

Preparation of sludge derived carbon with Fenton and NaClO activated and the application on the odor abatement

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Abstract:

Sewage sludge could be disposed to prepare the sludge derived carbon (SBC) through pyrolysis, while the SBC quality is poor without any pretreatment, and activation process is necessary to applied to destroy the cell wall barrier and heterogeneous structure in sludge. Two activators of Fenton and NaClO are applied to prepare the precursors, and the SBC obtained are characterized and compared in terms of SEM, FTIR, BET and porous distribution. Under the optimum conditions, the maximum BET in the SBC-Fenton and SBC-NaClO reach to 253 and 423 m² g⁻¹, respectively, while that in control group is 38 m² g⁻¹ only. The corresponding V_{micro}/V_{total} are 42 and 46% in the SBC-Fenton and SBC-NaClO, higher than that of 6% in control group. The saturation adsorption capacity is around 71.5, 67.8 and 33.10 mg g⁻¹ in SBC-Fenton, SBC-NaClO and SBC-control in series based on Langmuir isotherms using Methylene Blue. Thus, SBC might be one of the suitable substitutions for the soil cover in landfill, to realize carbon storage and reduce odor emission.

Keywords: Sludge derived carbon; Activation process; Adsorption capacity; Carbonization process

1 1. Introduction

2 Waste activated sludge (WAS) is the inevitable byproduct from waste water
3 treatment plants, and increases greatly with the growing quantity of wastewater
4 collected and more stringent sewage discharge standard implemented. Around 46.5
5 billion tons of municipal waste water was collected and treated in 2013, with around 35
6 Million ton sewage sludge generated (80% water content) in China (NBS, 2014). The
7 sludge disposal is a big headache problem for the local government.

8 Landfill could be used as the emergency way for the sludge disposal with so much
9 sludge generation. In order to implement the sludge landfilling, the water content of
10 sludge is supported to be below 60% according to Standard for Pollution Control on the
11 Landfill Site of Municipal Solid Waste (GB16889-2008) (MEP, 2008). However,
12 sludge landfilling has its own inherent problems, such as huge landfill volume occupied
13 and amounts of greenhouse gas (GHG)/odor emission (Chan et al., 2002; Tony et al.,
14 2014). Odor emission from the sludge landfilling is also different from the municipal
15 solid waste disposal in landfill, where sulfur compound and ammonia are the two main
16 causes for the former one, while aromatic, sulfur compound, and oxygenated
17 compound are the main contributions in the latter one (Fang et al., 2012). Generally, the
18 landfill volume is limited due to the sharply increase of municipal solid waste, and the
19 saving of the space is another requirement for the implement of the sludge landfilling.
20 Therefore, how to make a balance between the volume consuming for sludge
21 landfilling and the rapid increase of municipal solid waste is another challenge for the
22 landfill manager.

23 Soil covers in landfill, including the daily soil cover, intermediate soil cover and
24 the final soil cover, are the important part for landfill, while around 1/5-1/3 of the total
25 landfill volume will be occupied by these covers (George 2000). On the one hand,
26 sludge landfilling is the emergency disposal way due to the rapid increase of the
27 generation amounts in China, while the landfill volume is limited. On the other hands,
28 the soil cover will consume amounts of materials and landfill volume simultaneously. It
29 is interesting to know whether the sewage sludge could substitute the traditional
30 materials for the soil cover in landfill.

31 The direct utilization of sludge in landfill soil cover has been proven to be
32 impossible due to the low mechanical strength and the serous odor emission (Tan 2004).
33 The conversion of sludge into sludge derived carbon might be the suitable way though
34 pyrolysis. As the microorganism aggregative, sewage sludge contains amounts of
35 organic matter, such as lignin, cellulose, which provide the basic construction for the
36 carbon preparation (Liu 2003; Smith et al., 2009). The application of SBC in landfill
37 could reduce the sludge occupied volume, provide the suitable basement for the plant
38 growth in the final soil cover, and enhance the odor adsorption process together.
39 Green-house gas (GHG) of CO₂ and CH₄ could be also reduced greatly through the
40 carbon storage in sludge derivate carbon. Most of important, the introduction of Sludge
41 derived carbon (SBC) in the landfill might be also contribute to the landfill stabilization
42 process though the neutral of pH value, adsorb the acidic compounds and toxicity
43 compounds. Therefore, SBC might be the suitable substitute for the soil cover in
44 landfill, and also be used as the adsorbent or the catalyst for odor removal (Dominic et
45 al., 2012; Fontaine et al., 2012; Manyà. 2012).

46 Generally, the SBC preparation includes the activation process and carbonization
47 process, and the most common activation reagents used are ZnCl₂, H₃PO₄·KOH and
48 KCl (Meyer et al., 2011; Raymundo-Piñero et al., 2005). For example, KOH has been
49 intensive reported based on a hypothesis that the reactions between KOH and carbon (C)
50 would improve the surface area and porosity, while the results showed that the
51 corresponding BET are still as low as 100-200 m² g⁻¹ (Zhu, 2013). To find an effective
52 activation reagent is a big challenge for SBC products, even it used in the landfill.

53 The destruction of the macro-molecular weight organic matters might be useful for
54 the porous carbon generated in SBC. Fenton oxidants could destroy the cell wall due to
55 the generation of hydrogen radical (HO•) with the EV of +2.8 eV (Ema and Malay,
56 2012; Gu et al., 2013), which might contribute to the carbon porosities generated. The
57 introduction of NaClO could also enhance the indirect oxidation through the generation
58 of active chlorine (Cl₂, HOCl, and OCl⁻) and NaOH (Zhang et al., 2011). Both of the
59 powerful oxidants could convert the high biopolymer substances in sludge to
60 low-molecular-weight products efficiently. Besides, the intermediate products of

61 Fe₂O₃ and NaOH could react with carbon in sludge, and produce CO₂ and other gas
62 emission, which will benefit for the porous generated in the SBC.

63 In this work, two activation reagents of Fenton, and NaClO were introduced to
64 improve the SBC quality, and the morphology and structure property in SBC were
65 compared. The adsorption capacity was tested using the methyl blue (MB) simulated
66 dying wastewater. The removal efficiency of odor was simulated and the potential
67 utilization routes for SBC in landfill were also proposed.

68

69 2. Materials and methods

70 2.1 Sludge samples

71 Sludge samples were collected in the secondary sludge tank from Minhang
72 municipal wastewater treatment plant in Shanghai, China, with a typical A/O activated
73 sludge treatment process. The sludge obtained was dewatered by the centrifuge at the
74 rate of 4,000 rpm (round per minute) for 5 minutes in laboratory. The sewage sludge
75 properties are listed in Table 1.

76

77 Table 1 Properties of sewage sludge

TS (%)	pH	VSS/TSS (%)	TCOD (mg L ⁻¹)	TN(mg L ⁻¹)	TP(mg L ⁻¹)
0.8-1.05	6.00-6.66	68.00-69.58	25000-37000	92-130	217-268

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79

80 2.2 Activation and preparation processes

81 SBC was prepared with chemical activation methods, involving pre-drying,
82 preparation, carbonization, and washing processes (Lillo-Ródenas et al., 2008; Meyer
83 et al., 2011). Dewatered sludge was dried at 105 °C until constant weight obtained.
84 Sludge was then soaked in 0.8 mol L⁻¹ NaClO solution (Sinopharm Chemical Reagent
85 Co., Ltd, active chlorine, 5.68% w/v, aqueous solution), with the optimum ratio of 0.5
86 according to our previous works (Zhu, 2013). Samples of 500 mL raw sludge solution
87 were placed in the reactor at room temperature and stirred with the dropwise addition of
88 1.0 M H₂SO₄ until a desired pH of 3 reached. The H₂O₂/FeSO₄·7H₂O molar ratio of

89 5:1, and H₂O₂ dosage of 5% were added into the solution based on our preliminary
90 work (Gu et al., 2013). Both of sludge activated by NaClO and Fenton were stored as
91 the precursors for the next step.

92 The dried mixtures were pyrolysis in a horizontal quartz glass tube furnace
93 (HTL1100-60, HAOYUE, Shanghai, China) at 600°C for 2 h, taking N₂ as protect gas
94 with flow rate of 400 mL min⁻¹. The pyrolysis carbon was washed by 10% (v/v) HCl at
95 105°C and successive soaking in distilled water until constant pH reached. The final
96 SBC products were obtained after dried at 105°C. All the samples were labeled as
97 number and reagent. Meanwhile, a control sample was prepared in the same processes
98 without reagent impregnation, and the same carbonization process was implemented to
99 produce SBC.

100 2.3. Characterization of SBC-carbon

101 SBC surface is an interconnection network of micro pores, meso pores, and macro
102 pores (Nguyen et al., 2010). The porous structure was observed by scanning electron
103 microscopy (SEM) at 15.0 kV. Pore size distribution and specific surface area were
104 measured by N₂ adsorption and desorption isotherms at 77 K by Quantachrome
105 Instruments. Desorption data of N₂ isotherm were used to determine pore size
106 distribution with Barrett-Joyner-Halenda (BJH) method. Evaluated pore sizes range
107 from approximately 1.5 to 100 nm in radius. Specific surface area of activated SBC was
108 calculated with BET function, and dubinin-radiuskevitch (DR) method was used to
109 evaluate the micro pore volume.

110 Percentage of elements carbon (C), hydrogen (H), and oxygen (O) were
111 determined, and C was oxidized to CO₂ and analyzed by CS analyzer (CS-3000, NCS
112 Testing Technology, Shanghai, China). Elements H and O were tested using ONH
113 analyzer (ONH-3000, NCS Testing Technology, Shanghai, China), which H in samples
114 was released in form of H₂ and content was determined by a thermal conductivity cell,
115 while O was converted into CO at 2300°C and measured by infrared spectroscopy.
116 Activated SBC was measured by a FTIR spectrometer (Nicolet 6700, ThermoFisher) at
117 25°C. Samples were diluted in potassium bromide (KBr) and compacted into a thin
118 membrane at 8.0 T cm⁻² for 2 min.

119

120 2.4 Adsorption capacity and adsorption isotherms

121 Varied dose (0.5 to 2.5 g L⁻¹) of SBC was added into 100 mL Methylene Blue (MB)
122 solution (with the initial concentration of 20-125 mg L⁻¹) in a 250 mL flask and shaken
123 for 60-120 min until the equilibrium obtained at 25°C. The exhausted adsorbent was
124 filtered by 0.45 µm filter. Batch experiments were performed at 100 rpm. Solution
125 samples were taken at a given time and immediately centrifuged at 14,000 rpm for 3
126 min to remove the adsorbent. MB concentrations were measured by UV
127 spectrophotometer (Unico, UV 2102, Shanghai) at 664 nm and the effect of dose of
128 SBC was determined accordingly.

129 The amount of adsorbed at equilibrium was estimated by:

$$130 \quad q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

131 where q_e (mg g⁻¹) is the amount of adsorbed at equilibrium, C_0 and C_e (mg L⁻¹) are the
132 initial and equilibrium MB concentration respectively. V (L) is the volume of the
133 solution and W (g) is the mass of adsorbent. MB removal efficiency is estimated as:

$$134 \quad \text{MB Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

135 where C_0 and C_e (mg L⁻¹) are the initial and equilibrium MB concentration respectively.
136 Langmuir isotherm was used to analyze equilibrium based on the assumption of
137 monolayer coverage of adsorbate over an adsorbent surface, which has been
138 successfully used to explain the adsorption of dyes from solutions (Hameed, et al.,
139 2007).

140 Langmuir isotherm is shown as:

$$141 \quad q_e = \frac{q_m K_1 C_e}{1 + K_1 C_e} \quad (3)$$

142 where q_m (mg g^{-1}) represents maximum monolayer coverage capacity of adsorbent and
 143 K_l (l mg^{-1}) is Langmuir isotherm constant. The essential features of Langmuir isotherm
 144 would be expressed in terms of equilibrium parameter R_l :

$$145 \quad R_l = \frac{1}{1+(1+K_l C_0)} \quad (4)$$

146 in which value of R_l indicates the adsorption nature be either unfavorable ($R_l > 1$),
 147 linear ($R_l = 1$), favorable ($0 < R_l < 1$), or irreversible ($R_l = 0$).

148

149 3. Results and discussion

150 3.1. Effect on porous structure of SBC

151 The porous structure and morphology of SBC are shown in Table 2. It could be
 152 found that BET in SBC increased from 38 to 253 and 423 $\text{m}^2 \text{g}^{-1}$ after activated by
 153 Fenton and NaClO, respectively. The total pore volume increased from 0.066
 154 (SBC-control) to 0.184 (SBC-Fenton) and 0.513 $\text{cm}^3 \text{g}^{-1}$ (SBC-NaClO), and the
 155 corresponding micropore volume increased from 0.004 to 0.078 $\text{cm}^3 \text{g}^{-1}$ and 0.238 cm^3
 156 g^{-1} . The highest $V_{\text{micro}}/V_{\text{total}}$ ratio of 46% was observed in SBC-NaClO, and the
 157 corresponding ratio in control and Fenton were 6 and 42%, respectively.

158

159 Table.2. Surface Characteristics of porous structure of sludge-based carbon

	BET ($\text{m}^2 \text{g}^{-1}$)	V_{total} (cm^3 g^{-1})	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{micro}}/$ V_{total} (%)
Control	38.7	0.066	0.004	6
SBC-Fenton	253	0.184	0.078	42
SBC-NaClO	423	0.513	0.238	46.39

160

161 It could be found that SBC-NaClO had more uniform pores, and the radius was
 162 small but its cumulative volume was large, which resulted in a large BET area. Radii of
 163 all samples were mainly arranged between 15-25Å. SEM images of SBC-activated are
 164 shown in Fig. 1. Surface of control sample (Fig. 1a, 1c) was smoother than the other
 165 SBC samples. SBC-NaClO (Fig. 1b) contained much more small pores. For

166 SBC-Fenton sample (Fig. 1d), the surface showed more rough, with the presence of
167 irregular coral, and the micro and mesopore predominated in the structure.

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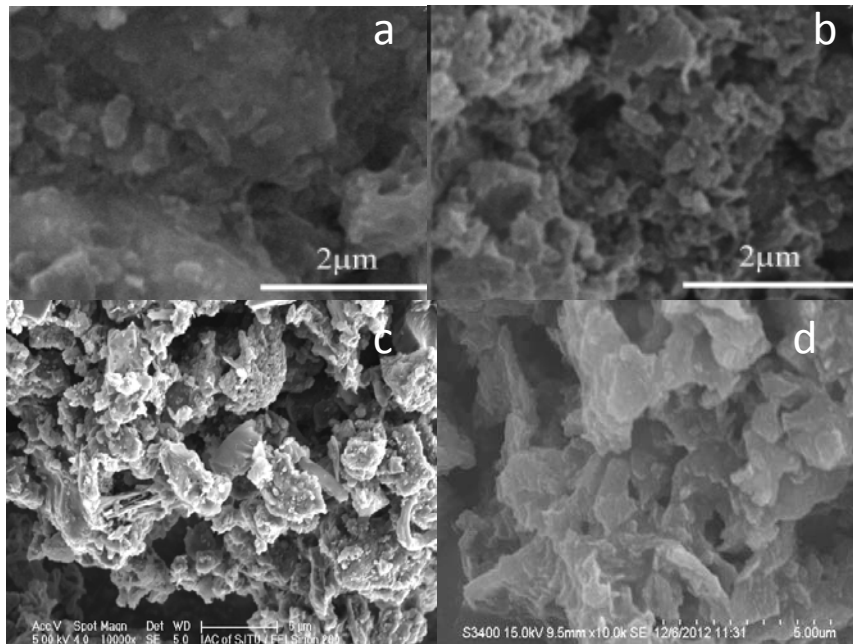
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190 Fig. 1 SEM image of SBC, a) SBC-control and b) SBC-NaClO; c) SBC-control and d)
191 SBC-Fenton

192

193 3.2 Elements distribution

194 Element distribution could be used to reflect the efficiency of activation process.

195 The generation rate, ash content and main elements in SBC-Fenton and SBC-NaClO

196 are shown in Table 3. Percentages of C, H, and O in control sample were 32.45, 2.11,

197 and 13.25%, respectively. The C ratio increased after activated by NaClO, since NaClO

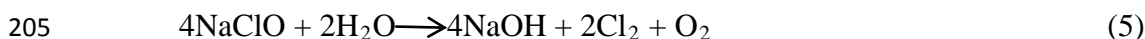
198 was able to disrupt the binding interaction between extracellular polymeric substances

199 (EPS) and cell, and the detached EPS could furthermore dissolve into solution under

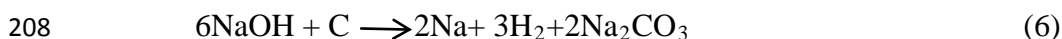
200 the centrifugal force (Abelleira et al., 2012), although parts of element C might lose in

201 the preparation process. The amount of O contents in SBC-NaClO was evidently higher

202 than the control group, because some water was added with the activation reagent
 203 solution during preparation and increased the percentage of O and H, which was shown
 204 in Eq. (5)



206 Then, the intermediate product of NaOH reacted with C during the activation at
 207 600 °C as follows (Raymundo-Piñero et al., 2005):



209 Residual of Na₂CO₃ might also contribute to the high O contents in SBC-NaClO.

210 Table.3 The element distribution in SBC

	SBC-Control	SBC-NaClO	SBC-Fenton
Yield(%)	32.3	31.2	35.7
Ash content(w%)	52.8	50.4	60.9
C(w%)	35.6	37.51	32.3
N(w%)	1.75	1.65	1.57
S(w%)	0.44	0.72	0.56
H(w%)	0.99	3.30	0.83
O(w%)	14.5	15.77	17.3
Fe(w% in the ash)	18.9	20.1	49.7

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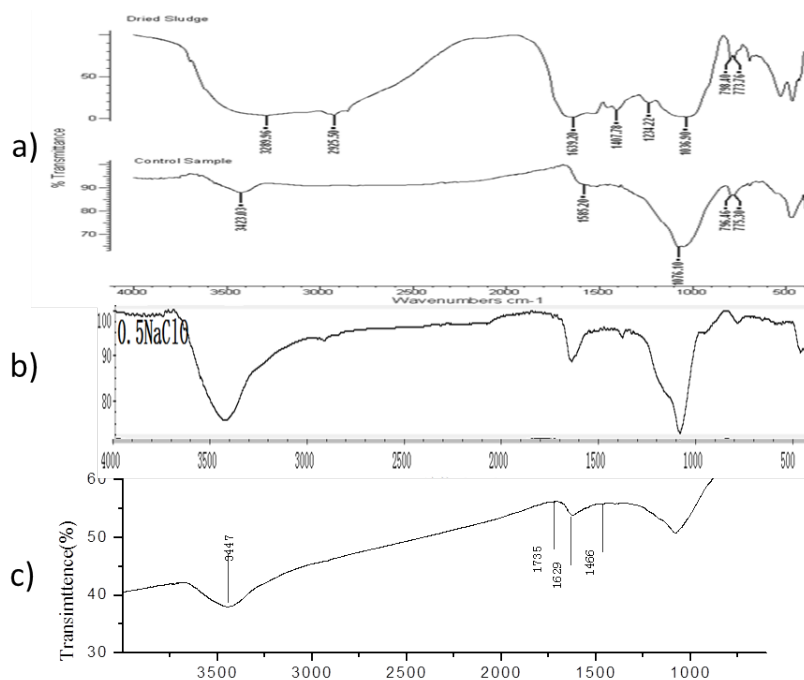
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213 Compared to the control group, the ash content in SBC-Fenton increased from
 214 52.8 to 60.9%, and the C/H/N decreased apparently, among which C content decreased
 215 from 35.6 to 32.3%, since some carbon was released in terms of CO₂ during the Fenton
 216 reaction. It should point out that the oxidation capacity of ·OH (2.85 mV) was higher
 217 than that of ClO⁻ (1.61 mV), which lead to the decrease of C ratio and the increase of
 218 ash ratio in SBC-Fenton, compared to the SBC-NaClO, meaning that the oxidant
 219 capacity is an important factor from the SBC generation rate perspective. In addition, S
 220 in sludge could convert into SO₄²⁻ in Fenton reaction system, instead of H₂S, and thus
 221 increase S percentage. Fe content in SBC- Fenton increased apparently from 18.9 to
 222 49.7% in the ash due to the introduction of FeSO₄.

223

224 3.3 FTIR Spectroscopy

225 FTIR spectra of dried sludge and control sample are shown in Fig. 2a. All of
 226 samples spectra exhibited a prominent peak located at 3300–3500 cm^{-1} , which was
 227 associated with the presence hydroxyl groups. As seen from spectrum of dried sludge,
 228 transmittance peak at about 2925 cm^{-1} was assigned to vibration of O-H stretching.
 229 Peak of O-H deformation was found at 1407 cm^{-1} . Peak at 1234 cm^{-1} was related to the
 230 strong infrared vibration of the C-O stretching. Those peaks could not be found at
 231 spectrum of SBC, since the carbonization process destroyed the structure of SBC
 232 greatly. Peak at 3289 cm^{-1} was the vibration of O-H stretching in broad region of
 233 3700-3200 cm^{-1} , which shifted to 3423 cm^{-1} in spectra of SBC (Gómez-Serrano et al.,
 234 2002). C=O stretching in spectrum of dried sludge was found at 1639 cm^{-1} , whereas it
 235 was detected at 1585 cm^{-1} in spectrum of SBC. The frequency range of 1100-1000 cm^{-1}
 236 was associated with C-O stretching. It could be seen at 1036 and 1076 cm^{-1} in spectrum
 237 of dried sludge and SBC respectively. There were two vibration of C-H deformation at
 238 aromatics in dried sludge and SBC, which moved from the peak of 798 and 773 cm^{-1} in
 239 dried sludge to 796 and 775 cm^{-1} slightly in SBC.



240 (a) Dried sludge and SBC-control, (b)SBC-NaClO (c)SBC-Fenton

241 Fig.2 FTIR spectra scan of SBC with and without activation

242 FTIR spectra of SBC-NaClO are shown in Fig. 2b. The stretching vibration of

245 O-H bond, C=O bond, and C-O bond could be found at 3423, 1585, and 1076 cm^{-1} ,
246 compatible with those in the spectrum of SBC. There was one deformation of C-H bond
247 in the range of 760-800 cm^{-1} in SBC-NaClO sample. NaClO solution might modify a
248 C-H bond of SBC during activation process. On the other sides, more peaks were
249 disappeared in SBC-Fenton (Fig. 2c). The stretching vibration of O-H bond could be
250 seen at frequency of 3300-3500 cm^{-1} in SBC-Fenton, while peaks of $-\text{CH}_3$ and $-\text{CH}_2$
251 were disappeared at 2920 cm^{-1} , meaning that the polysaccharide, protein and high
252 molecular polymer etc., in sludge were decomposed into small-molecular weight
253 substances after Fenton reactions. The transmittance at 1735, 1629 and 1466 cm^{-1}
254 decreased in the SBC-Fenton samples, which was related to the stretching vibration of
255 C=O, O-H and C-O bond, ascribed that the polycyclic organic matter might be
256 decomposed (Kaçan et al., 2012). Band at 1629 cm^{-1} was believed to arise from
257 aromatic C-C bonds which were polarized by oxygen atoms bond. This might be
258 related to the oxygen groups incorporated to the carbonaceous phase attacked by the
259 hydroxyl radicals. The region near 1466 cm^{-1} was commonly associated with carbonyl
260 (C=O) and alkene (C=C) bonds, which were normally from the vibration of small
261 molecule organics.

262

263 3.4 The adsorption capacity of MB

264 NaClO activation could destroy the EPS and cell wall in sludge, and reduce the
265 volatilization during pyrolysis of mesopores and macropores simultaneously. It was
266 found that around 95 and 99% of MB could be adsorbed by the SBC-Fenton and
267 SBC-NaClO under the dosage range of 0.5-2.5 g L^{-1} , respectively, with the initial MB
268 concentration of 20-40 mg L^{-1} at 25 $^{\circ}\text{C}$.

269 The adsorption balance between the agent and the adsorbent, affinity, adsorption
270 mechanism and adsorption capacity could be measured by adsorption isotherms, and
271 used to test the adsorption capacity of SBC. Langmuir and Freundlich model were
272 applied to simulate the adsorbent capacity of SBC obtained, and the parameters of
273 Langmuir and Freundlich model are listed in Table 4. Both of SBC-NaClO and
274 SBC-Fenton have a good monolayer adsorbent capacity, with the value of 67.83 and

275 71.50 mg g⁻¹, while that in SBC-control was only 33.10 mg g⁻¹.

276 Table 4. Parameters of adsorption models of MB on SBC

Isotherms	Parameters	SBC-Fenton	SBC-NaClO	SBC-Control
	q _m (mg g ⁻¹)	71.50	67.83	33.10
Langmuir	K _l (L mg ⁻¹)	0.0148	2.01	0.03
	R ²	0.995	0.980	0.990
	K _f (mg g ⁻¹)	56.6	38.23	2.67
Freundlich	1/n	0.0534	0.20	0.50
	R ²	0.661	0.92	0.98

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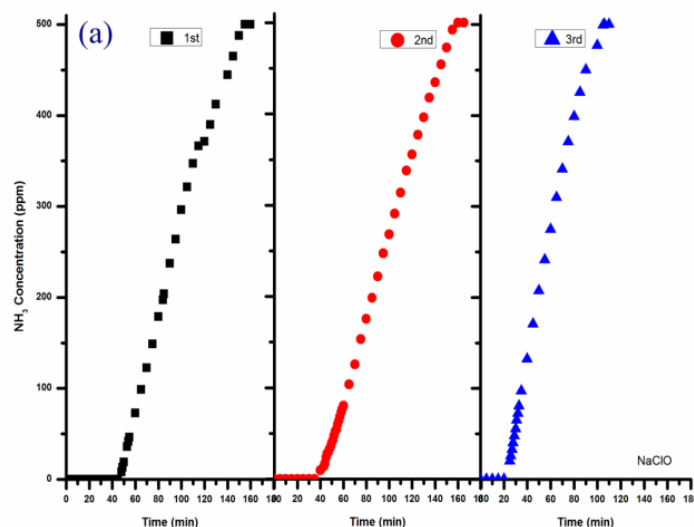
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279 3.5 The odorous removal capacity of SBC

280 Odorous compounds from municipal solid waste (MSW) usually include
281 reduced sulfur, nitrogen compounds, organic acids, aldehydes, and ketones, where
282 hydrogen sulphide (H₂S) and ammonia (NH₃) are identified as the two predominant
283 odorants (Dincer et al., 2006; Ding et al., 2012; Fang et al., 2012). Both of these two
284 odors were considered for the potential odor reduction. SBC-NaClO was used to
285 adsorb NH₃, and SBC-Fenton was used to remove H₂S according to their respective
286 property.

287 Dynamic NH₃ adsorption was carried out in a fixed bed configuration at 20°C. 1
288 g of SBC-NaClO samples were packed into a U shape glass tube (9 mm of internal
289 diameter) as the adsorbent. The input gas consisted of 500 ppmv (mol mol⁻¹) of NH₃
290 passed through the bed at flow rate of 100 mL min⁻¹, combined with the carrier gas of
291 N₂. Concentration of input and outlet NH₃ was monitor by a gas detector (pGas200,
292 Cnshsh Ltd.). Adsorption experiments were performed until the bed exhaustion, which
293 50 ppmv (mol mol⁻¹) NH₃ breakthrough capacities (mg of NH₃ per gram of carbon)
294 were calculated by integration of the breakthrough curves taking into account the input
295 concentration of NH₃, flow rate, breakthrough time and the mass of used carbon
296 (ASTM, 2008). Three cycles of NH₃ adsorption breakthrough curves are shown in Fig.
297 3, and all samples presented a sharp adsorption profile, indicating fast kinetics of

298 interactions between SBC and NH₃.



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Fig.3 The isothermal equation of NH₃ adsorbent using SBC-NaClO

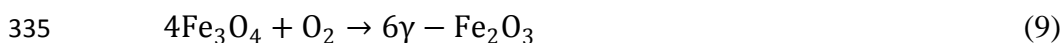
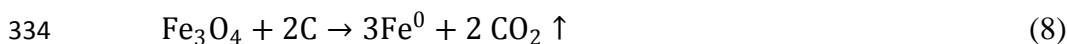
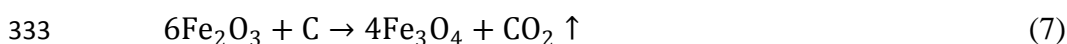
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302 The regeneration was implemented using thermal treatment at 105 °C. A small
303 decrease was observed in the secondly round, while the amount of adsorbed was 52%
304 of the original adsorption in the third cycle. The NH₃ breakthrough capacity for
305 SBC-NaClO was around 2.1, 2.0 and 1.1 mg g⁻¹ in the first 3 cycle, respectively. The
306 effect of heating on regeneration reduced with cycle times increasing, suggesting that
307 the preferential interactions between NH₃ and oxygen surface groups, especially the
308 acidic groups, on carbon surface were the key factor of determining adsorption capacity.
309 Generally, the adsorption capacity of SBC-NaClO for ammonia was relatively weak,
310 and the amount of less stable oxygen surface groups played a crucial role in the
311 adsorption-regeneration cycles, which resulted in a good regeneration effect due to the
312 ammonia desorption ability.

313 SBC-Fenton could be the good adsorbent for H₂S removal (Ros et al., 2006). It
314 was found that H₂S removal rate increased as the SBC-Fenton dosage increased, and
315 around 29.2, 34.9, 37.1, 42.5 and 44.2% of H₂S were removed, with the SBC-Fenton
316 additive of 2, 4, 6, 8 and 10 g and 10 mL H₂S in the initial stage. The high micro pore
317 rate of 47% in SBC-Fenton contributes to the H₂S removal, and the presence of Fe is
318 also helpful for the form the crystal as Ca₂Fe₂O₅ during the carbonization process. The
319 formation of Ca₂Fe₂O₅ and other Fe form in SBC-Fenton was useful for H₂S reduction.

320 Therefore, the mixture of the SBC-Fenton and SBC-NaClO might be a good soil cover
321 for landfill.

322 Generally, sewage sludge was the aggregation of microorganisms, which the cell
323 wall was wrapped by EPS, and the binding water presented between polymer in the
324 extracellular and cell wall. Polysaccharide and the binding water were decomposed and
325 evaporated during the carbonization process between 550 and 650 °C, which lead to
326 the formation of large pores, and low BET value without any activation process.
327 However, activation process by Fenton could improve the SBC property greatly, since
328 the generation of ·OH destroyed the microorganism structure, and decomposed the
329 large molecular weight organic matter into the small and medium organic matter. These
330 intermediate organic matters were helpful for the formation of CO₂ and H₂O during the
331 carbonization process. The SBC property benefit from the introduction of Fe, since the
332 Fe₂O₃ and Fe₃O₄ in the precursor react with C in a high temperature as follows:



337 All of these reactions produced CO₂, with the molecular diameter of 0.33 nm,
338 which contributed to form the micro-pore in SBC obtained.

339 For the NaClO additive, it could produce Cl₂ and NaOH during the activation
340 process, and contributed to the generation of more porosities as shown in Eq. (5). The
341 ClO destroyed the C-C bond in EPS and thus dewater the binding water between
342 polymer EPS and cell wall. The intermediate product of NaOH could react with C
343 during the carbonization process (550-650 °C), and thus produce micro-pores, as
344 shown in Eq. (6).

345

346 **4. Conclusions**

347 Higher quality SBC was prepared with the activators of Fenton and NaClO. Both
348 of them contributed to the increase of BET and $V_{\text{micro}}/V_{\text{total}}$, which were 6.7 and 11
349 times higher than SBC-control. Activation process was necessary to applied to improve

350 the SBC quality by destroying of cell wall barrier and decompose of the complex macro
351 compounds. The intermediate products of Fe and NaOH contributed to SBC-activated
352 structure. The saturation adsorption capacity could be around 71.5, 67.8 and 33.1 mg
353 g⁻¹ in SBC-Fenton, SBC-NaClO and SBC-control using MB. SBC could be a promising
354 substitute soil cover in landfill, instead of volume occupied.

355

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363 **References :**

- 364 [1]. Abelleira, J., Pérez-Elvira, S.I., Sánchez-Oneto, J., Portela, J.R., Nebot, E. (2012)
365 Advanced thermal hydrolysis of secondary sewage sludge: a novel process
366 combining thermal hydrolysis and hydrogen peroxide addition. *Resour. Conserv.*
367 *Recy.* 59:52-57
- 368 [2]. ASTM standard (2008) Standard test methods for determination of the accelerated
369 hydrogen sulfide breakthrough capacity of granular and pelletized activated carbon.
370 D6646-03.
- 371 [3]. Chan G.Y.S., L.M. Chu, M.H. Wong (2002) Effects of leachate recirculation on
372 biogas production from landfill co-disposal of municipal solid waste, sewage
373 sludge and marine sediment. *Environ. Pollut.* 118: 393-399
- 374 [4]. Ding, Y., Cai, C. Y., Hu, B., Xu, Y. E., Zhe, X. J., Chen, Y. X., Wu, W. X. (2012)
375 Characterization and control of odorous gases at a landfill site: A case study in
376 Hangzhou, China. *Waste Manage.* 32: 317-326.
- 377 [5]. Dominic Woolf, James E. Amonette, F. Alayne Street-Perrott, Johannes Lehmann,
378 Stephen Joseph (2010) Sustainable biochar to mitigate global climate change.

- 379 Nature Commun. 1: 1–9.
- 380 [6]. Ema, S. Elmolla, Malay Chaudhuri (2012) The feasibility of using combined
381 Fenton-SBR for antibiotic wastewater treatment. *Desalination*. 285:14-21.
- 382 [7]. Fang J., Yang N., Cen D., Shao L., He P. (2012) Odor compounds from different
383 sources of landfill: Characterization and source identification. *Waste Manage.*
384 32:1401–1410
- 385 [8]. Fontaine S., S. Barot, P. Barre, N. Bdioui, B. Mary, C. Rumpel (2007) Stability of
386 organic carbon in deep soil layers controlled by fresh carbon supply, *Nature*. 450:
387 277-280
- 388 [9]. George Tchobanoglous (2000) Hilary Theisen, Samuel Vigil, *Integrated solid*
389 *waste management*. McGraw-Hill
- 390 [10]. Gómez-Serrano V., Álvarez, P.M., Jaramillo, J., Beltrán, F.J. (2002) Formation
391 of oxygen complexes by ozonation of carbonaceous materials prepared from
392 cherry stones I. thermal effects. *Carbon*. 40:513-522.
- 393 [11]. Gu L., Wang Y., Zhu N., D. Zhang, S. Huang, H. Yuan, Z. Lou, M. Wang
394 (2013) Preparation of sewage sludge derived activated carbon by using Fenton's
395 reagent and their use in 2-Naphthol adsorption. *Bioresour. Technol.* 146:779-784.
- 396 [12]. Hameed B H, Din A T M, Ahmad A L. (2007) Adsorption of methylene blue
397 onto bamboo-based activated carbon: kinetics and equilibrium studies. *J. Hazard.*
398 *Mater.* 141:819-825.
- 399 [13]. Kaçan E., C.Kütahyalı (2012) Adsorption of strontium from aqueous solution
400 using activated carbon produced from textile sewage sludge. *J. Anal. Appl. Pyrol.*
401 97:149–157.
- 402 [14]. Liu, Y. (2003) Chemically reduced excess sludge production in the activated
403 sludge process. *Chemosphere*. 50:1-7.
- 404 [15]. Manyà., J.J. (2012) Pyrolysis for SBC purposes: a review to establish current
405 knowledge gaps and research needs. *Environ. Sci. Technol.* 46:7939–7954.
- 406 [16]. Meyer, S., Glaser, B., Quicker, P. (2011) Technical, economical, and
407 climate-related aspects of SBC production technologies: a literature review.
408 *Environ. Sci. Technol.* 45: 473–9483.
- 409 [17]. Ministry of Environment protection/ General Administration of Quality

- 410 Supervision, Inspection and Quarantine of the People's Republic of China (AQSIQ)
411 (2008) Standard for Pollution Control on the Landfill Site of Municipal Solid
412 Waste (GB16889-2008). China Environmental Science Press. Beijing.
- 413 [18]. National Bureau of Statistics of the People's Republic of China/Ministry of
414 Environment protection (2014) China Environmental Statistics 2013. China
415 statistics press. Beijing.
- 416 [19]. Nguyen, B.T., Lehmann, J., Hockaday, W.C., Joseph, S., Masiello, C.A. (2010)
417 Temperature sensitivity of black carbon decomposition and oxidation. *Environ. Sci.*
418 *Technol.* 44: 3324–3331.
- 419 [20]. Raymundo-Piñero, E., Azaïs, P., Cacciaguerra, T., Cazorla-Amórs, D.,
420 Linares-Solano, A., Béguin, F. (2005) KOH and NaOH activation mechanisms of
421 multiwalled carbon nanotubes with different structural organization. *Carbon.*
422 43:786–795.
- 423 [21]. Ros, A., Montes-Moran, M.A., Fuente, E., Nevskaia, D.M., Martin, M.J.
424 (2006) Dried sludges and sludge derived chars for H₂S removal at low temperature:
425 influence of sewage sludge characteristics. *Environ. Sci. Technol.* 40:302-309.
- 426 [22]. Smith, K.M., Fowler, G.D., Pullket, S., Graham, N.J.D. (2009) Sewage sludge
427 derived adsorbents: a review of their production, properties and use in water
428 treatment applications. *Water Res.* 43: 2569-2594.
- 429 [23]. Tan Shenjun (2004) Engineering Application of Sewage Sludge as Daily
430 Cover Material in Refuse Landfills. Master Dissertation. Tongji University. (in
431 Chinese)
- 432 [24]. Tony Liangtong Zhan, Xinjie Zhan, Weian Lin, Xiaoyong Luo, Yunmin Chen
433 (2014) Field and laboratory investigation on geotechnical properties of sewage
434 sludge disposed in a pit at Changan landfill, Chengdu, China. *Eng. Geol.*
435 170:24-32
- 436 [25]. Zhang HaiYing, HongTao Hu, Yi Zheng, Dong Hui Chen (2011) Advanced
437 Treatment of Stabilized Leachate by Sodium Hypochlorite Composite Chemicals.
438 *Key Engineering Materials.* 474-476: 1272-1276
- 439 [26]. Zhu Tianxing (2013) Production and characterization of sludge derived
440 biochar with hypochlorite activation. Bachelor Dissertation. Shanghai Jiao Tong

441 University. (in Chinese)