; S_{mic}: micropore area; S_{ext}: external surface area.

at outlet [7]. The combustible sulfur could be any reduced sulfur species (but excluding S (VI), such as sulfate) which can be potentially utilized by bacteria. The content of combustible sulfur was obviously higher than the sulfate in the corresponding exhausted carbon.

In Table 1, BET surface area (S_{BET}) reduced significantly from top to bottom carbon, due to the much larger deposition of sulfur products in carbon pores at inlet than at outlet of the bed [10]. The micropore volume (V_{mic}) and surface area (S_{mic}) decreased from top to bottom carbon, indicating potentially a higher physical adsorption capacity of top carbon in re-use process. Meanwhile, the external surface area (S_{ext}) can be used to indicate the available surface for bacteria growth as nearly all internal surface areas are inaccessible, due to the large size of microorganisms (~1 μm) [11]. There was not much change in S_{ext} for VA-exhausted carbon in comparison to fresh carbon, implying a large space still available for bacterial attachment on the exhausted carbon.

3.2. Biofilm development on exhausted carbon

The different exhausted carbon (Table 1) could result in different biofilm development. It is worthy to investigate the suitability of exhausted carbon for developing BAC. The effectiveness of microbial sulfur oxidation was confirmed through the comparison of batch incubation of exhausted carbon with and without bacterial culture. The sulfate concentration and pH were employed as two indicators to monitor the sulfur bio-oxidation during biofilm development on exhausted carbon (Fig. 1A), and results of pH were not shown here. Three experiments (with bacteria) were referred to BVA1, -2 and -3 while correspondingly their controls (without bacteria) were VA1, -2 and -3 involving the top, middle and bottom exhausted carbon, respectively.

Fig. 1A showed abrupt change in sulfate concentration in the solution after 1-day incubation for all experiments and controls, attributing to different sulfate contents of exhausted carbon (Table 1). The sulfate contents of controls (VA1, -2 and -3) appeared relatively constant with time after the 1st day up to the 28th day. There was no significant difference in sulfate content between control and experiment solution for the top carbon (VA1 and BVA1). It most likely attributed to the very low sulfur content (Table 1), resulting in little sulfur available for bacteria. Nevertheless, sulfate contents of BVA2 and BVA3 increased obviously with time, accompanied by a gradual pH drop, in comparison to their controls (VA2 and VA3). The widening deviation of both sulfate content and pH value with time between the experiment and control trials indicated the occurrence of microbial sulfur oxidation clearly.

On the 14th day, the pH in liquid with bottom carbon was adjusted from 5.2 and 6.2 to 7.0 for experiment and control, respectively, to verify the bacterial function again. Results showed that more sulfate was produced in the experiment than control flasks right after the change made, confirming that the bacteria indeed played an important role in sulfur release from the exhausted carbon.

After 28 days of biofilm development, combustible sulfur of the control and experimental carbon was analyzed, in comparison with that of exhausted carbon (Fig. 2A). The difference of sulfur content between the exhausted and control was attributed to wash sulfur compound into aquatic solution. A clear decrease of combustible sulfur in experiment from that in control indicated that bacteria could play an important role in releasing combustible sulfur from exhausted carbon, followed by bio-oxidation to sulfate in the liquid phase (Fig. 1A). A thorough study of sulfur balance and distribution in carbon and solution is thus worthy, and it will be carried out in a near future.

Morphological observation, carried out after 15 days of biofilm development, showed that rod-shaped bacteria (~1 μm in length) distributed partially on carbon surface (Fig. 3A). Bacterial counts

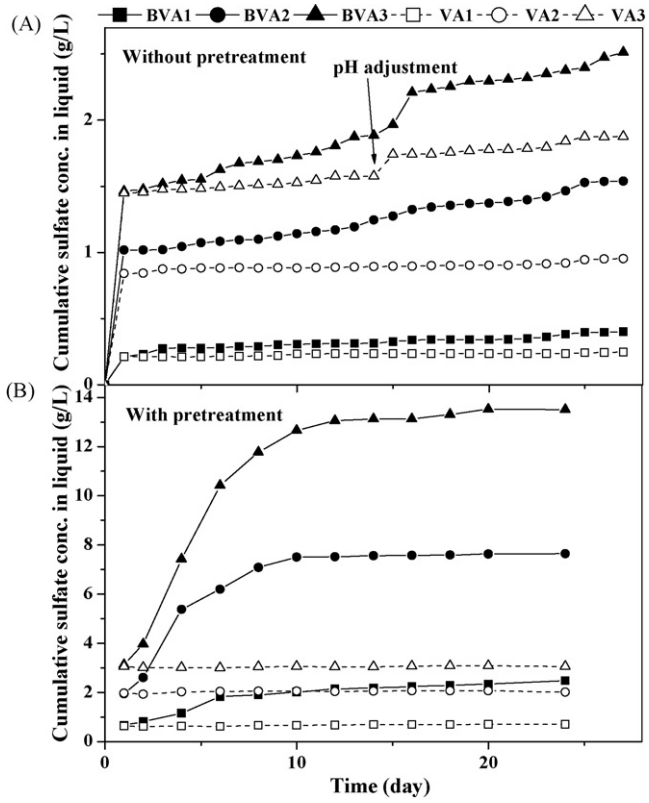

Fig. 1. Sulfate concentration profile during biofilm development without pre-treatment (A) and with pre-treatment (B).

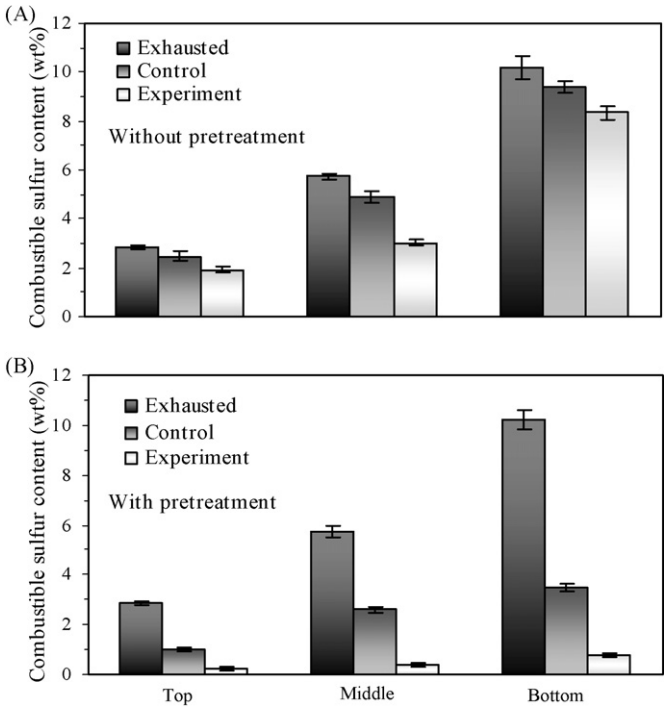

Fig. 2. Combustible sulfur content after 28 days without pre-treatment (A) and after 24 days with pre-treatment (B).

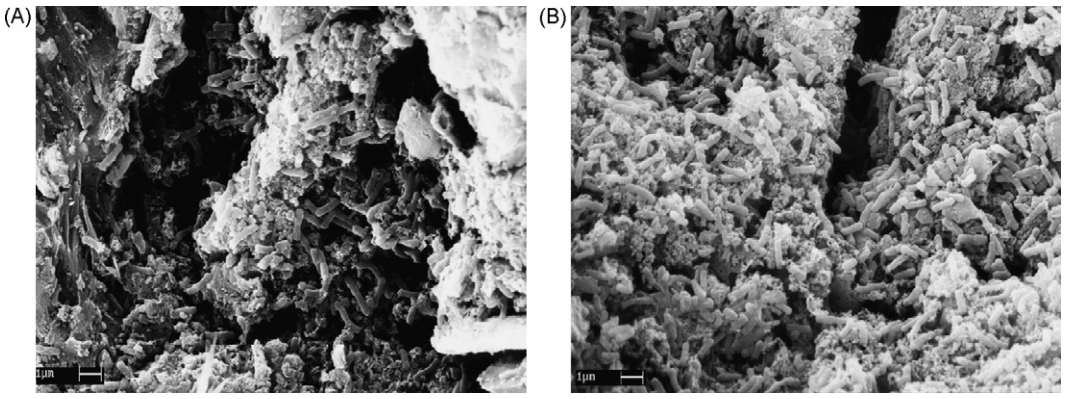

Fig. 3. Micrographs of microorganism grown on BVA3 surface for 15 days without pre-treatment (A) and for 8 days with pre-treatment (B).

from the 5th to 28th day of biofilm development revealed that there were SOB approximately 1.0 to 5.8 × 10^5 CFU/g dry AC presented on these BAC. BVA1 with low deposited sulfur content presented relatively less bacteria attachment, while for BVA3 with higher sulfur content, higher numbers of bacteria could be observed. SEM pictures were also taken from control carbon, with no bacteria but only chemical crystals shown.

Similar trials were conducted with exhausted carbon from virgin AP460 (Calgon Carbon Corporation), but there was no difference found between control and experiments, in terms of sulfate content in liquid and combustible sulfur in carbon (data not shown). The possible reasons are due to different adsorption mechanisms associated for the two types of carbon [12,13] which could result in different release of pre-deposited sulfur. Carbon type was also reported to be a key issue for desorption and bio-regeneration of other adsorbed chemicals [14]. In the study, the difference resulting from carbon types will not be discussed in detail.

3.3. Enhanced biofilm development on exhausted carbon by adding NaOH

Although a green light of developing biofilm on VA-exhausted carbon was seen based on pre-deposited sulfur as the sole energy source, the development process was slow and the amounts of bacteria attached on the surface of exhausted carbon were significantly lower than those of other studies where external energy source was provided continuously [4]. A large amount of reduced sulfur was still remained in AC (Fig. 2A). Therefore, it is critical to significantly enhance the release of these reduced sulfur compounds so as to ensure a good biofilm development.

NaOH solution was added as a pre-treatment step to enhance the desorption of sulfur compounds in exhausted carbon into aquatics phase, followed by the normal biofilm development procedure. As shown in Fig. 1B, the sulfate contents in three BVA flasks increased largely with time at the first 8 days while those of controls remained constant. In addition, compared to Fig. 1A, pre-treatment indeed increased greatly the quantity of sulfur bio-oxidized. In a quantitative comparison, sulfate generated in liquid on the 24th day was found at 8.56% S-sulfate/AC for BVA3 with adding NaOH, while it was only 1.85% S-sulfate/AC without pre-treatment on the 28th day. The pH (data not shown here) in experimental flasks decreased and was adjusted to 7 when it dropped to below 3 while in the controls, the pH remained always constant.

As shown in Fig. 2B, a large amount of combustible sulfur in exhausted carbon was removed by NaOH adding. Further release of sulfur was achieved by bacterial function, resulting in much less sulfur remained in experiments than those in controls. Compared with the case without pre-treatment (Fig. 2A), the remaining combustible sulfur of BVA was much fewer for the case with pre-treatment.

After the pre-treatment followed by biofilm development run for 8 days, the carbon pellet was collected for SEM observation (Fig. 3B). The result showed that biofilm was well developed on BVA3, supported by the plate count of SOB attached: 2.6 × 10^8 CFU/g dry AC, much higher than those of BVA without pre-treatment. The reason associated is that, due to NaOH adding, much more reduced sulfur released (Fig. 2B), which benefited to the initial formation of a biofilm on carbon surface. It could then be much easier for the immobilized bacteria than suspended ones to access the pre-deposited sulfur on exhausted carbon, evidenced by much higher combustible sulfur released due to bacterial contribution (Fig. 2B). Bacterial cell attachment on an adsorbent was previously shown to facilitate the biodegradation of other pre-adsorbed chemicals [15,16]. It is possible that the attached bacteria may be exposed to a higher chemical concentration (i.e. sulfur compounds in this study) within the inner boundary diffusion film compared to that of bulk solution, resulting in enhanced biodegradation.

3.4. Sulfur reactions associated in developing biofilm with pre-treatment

Sulfur deposits in exhausted carbon were previously formed in the H_2S adsorption process. The transformation of these sulfur species is the basis for understanding the biofilm development mechanism.

3.4.1. Identification of sulfur species on carbon

Thermal analysis was conducted to identify the deposited sulfur species on the AC. The results of the bottom carbon are presented in Fig. 4, as a representative. From previous work, it was learnt that the peak centered at about 240–300 °C was assigned to the presence of bonded SO_2, and the peak centered at about 380–400 °C represented elemental sulfur [10,17]. In this study, the DTG curve of the fresh carbon (VA) was almost featureless in the temperature range of 200–500 °C. For exhausted (VA-E3), control (VA3) and experimental samples (BVA3) without pre-treatment, one peak was observed at about 380–400 °C, suggesting elemental sulfur probably dominated. Moreover, the DTG peak of control was smaller than that of the exhausted one, showing the effects of nutrient water and shaking to wash off some sulfur into liquid phase, possibly in the colloidal form [10,18]. It was also suggested that some elemental sulfur (sulfur radicals) might be capable of interactions with carbon surface during water washing, resulting in oxidation along with creation of more water-soluble sulfur species [17]. Furthermore, an even smaller DTG peak was found for experimental carbon than that of control, indicating some sulfur compounds removed from

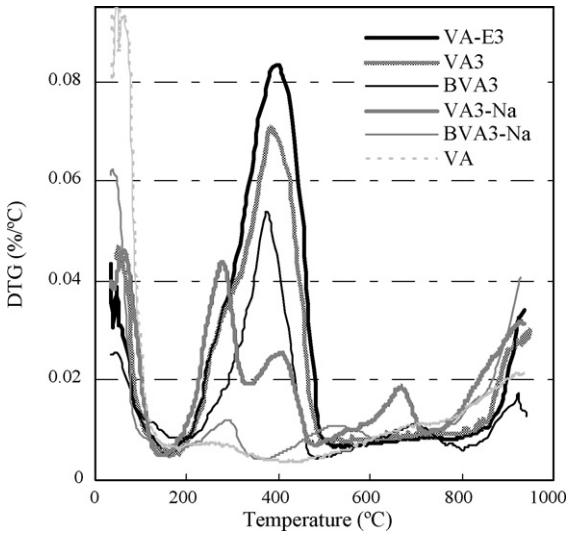

Fig. 4. DTG curves for bottom samples without and with pre-treatment.

the carbon through bacterial degradation. The contents of sulfur compounds on carbon were estimated from DTG curves via separation of both S-SO_2, elemental sulfur peaks (S^{el}) and others in different temperature ranges [17] (Table 2). It can be seen that 26.2 and 29.4% of S-SO_2 and S^{el} were reduced in control (VA3), respectively, compared to exhausted carbon (VA-E3). Meanwhile they were decreased further by biodegradation (BVA3) for 50.0 and 48.7%, respectively.

Curves VA3-Na and BVA3-Na represented the control and experimental samples with pre-treatment, respectively. Three well-defined peaks were found around 280, 410 and 680 °C in the curve of VA3-Na control. It showed that NaOH adding resulted in the removal of a large quantity of elemental sulfur (75.8% in Table 2) from exhausted carbon, and generated some products including possibly sulfur oxide (at peak 280 °C) and new sulfur species (at peak 680 °C). For BVA3-Na, only a small peak around 300 °C (0.37%) remained, which might be the remaining bonded SO_2 that cannot be used by bacteria or the sulfate adsorbed in biofilm.

3.4.2. Identification of sulfur species in liquid

After adding NaOH solution into carbon samples and shaking for 24 h, the solution became yellow color in the flasks containing middle and bottom carbon with higher sulfur content, while for fresh carbon without sulfur and top carbon with little sulfur, solution color did not change. After that, HCl solution was added to adjust the pH back to neutral, and then white precipitates were produced in the flasks containing middle and bottom carbon. And again, no evident change was found for solutions with fresh and top carbon. Preliminary sulfur analysis using standard methods [9] found that the yellow solution contained mainly $S_2O_3^{2-}$, S^{2-} and a little of elemental sulfur (data not shown), but after the addition of HCl solution, the main sulfur species in solution was elemental sulfur.

Table 2
Sulfur content on bottom samples without and with pre-treatment (%)

Sample	S-SO_2 (240–340 °C)	S^{el} (340–480 °C)	Other S (600–700 °C)
VA-E3	2.10	7.65	0.00
VA3	1.55	5.40	0.00
BVA3	1.05	3.92	0.00
VA3-Na	2.86	1.85	0.43
BVA3-Na	0.37	0.19	0.00

According to the pathway of H_2S adsorption on the alkaline activated carbon [10], there were possibly several sulfur species (H_2S, HS^-, S, SO_2) deposited on carbon. The dissolved sulfide (H_2S/HS) in caustic solution reacted with the elemental sulfur to form polysulfides S_x^{2-}. Lower molecular weight polysulfides in caustic solution reacted with elemental sulfur to form higher molecular polysulfides [19,20]. Therefore, the possible sulfur reactions associated in developing biofilm with pre-treatment were proposed as the following [19,21,22]:

(1) After adding NaOH solution into exhausted carbon:

$$H_2S(ads) + OH^{-1}(aq) \rightarrow HS^-(aq) + H_2O$$

$$SO_2(ads) + 2OH^{-1}(aq) \rightarrow SO_3^{2-}(aq) + H_2O$$

$$S^0(ads) + SO_3^{2-}(aq) \rightarrow S_2O_3^{2-}(aq)$$

Then, elemental sulfur reacted with sulfide in caustic condition to yield polysulfide compounds (yellow color):

$$(x-1)S^0(ads) + HS^-(aq) \leftrightarrows S_x^{2-} + H^+$$

(2) After adding HCl to neutralize the solution:

$$S_x^{2-}(aq) + 2H^+ \rightarrow H_2S + (x-1)S(\text{white precipitates})$$

$$S_2O_3^{2-}(aq) + 2H^+ \rightarrow SO_2 + H_2O + S(\text{white precipitates})$$

(3) Formation of biofilm initially on the carbon surface by utilizing reduced sulfur in liquid as energy for bacteria:

$$H_2S + 2O_2 \rightarrow 2H^+ + SO_4^{2-}(\text{with SOB})$$

$$S + (3/2)O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-}(\text{with SOB})$$

$$SO_3^{2-} + (1/2)O_2 \rightarrow SO_4^{2-}(\text{with SOB})$$

$$\text{Suspended bacteria} + \text{desorbed reduced sulfur} \rightarrow \text{a thin layer of biofilm on carbon}$$

(4) Further enhanced the release of sulfur compounds from exhausted carbon due to the presence of initial biofilm on carbon, resulting in more bacteria growth on carbon surface:

$$\text{The thin layer of biofilm} + \text{sulfur deposits on carbon} \rightarrow \text{well developed biofilm}$$

Based on the above results, the biofilm development on exhausted carbon could be considered as a combination of the following aspects: (1) part of the sulfur compounds could release from the exhausted carbon into liquid phase by water washing or pre-treatment; (2) the desorbed reduced sulfur compounds can be biodegraded by suspending bacteria in liquid phase, thus allowing SOB to grow in the solution; (3) some active bacteria might attach on the carbon surface to form a biofilm initially at external surface of carbon, and then they were exposed to a steeper concentration gradient of sulfur compounds; (4) following that, further

Table 3
Regeneration efficiency of combustible sulfur in VA exhausted carbon (%)

Sample	Without pre-treatment			With pre-treatment		
	Control	Experiment	Net contribution of bacteria	Control	Experiment	Net contribution of bacteria
Top	13.7	33.0	19.3	65.6	93.0	27.4
Middle	14.5	47.3	32.8	54.5	93.4	38.9
Bottom	7.8	18.0	10.2	65.8	92.3	26.5

desorbed sulfur compounds resulted in more bacteria growth on carbon surface.

It was reported that too much biomass attachment could block the carbon external pores and make the adsorption capacity loss, resulting in limited buffer capacity of BAC during transient loading [23]. Therefore, the free biofilm coverage on the carbon with exposure areas can benefit to keep adsorption capacity in odor biofiltration process. Alternatively, a weak biofilm is not efficiently enough regarding contaminates removal [8,24]. Hence, the overall consideration of the biofilm development is to optimize the combination of the two effects, biodegradation and adsorption. Further work should be conducted to investigate the odor removal performance of these developed BAC. It is expected that the start-up time of using exhausted carbon in biofiltration will be much shorten compared to fresh carbon, as energy source (the sulfur deposits) already existed in exhausted carbon surface.

Besides, although adding NaOH demonstrated an essential pre-treatment for the release of sulfur from exhausted carbon and enhancement of biofilm development on exhausted carbon in off-line trials, an on-line biofiltration showed that it was not necessary for the pre-treatment of reduced sulfur from exhausted carbon (data not shown). It was because supplied H_2S could be used as the initial energy for bacteria growth on carbon. And later, attached bacteria facilitated the release of deposited sulfur from exhausted carbon.

3.5. Bio-regeneration

The simultaneous bio-regeneration of exhausted carbon in the course of biofilm development was preliminarily assessed through analyzing sulfur compounds and BET porosity of the developed BAC. It was evidenced that there was less combustible sulfur found in experimental samples than those in controls (Fig. 2), corresponding to higher sulfate contents detected from experimental flasks than those from control ones (Fig. 1). Regeneration efficiencies of combustible sulfur in exhausted carbon are shown in Table 3. Around 18–47% of overall regeneration efficiencies were achieved for exhausted VA carbon without any pre-treatment, among which ~10–33% of sulfur removal was attributed to biodegradation. Pre-treatment of adding NaOH enhanced the overall regeneration efficiency of combustible sulfur in exhausted carbon to 92–93%, with the net contribution of bio-regeneration increased to ~26–39%. It confirmed the effect of attached bacterial occurrence in enhancing the release of sulfur. A decrease in intensities of the sulfur peak in DTG curves (Fig. 4) also showed directly the effect of biological regeneration of VA exhausted carbon.

Removal of pre-deposited sulfur compounds on exhausted carbon can re-open adsorption sites or free carbon pores, which can be re-used for further adsorption of targeted contaminants. V_{mic} and S_{mic} of different samples, including fresh, exhausted carbon and BVA without and with pre-treatment, are shown in Fig. 5. In developing biofilm without pre-treatment, the V_{mic} and S_{mic} of BVA increased from those of exhausted carbon, indicating the regeneration effects. Furthermore, with pre-treatment the generated BAC (BVA-Na) had further enlarged V_{mic} and S_{mic} which reached almost the similar level as that of fresh carbon. In more details, the bottom

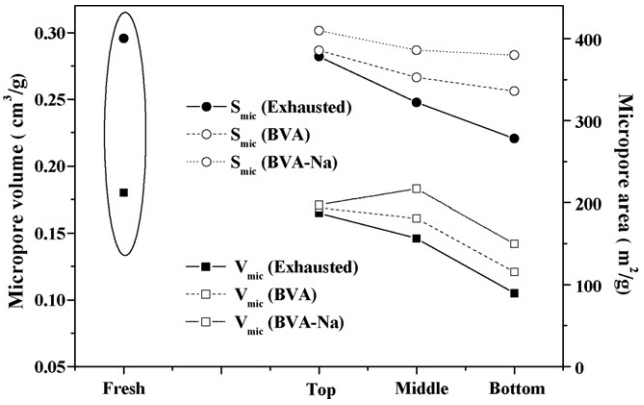

Fig. 5. Micropore volume and area for VA samples without and with pre-treatment.

exhausted carbon remained only about 40% of the initial V_{mic} and S_{mic} of fresh carbon, which were renewed in BAC generated without pre-treatment to 67 and 74% of the initial V_{mic} and S_{mic}, respectively. With pre-treatment, the V_{mic} and S_{mic} of the developed BAC were further increased to 80 and 95% of initial ones, respectively, demonstrating a significant recovery of adsorption capacity. This resulted from the removal of sulfur deposited in the micropores of the carbon earlier [25].

4. Conclusions

In summary, this study directly confirmed that, without supplying any external energy source, the sulfide-oxidizing bacteria could access partially the pre-adsorbed sulfur in VA exhausted carbon for bacterial growth and then form a biofilm on carbon surface. Therefore, it is highly feasible to develop BAC from exhausted carbon, benefiting to sustainable bio-regeneration and re-use of these carbon in odor biofiltration. The guideline of developing BAC from exhausted carbon was investigated, including utilizable sulfur compounds (i.e. energy for bacterial growth), carbon external surface area (space for bacterial attachment), and micropore volume and area (active site for physical/chemical adsorption). Pre-treatment trials by adding NaOH proved to be effective to enhance the development of biofilm on exhausted carbon. Additionally, the function of bio-regeneration in the course of biofilm development on exhausted carbon supported the idea of simultaneous bio-regeneration of exhausted carbon for a sustainable biofiltration system.

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