



## Characterization of adsorption removal of hydrogen sulfide by waste biocover soil, an alternative landfill cover

Ruo He<sup>a,\*</sup>, Fang-Fang Xia<sup>a</sup>, Jing Wang<sup>a</sup>, Chang-Liang Pan<sup>a</sup>, Cheng-Ran Fang<sup>b</sup>

<sup>a</sup> Department of Environmental Engineering, Zhejiang University, Hangzhou 310029, China

<sup>b</sup> School of Civil Engineering and Architecture, Zhejiang University of Science and Technology, Hangzhou 310023, China

### ARTICLE INFO

#### Article history:

Received 25 June 2010

Received in revised form 6 November 2010

Accepted 16 November 2010

Available online 23 November 2010

#### Keywords:

Waste biocover soil

Adsorption

Hydrogen sulfide

### ABSTRACT

Landfill is an important anthropogenic source of odorous gases. In this work, the adsorption characteristics of H<sub>2</sub>S on waste biocover soil, an alternative landfill cover, were investigated. The results showed that the adsorption capacity of H<sub>2</sub>S increased with the reduction of particle size, the increase of pH value and water content of waste biocover soil. The optimal composition of waste biocover soil, in regard to operation cost and H<sub>2</sub>S removal performance, was original pH value, water content of 40% (w/w) and particle size of  $\leq 4$  mm. A net increase was observed in the adsorption capacity of H<sub>2</sub>S with temperatures in the range of 4–35 °C. The adsorption capacity of H<sub>2</sub>S on waste biocover soil with optimal composition reached the maximum value of  $60 \pm 1$  mg/kg at oxygen concentration of 10% (v/v). When H<sub>2</sub>S concentration was about 5% (v/v), the adsorption capacity was near saturation, maintaining at  $383 \pm 40$  mg/kg. Among the four experimental soils, the highest adsorption capacity of H<sub>2</sub>S was observed on waste biocover soil, followed by landfill cover soil, mulberry soil, and sand soil, which was only 9.8% of that of waste biocover soil.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

Odor is considered one of the most important environmental pollution issues, and has recently received increasing attention. Landfill is an important anthropogenic source of odorous gases. Odor pollution impact from landfill sites is often within 2.0 km, but under bad conditions, such as temperature inversion, it can reach above 6.0 km [1]. With the development of society and economy, more and more solid waste is produced. Many landfills in China are surrounded by villages, and odor pollution from landfills has become one of the most common pollution complaints by citizens. Odorous gases from landfills include ammonia, hydrogen sulfide (H<sub>2</sub>S), methyl mercaptan, methyl sulfide, and so on, of which sulfur compounds is a typical odorous gas and comprises about 1% of landfill gas. H<sub>2</sub>S is an important sulfur compound in landfill gas [2,3]. It was reported that landfills where H<sub>2</sub>S concentration was above the standard (0.5–24 times higher than the standard value, 60 ppbv for new landfills established after 1994 and 100 ppbv for old landfills established before 1994) accounted for 7.6% of 329 investigated landfills in China [4]. H<sub>2</sub>S has a characteristic rotten egg odor even at low concentrations. About half of the population can smell it at concentrations as low as 8 parts per billion by volume (ppbv) in

the air, and more than 90% can smell it at levels of 50 ppbv [5]. H<sub>2</sub>S concentration in the landfill bounds reaches the standard level (60–100 ppbv), but people living near landfills still can smell the odor. Moreover, H<sub>2</sub>S concentration is very high in landfill cells, and it can reach 450 ppmv and even more in landfill gas collection tubes [6]. H<sub>2</sub>S not only makes people feel unhappy and disgusted, but also does harm to people [5,7,8]. At levels up to 30–40 ppmv, H<sub>2</sub>S can cause acute poisoning. Instantaneous loss of consciousness, rapid apnea (slowed or temporarily stopped breathing), and death may result from acute exposure to H<sub>2</sub>S levels of 100–200 ppmv [5,9]. Therefore, it is imperative to take effective steps to control H<sub>2</sub>S emission from landfills.

Landfill cover soil is the interface between landfill gas and the atmosphere. A part of H<sub>2</sub>S is removed in landfill cover soil while it is escaping from landfills. The action of landfill cover soil to H<sub>2</sub>S was similar to an open biofilter in passive ventilation. Landfill cover materials act as packed stuff in the biofilter, which directly affect the removal efficiency of H<sub>2</sub>S. Waste biocover soil is much like humus soil, such as compost and stable landfill waste, which has good porous structure, large surface area, high cation-exchange capacity (CEC) and large biomass [10,11]. The previous estimations of its permeability, shear performance, leaching toxicity and expansion and contraction have proved that organic biocover soil is a good alternative cover for landfills [12,13]. Recently, the environmental effects of waste biocover soil as landfill alternative cover have aroused extensive interest from researchers. However, it has focused mainly on the reduction of

\* Corresponding author. Tel.: +86 571 86971156; fax: +86 571 86971156.  
E-mail address: [heruo@zju.edu.cn](mailto:heruo@zju.edu.cn) (R. He).

CH<sub>4</sub> emission [14–16], while its effects on H<sub>2</sub>S removal are poorly understood.

The removal process of H<sub>2</sub>S by waste biocover soil in landfills is similar to that of a biofilter, occurring in two phases: adsorption onto the liquid–solid phase and biodegradation [17,18]. Of these, the adsorption of H<sub>2</sub>S on waste biocover soil, from the air phase to the liquid–solid phase, is the first stage of H<sub>2</sub>S removal when it escapes from landfills. H<sub>2</sub>S removal performance can be significantly improved by combining the biological action of microorganisms with the adsorption of waste biocover soil.

In the paper, batch adsorption studies were conducted to investigate the optimal composition of waste biocover soil, including particle size, water content and pH value. The adsorption isotherm of H<sub>2</sub>S on waste biocover soil as well as the effects of ambient conditions (temperature, oxygen concentration) on the adsorption capacity of H<sub>2</sub>S was studied. Compared with mulberry soil (a soil appropriate for growing mulberry trees), sand soil and landfill cover soil, the adsorption performance of H<sub>2</sub>S on waste biocover soil was estimated.

## 2. Materials and methods

### 2.1. Soil characteristics

Four soils were used in the experiment: waste biocover soil, mulberry soil, landfill cover soil and sand soil. Waste biocover soil was collected from a rural waste bioreactor. After removing large particles, such as stones, plastic, and cellulose textile, waste biocover soil was air-dried and used as experimental material. Landfill cover soil was taken from the top 30 cm of cover soil in Hangzhou Tianziling landfill cell, where municipal solid waste had been landfilled for over 8 years. Sand soil and mulberry soil were taken from Huajiachi campus of Zhejiang University. Physico-chemical properties of experimental soils are shown in Table 1.

### 2.2. Batch experiments of the composition of waste biocover soil

- (1) *Particle size.* Air-dried waste biocover soil was sieved through 0.45 mm, 1 mm, 4 mm, 10 mm, 25 mm mesh, respectively, and the corresponding granules were named as particle size  $\leq 0.45$  mm,  $\leq 1$  mm,  $\leq 4$  mm,  $\leq 10$  mm and  $\leq 25$  mm in the study. The effect of particle size of waste biocover soil on adsorption of H<sub>2</sub>S was determined with the particle size range from  $\leq 0.45$  mm to  $\leq 25$  mm. About 10 g of air-dried waste biocover soil of each particle size was placed into 150 ml serum vials, and adjusted to water content of 40% (w/w) with 200 mg/l NaN<sub>3</sub> (NaN<sub>3</sub> content of 0.13 mg/g (dry weight), as the bioinhibitor).
- (2) *Water content.* The effect of soil water content on adsorption of H<sub>2</sub>S was examined by adjusting the water content from 2% (w/w) to 60% (w/w) with 200 mg/l NaN<sub>3</sub>.
- (3) *pH value.* The influence of pH value on adsorption of H<sub>2</sub>S was determined under the premise of water content of 40% (w/w) and NaN<sub>3</sub> content of 0.13 mg/g (dry weight). Variation of pH value in waste biocover soil was adjusted by addition of HCl and NaOH solutions. Due to high buffer capacity of the soil, soil pH value was measured again at the end of the experiment. The pH value in the soil at the beginning varied between 3 and 11. pH value of waste biocover soil changed a little between the beginning and the end at high pH values (10 and 11), but it was within 0.5.
- (4) *Orthogonal experiment.* Combining the experiments of single-factor (particle size, water content and pH value) with subsequent biodegradation of H<sub>2</sub>S, orthogonal experiment L16(4<sup>3</sup>) in four levels of three factors (particle size, pH and water content) was designed by date processing system (DPS)

software to optimize the composition of waste biocover soil for adsorption removal of H<sub>2</sub>S (Table 2).

About 10 g of air-dried waste biocover soil ( $\leq 4$  mm) was placed into 150 ml serum vials for above batch tests (unless stated otherwise). The serum vials in batch experiments were covered with cling film and allowed to equilibrate after the adjustment of water content and pH value overnight (approximately 12–14 h) at 30 °C, and then sealed with butyl rubber stoppers. Pure H<sub>2</sub>S (minimum purity 99.0%) was injected by a gas syringe into the vials to a concentration of 1% (v/v) in the gas phase. All treatments were performed in three replications and placed at 30 °C on a shaker (100 rpm). After 3 h, about 1 g soil subsample was taken for analysis of the adsorption capacity of H<sub>2</sub>S (a preliminary experiment showed that adsorption equilibrium of H<sub>2</sub>S was achieved within 2–3 h).

### 2.3. Experiments of ambient conditions and adsorption isotherm

- (1) *Temperature.* The effect of temperature on adsorption of H<sub>2</sub>S was determined by incubating waste biocover soil microcosms on temperature-controlled shakers with temperatures ranging from 4 °C to 45 °C. The serum vials were allowed to equilibrate after the adjustment of water content overnight (approximately 12–14 h) at different temperatures.
- (2) *Oxygen concentration.* The gas in the headspace of serum vials was exchanged by N<sub>2</sub> (minimum purity 99.99%) to establish anaerobic condition. Then pure oxygen (minimum purity 99.99%) and H<sub>2</sub>S in order were injected into the vials to H<sub>2</sub>S concentration of 1% (v/v) and oxygen concentration range from 0 to 21% (v/v).
- (3) *Adsorption isotherm.* The adsorption isotherm of H<sub>2</sub>S was determined under a range of H<sub>2</sub>S concentrations varying from 0.1% (v/v) to 10% (v/v). Approximately 1 g soil subsample was taken to analyze the adsorbed amount of H<sub>2</sub>S on waste biocover soil every 15 min. The serum vials were flushed with 5 volumes of serum vial air, and the initial H<sub>2</sub>S concentration (the same H<sub>2</sub>S volume as the first time) was reestablished until the soil reached the adsorption equilibrium (about 3 h).

In addition, about 16.3 g (wet weight) of landfill cover soil, sand soil and mulberry soil, respectively, was placed into 150 ml serum vials and used for comparison.

Each treatment was performed in the same way as the batch experiments: about 10 g of air-dried waste biocover soil ( $\leq 4$  mm), water content of 40% (w/w), NaN<sub>3</sub> content of 0.13 mg/g (dry weight) and incubation at 30 °C (unless stated otherwise).

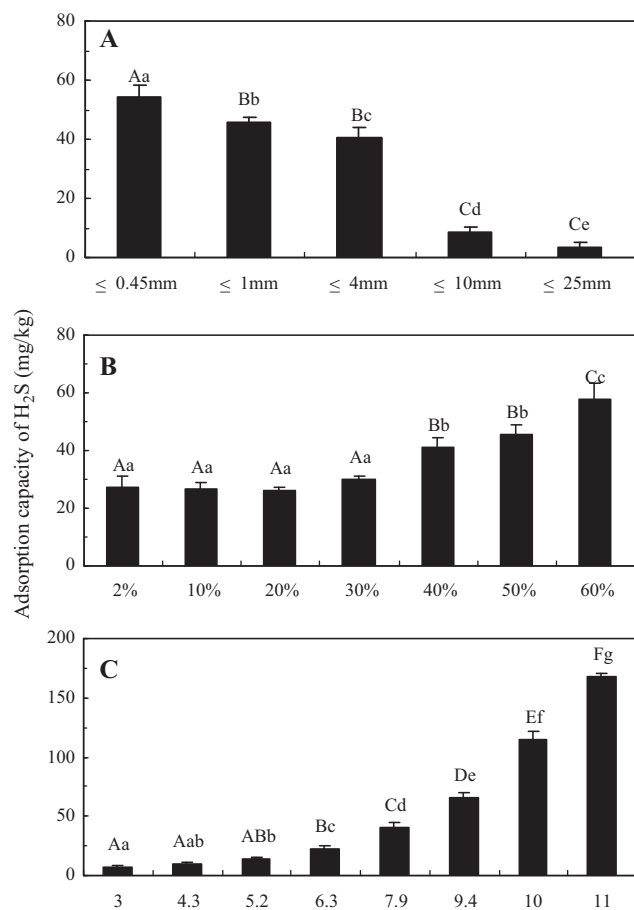
### 2.4. Analysis of adsorptive capacity of H<sub>2</sub>S

The sulfide content of waste biocover soil was determined by the method described by Qiu et al. [19]. The apparatus includes three parts: arsine generator, gas-guide tube with some absorbent cotton, and absorbing tube with 25 ml of 0.1 mol/l zinc acetate. About 1 g soil sample in an arsine generator was mixed thoroughly with 20 ml of 0.055 mol/l zinc acetate, 2.5 ml of 0.63 mol/l vitamin C, 2 ml of 0.083 mol/l cysteine. Then, about 5 g zinc granules and 20 ml of 1:1 hydrochloric acid were put into the generator quickly. After 1 h, 5 ml of 5 mmol/l 1,4-amino-N,N-dimethylaniline dihydrochloride was added in the absorbing tube, and followed by 1 ml of 0.25 mol/l ammonium ferric sulfate. The optical density was measured after 10 min on a spectrophotometer at wavelength of 665 nm. The adsorptive capacity of H<sub>2</sub>S on soil ( $Q_e$ , mg/kg (dry)) was calculated by the following Eq. (1):

$$Q_e = \frac{34(C_e - C_0)}{32m(1 - p)} \quad (1)$$

**Table 1**  
Physico-chemical properties of experimental soils.

Soil types	Water content (%)	pH	Organic matter content (g/kg dry weight)	Total phosphorus (g/kg dry weight)	Total nitrogen (g/kg dry weight)	Sulfide content (mg/kg dry weight)
Waste biocover soil	2.0 ± 0.1 <sup>a</sup>	7.9 ± 0.1	31.4 ± 0.4	1.5 ± 0.1	1.3 ± 0.2	8.6 ± 0.1
Mulberry soil	13.9 ± 0.2	6.8 ± 0.1	5.4 ± 0.1	1.1 ± 0.2	1.2 ± 0.1	8.0 ± 0.0
Landfill cover soil	20.3 ± 0.4	4.9 ± 0.1	15.5 ± 0.3	0.8 ± 0.0	0.5 ± 0.1	7.8 ± 0.2
Sand soil	8.6 ± 0.1	8.6 ± 0.0	1.3 ± 0.1	0.6 ± 0.0	0.1 ± 0.0	4.5 ± 0.1

<sup>a</sup> Mean ± standard deviation (n = 3).**Fig. 1.** Effects of the composition of waste biocover soil on the adsorption capacity of H<sub>2</sub>S. (A) Particle size; (B) water content; (C) pH value. Means with the same small letter(s) and capital letter(s) are not significantly different at  $p < 0.05$  and  $p < 0.01$ , respectively, based on LSD multiple range test.

where  $C_e$  is the sulfide amount of soil after adsorption, mg;  $C_0$  is the initial sulfide amount of soil, mg;  $m$  is the wet mass of soil, kg;  $p$  is the water content of soil, %; and  $34/32$  is the calculated coefficient of H<sub>2</sub>S content based on sulfide content.

### 3. Results and discussion

#### 3.1. Effects of the composition of waste biocover soil on adsorption of H<sub>2</sub>S

The adsorption of H<sub>2</sub>S on waste biocover soil is a gas–solid reaction. Particle size of waste biocover soil influences diffusion, inner-diffusion, adsorption, desorption of gas [20]. The adsorption capacity of H<sub>2</sub>S decreased as particle size of waste biocover soil was increased (Fig. 1). When the particle size of waste biocover soil was ≤ 10 mm and ≤ 25 mm, the adsorption capacity of H<sub>2</sub>S was  $9 \pm 2$  mg/kg and  $3 \pm 1$  mg/kg, respectively, which was only 16.1%, 19.4%, 21.4% and 6.1%, 7.4%, 8.1% of that of particle size of

≤ 0.45 mm, ≤ 1 mm, and ≤ 4 mm. The effect of particle size on the removal capacity of H<sub>2</sub>S was mainly attributed to change in the specific surface area of waste biocover soil. A similar result was found by Delhoménie et al. [20] in toluene removal by a compost-based biological filter.

The adsorption capacity of H<sub>2</sub>S presented an increase trend when the water content of waste biocover soil increased from 30% (w/w) to 60% (w/w), but the soil became over-saturated and water-logged at a water content of 60% (w/w). When pH value of waste biocover soil was 3, the adsorption capacity of H<sub>2</sub>S was 8 mg/kg, which was only 18.4% of that of the original soil (pH 7.9). With the increase of pH value, the removal capacity of H<sub>2</sub>S on waste biocover soil increased sharply. When pH was 11, the removal capacity of H<sub>2</sub>S reached  $168 \pm 5$  mg/kg, about 4 times that of original soil. It has been demonstrated that the basic pH was one of the required conditions for an efficient desulfurization process [21]. The main reason for this was that H<sub>2</sub>S was a soluble weak acid gas. When H<sub>2</sub>S was adsorbed onto waste biocover soil, an enhanced H<sub>2</sub>S dissociation into HS<sup>-</sup> and S<sup>2-</sup> occurred in the water film under strongly basic conditions (Eqs. (2) and (3)) [22].



The form of H<sub>2</sub>S in soils or solutions mainly depends on pH value of ambient conditions. It is mainly H<sub>2</sub>S in acidic solution and no H<sub>2</sub>S exists when pH value is higher than 9; when pH is between 8 and 9, HS<sup>-</sup> is predominant and no S<sup>2-</sup> exists in solution with pH under 8 [23,24]. Under acidic conditions, the adsorption of H<sub>2</sub>S on waste biocover soil is mainly in the form of H<sub>2</sub>S, which escapes easily from the surface. Under basic conditions, however, H<sub>2</sub>S either as liquid or adsorbed phases might participate in a reaction with alkali (OH<sup>-</sup>) on waste biocover soil (Eq. (4)).



Analysis of orthogonal experiment of particle size, water content and pH value of waste biocover soil with SPSS 16.0 showed particle size was the most dominant factor for the adsorption capacity of H<sub>2</sub>S, followed by water content and pH value (Tables 2 and 3). The smaller the particle size of waste biocover soil, the higher the adsorption capacity. As for the air-dried waste biocover soil, about 57.2% (w/w) of the particle was in the size of 1–4 mm, and particle size of 4–10 mm and 10–25 mm accounted for only 9.9% (w/w) and 12.3% (w/w), respectively. The adsorption capacity of H<sub>2</sub>S increased with the increase of water content, but waste biocover soil became slurry when the water content reached 60% (w/w). If such soil was used as an alternative cover soil for landfills, it would enhance leachate volume. So, it is unfeasible to use a saturated waste biocover soil for landfills despite its high removal capacity of H<sub>2</sub>S. Waste biocover soil pH levels in the orthogonal experiment was designed between 6 and 9 because most organisms grow best at neutral pH. Compared with the factors of particle size and water content of waste biocover soil, the effects of pH levels of 6–9 on the adsorption capacity of H<sub>2</sub>S was less ( $p = 0.137$ ). Therefore, the optimal composition of waste biocover soil, in regard to operation cost and removal performance of H<sub>2</sub>S, was original

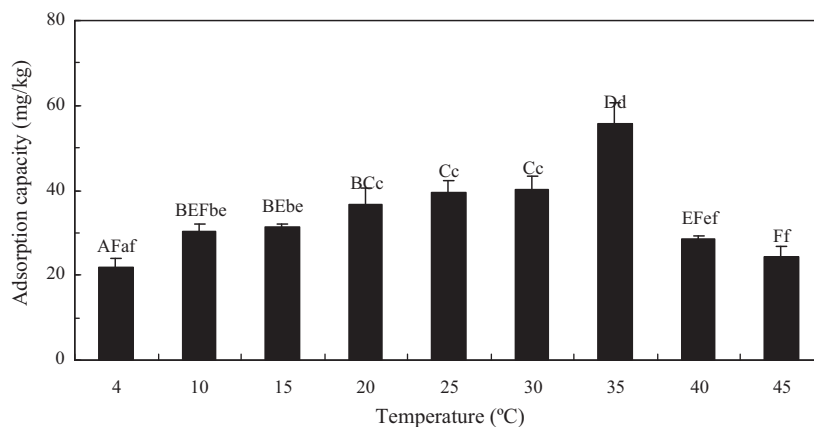


Fig. 2. Effect of temperature on the adsorption capacity of H<sub>2</sub>S on waste biocover soil. The meaning of small letter(s) and capital letter(s) is the same as in Fig. 1.

**Table 2**  
Orthogonal design of the composition of waste biocover soil [L<sub>16</sub> (4<sup>3</sup>)].

No.	Water content (%)	pH	Particle size (≤mm)	Adsorption capacity (mg/kg)
1	2 <sup>a</sup>	6	0.45	36 ± 3 <sup>c</sup>
2	2	7	1	40 ± 0
3	2	7.9 <sup>b</sup>	4	27 ± 1
4	2	9	10	20 ± 4
5	20	6	1	43 ± 3
6	20	7	4	35 ± 0
7	20	7.9	10	8 ± 2
8	20	9	0.45	83 ± 2
9	40	6	4	21 ± 0
10	40	7	10	12 ± 3
11	40	7.9	0.45	71 ± 8
12	40	9	1	94 ± 2
13	60	6	10	28 ± 1
14	60	7	0.45	85 ± 2
15	60	7.9	1	85 ± 3
16	60	9	4	77 ± 5

<sup>a</sup> The water content of the original soil after air drying.

<sup>b</sup> The pH value of the original soil.

<sup>c</sup> Mean ± standard deviation (*n* = 3).

pH value (pH 7.9), water content of 40% (w/w) and particle size of ≤4 mm.

### 3.2. Effect of temperature on adsorption of H<sub>2</sub>S

The transfer rate of the molecular (aqueous) form (H<sub>2</sub>S (aq)) into the gaseous form (H<sub>2</sub>S (g)) enhances with the increase of temperature [25]. A net increase was observed in the adsorption capacity of H<sub>2</sub>S with temperature in the range of 4–35 °C (Fig. 2). This is probably due to the slightly basic condition of waste biocover soil (pH value 7.9). When H<sub>2</sub>S was absorbed in the water film, it easily dissociated into HS<sup>-</sup> and the transfer rate of H<sub>2</sub>S from the water film into the gas decreased consequently. The effect of increasing temperature plays a more influential role in increase of transfer from H<sub>2</sub>S (g) to H<sub>2</sub>S (aq) than in decreased amounts of H<sub>2</sub>S (aq) over the temperature range from 4 °C to 35 °C. The adsorption capacity of

**Table 3**  
Analysis of variance of orthogonal experiment.

Source	Type III sum of squares	df	Mean square	F	Sig. (p)
Water content	3069.185	3	1023.062	4.225	0.063
pH value	1978.124	3	659.375	2.723	0.137
Particle size	5803.704	3	1934.568	7.990	0.016
Error	1452.800	6	242.133		

Note: df, degrees of freedom. F, Fischer's F statistic. Sig. (p), significance level.

H<sub>2</sub>S decreased when the temperature increased to 40 °C. The result was in contrast to Pipatmanomai's finding that the H<sub>2</sub>S capture on activated carbon increased with increasing the reaction temperature to 50 °C in a presence of air [26]. The reasons could be attributed by both physical adsorption and chemi-sorption view points. The moisture content in the gas was high due to high water vapor pressure at high temperatures (40 °C). Water vapor was difficult to condense as water film onto waste biocover soil during the adsorption process. Consequently, the competition adsorption between H<sub>2</sub>S and water onto waste biocover soil might occur when the moisture content in the gas was high [27]. Moreover, there was less reaction in aqueous phase between H<sub>2</sub>S and OH<sup>-</sup> because the liquid water film was thin and H<sub>2</sub>S was less soluble in liquid (water) at high temperature. In addition, the diffusion coefficient of H<sub>2</sub>S was lower when moisture content in gas was higher, which decreased the chances of gas–solid interface contact and depressed the chemi-sorption with metal and other chemicals in waste biocover soil.

### 3.3. Effect of oxygen concentration on adsorption of H<sub>2</sub>S

The effect of oxygen concentration on the adsorption capacity of H<sub>2</sub>S on waste biocover soil is shown in Fig. 3. The adsorption capacity of H<sub>2</sub>S on waste biocover soil was 34–36 mg/kg under anoxic condition. It increased a little with the increase of oxygen concentration, and reached the maximum value of 60 ± 1 mg/kg at oxygen concentration of 10% (v/v), and then decreased a little. Biological activity is one of the main factors controlling the floating equilibrium between loosening and compacting forces in soils [28]. Development of anoxic and anaerobic condition resulted in

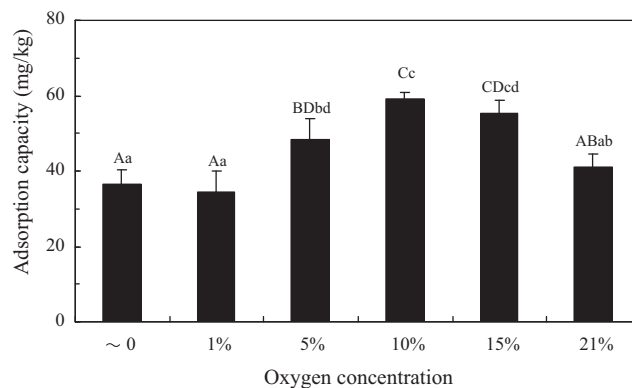
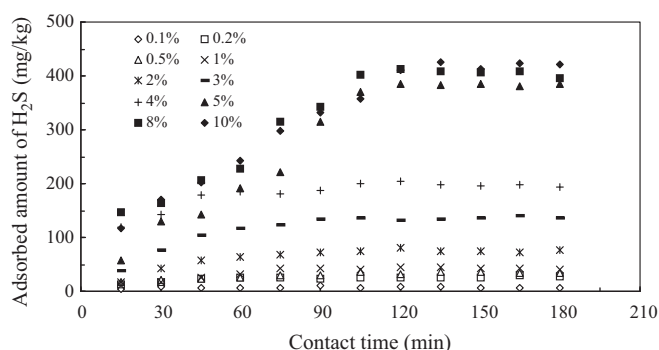


Fig. 3. Effect of oxygen concentration on the adsorption capacity of H<sub>2</sub>S on waste biocover soil. The meaning of small letter(s) and capital letter(s) is the same as in Fig. 1.



**Fig. 4.** Effect of contact time and concentration in the gaseous phase on the adsorbed amount of H<sub>2</sub>S on waste biocover soil.

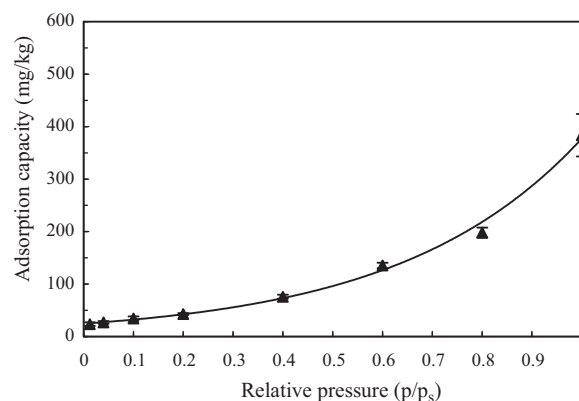
a shift in the soil microbial populations and community structure, which would influence waste biocover soil aggregated structure [29]. Experimental waste biocover soil was observed to become compacted lumps at low concentrations of oxygen. As a result, a low surface area made the adsorption capacity of H<sub>2</sub>S drop. At high concentrations of oxygen, H<sub>2</sub>S is easily oxidized to SO<sub>2</sub>, which resulted in lower concentrations of H<sub>2</sub>S in gas phase than the theoretical. Dissolved oxygen in the water film at the surface of waste biocover soil was enhanced at high concentrations of oxygen in the headspace of the serum vials. Hydrogen Sulfide (HS<sup>-</sup>) underwent chemical oxidation in the presence of excess dissolved oxygen (Eq. (5)) [24]. Moreover, waste biocover soil was rich in inorganic impurities catalyst (silica, alumina, iron oxide, calcium oxide and magnesia), which could catalyze H<sub>2</sub>S oxidation and convert it to elemental sulfur in the presence of oxygen [27,30,31]. Meanwhile, elemental sulfur would be oxidized to sulfate at a slow rate (Eq. (6)) [32]. It was also previously demonstrated that, besides elemental sulfur as the predominant product during the oxidation of H<sub>2</sub>S on activated carbons, around 30% (w/w) of the sulfur was in the form of sulfuric acid [33]. However, further studies are needed in this case to understand the form of deposited sulfur in waste biocover soil.



### 3.4. Adsorption isotherm

The adsorption isotherm was studied using concentrations of H<sub>2</sub>S in the headspace of the serum vials between 0.1% (v/v) and 10% (v/v). The equilibrium time was prolonged with the increase of H<sub>2</sub>S concentration (Fig. 4). Adsorption equilibrium for H<sub>2</sub>S on waste biocover soil was achieved within 2–3 h. When H<sub>2</sub>S concentration was about 5% (v/v), the adsorption capacity was near saturation, maintaining at  $383 \pm 40$  mg/kg. Although the adsorption capacity of H<sub>2</sub>S on waste biocover soil was very limited, it fostered more favorable condition with organic matter content (Table 1), optimal pH for the biodegradation of H<sub>2</sub>S in comparison with other adsorbents such as activated carbons with metal containing bentonite binders, alkaline activated carbon [34,35].

The adsorption capacity of H<sub>2</sub>S on waste biocover soil mainly depended upon three main factors: (a) H<sub>2</sub>S concentration; (b) the characteristics of the water film, such as pH, temperature and ionic strength; (c) the characteristics of waste biocover soil, such as surface area, organic matter, mineral composition, and pore size. Many theories and models have been presented in the literature to describe adsorption isotherms of gases on a wide variety of solids [36–38]. In the study, adsorption characteristics of H<sub>2</sub>S were measured over H<sub>2</sub>S concentrations range from 0.1% (v/v) to 10% (v/v).

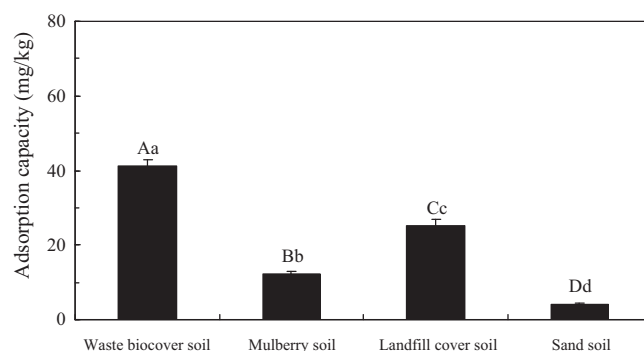


**Fig. 5.** Adsorption of H<sub>2</sub>S at T=303 K on waste biocover soil.  $p_s$  (H<sub>2</sub>S saturation pressure = 5.6 kPa) in the study.

The initial H<sub>2</sub>S concentration in the headspace was reestablished every 15 min, and the gas in the headspace of the serum vials was treated as ideal-gas system. The adsorption of H<sub>2</sub>S at T=303 K on waste biocover soil is shown in Fig. 5. The adsorption isotherm of H<sub>2</sub>S on waste biocover soil differed from the dry adsorbent (activated carbon) isotherms in the presence of water and inorganic impurity catalysts. The adsorption capacity of H<sub>2</sub>S was small at low relative pressures, and enhanced as the relative pressure was increased. It presented that the adsorbate–adsorbent interaction was small compared to the adsorbate–adsorbate interaction, i.e. strongly associating admolecules [39], when H<sub>2</sub>S was adsorbed on waste biocover soil. Adsorption of H<sub>2</sub>S on waste biocover soil is a complicated process, including physical adsorption and chemisorption. Further study on the adsorption isotherm of H<sub>2</sub>S on waste biocover soil is required because the knowledge in this area is limited. The solubility of H<sub>2</sub>S into water film and the reactivity of H<sub>2</sub>S with metal and other chemicals are important issues that need to be explored further.

### 3.5. Adsorption removal of H<sub>2</sub>S on soils

The adsorption capacity of H<sub>2</sub>S was significantly different in the experimental soils (Fig. 6). The highest adsorption capacity of H<sub>2</sub>S was observed on waste biocover soil, followed by landfill cover soil and mulberry soil. The lowest was sand soil, which was only 9.8% of that of waste biocover soil. This was probably due to the different aggregate structure and active surface area of soils. The experimental waste biocover soil was similar to humus soil, which had high CEC and pore volume, and was a good alternative cover soil for removing odorous gas, such as H<sub>2</sub>S, from landfills. In addition, waste biocover soil had a high organic matter content (Table 1),



**Fig. 6.** The adsorption capacity of H<sub>2</sub>S on different soils. The meaning of small letter(s) and capital letter(s) is the same as in Fig. 1.

which provided a good substrate for the growth of microorganisms. The adsorbed capacity of H<sub>2</sub>S on waste biocover soil would be released to sustain microbiological consortia during nutrient-lean inlet condition.

#### 4. Conclusions

The removal performance of H<sub>2</sub>S on waste biocover soil depended on its composition and ambient conditions. The adsorption capacity of H<sub>2</sub>S decreased with the increase of particle size of waste biocover soil. A high water content and pH value enhanced the adsorption of H<sub>2</sub>S via providing a favorable condition for H<sub>2</sub>S dissociation and oxidation. The optimal composition of waste biocover soil, in regard to operational cost and removal performance of H<sub>2</sub>S, was original pH, water content of 40% (w/w) and particle size of ≤4 mm. The adsorption capacity of H<sub>2</sub>S on the waste biocover soil increased over the temperatures range from 4 °C to 35 °C. Waste biocover soil became compacted lumps, and the surface area was reduced, at low concentrations of oxygen. Compared with mulberry soil, sand soil and landfill cover soil, waste biocover soil showed an excellent performance on H<sub>2</sub>S removal and was a good alternative landfill cover for the removal of odorous gases.

#### Acknowledgements

This work was financially supported by National Natural Science Foundation of China with Grant No. 41001148, and Zhejiang Province Natural Science Foundation of China Grants with Nos. Y5090073 and Y5080154.

#### References

- [1] S. Guo, Y.J. Yu, R. Yuan, Effects of secondly pollutants from landfills on environment and resident health, *Foreign Med. Sci.* 34 (2007) 75–79 (in Chinese).
- [2] H.C. Shin, J.W. Park, K. Park, H.C. Song, Removal characteristics of trace compounds of landfill gas by activated carbon adsorption, *Environ. Pollut.* 119 (2002) 227–236.
- [3] K.H. Kim, Emissions of reduced sulfur compounds (RSC) as a landfill gas (LFG): A comparative study of young and old landfill facilities, *Atmos. Environ.* 40 (2006) 6567–6578.
- [4] G.G. Li, J.S. Chao, Z.G. Wang, Current situation of china urban garbage disposal and existing problems, *Environ. Protect.* (4) (2002) 35–38 (in Chinese).
- [5] J. Collins, D. Lewis, 2000. Hydrogen sulfide: evaluation of current California air quality standards with respect to protection of children, 2000. Available at <http://www.ust.is/media/ljosmyndir/mengun/H2S.Evaluation.of.CAAQS.pdf>.
- [6] R. Anderson, J.R. Jambeck, G.P. McCarron, Modeling of hydrogen sulfide generation from landfills beneficially utilizing processed construction and demolition material, Alexandria, VA, 2010. [http://erefdn.org/publications/uploads/H2S\\_Modeling\\_Jambeck-UNH.2-26-10.FINAL.pdf](http://erefdn.org/publications/uploads/H2S_Modeling_Jambeck-UNH.2-26-10.FINAL.pdf).
- [7] D.C. Glass, A review of the health effects of hydrogen sulphide exposure, *Ann. Occup. Hyg.* 34 (1990) 323–327.
- [8] M.S. Legator, C.R. Singleton, D.L. Morris, D.L. Philips, Health effects from chronic low-level exposure to hydrogen sulfide, *Arch. Environ. Health* (56) (2001) 123–131.
- [9] G. Busca, C. Pizarino, Technologies for the abatement of sulphide compounds from gaseous streams: a comparative overview, *J. Loss. Prev. Process Indust.* 16 (2003) 363–371.
- [10] X.L. Chai, S. Takayuki, X.Y. Cao, Q. Guo, Y.C. Zhao, Spectroscopic studies of the progress of humification processes in humic substances extracted from refuse in a landfill, *Chemosphere* 69 (2007) 1446–1453.
- [11] R. He, A.D. Ruan, D.S. Shen, Effects of methane on the microbial populations and oxidation rates in different landfill cover soil columns, *J. Environ. Sci. Health A* 42 (2007) 785–793.
- [12] F. Ingelmo, R. Canet, M.A. Ibañez, F. Pomares, J. García, Use of MSW compost, dried sewage sludge and other wastes as partial substitutes for peat and soil, *Bioresour. Technol.* 63 (1998) 123–129.
- [13] W.A. Elshorbagy, A.M.O. Mohamed, Evaluation of using municipal solid waste compost in landfill closure caps in arid areas, *Waste Manage.* 20 (2000) 499–507.
- [14] M.A. Barlaz, R.B. Green, J.P. Chanton, C.D. Goldsmith, G.R. Hater, Evaluation of a biologically active cover for mitigation of landfill gas emissions, *Environ. Sci. Technol.* 38 (2004) 4891–4899.
- [15] R. He, A.D. Ruan, C.J. Jiang, D.S. Shen, Responses of oxidation rate and microbial communities to methane in simulated landfill cover soil microcosms, *Bioresour. Technol.* 99 (2008) 7192–7199.
- [16] D. Han, Y.C. Zhao, B.J. Xue, X.L. Chai, Effect of bio-column composed of aged refuse on methane abatement – A novel configuration of biological oxidation in refuse landfill, *J. Environ. Sci.* 22 (2010) 769–776.
- [17] H.Q. Duan, L.C.C. Koe, R. Yan, Treatment of H<sub>2</sub>S using a horizontal biotrickling filter based on biological activated carbon: reactor setup and performance evaluation, *Appl. Microbiol. Biotechnol.* 67 (2005) 143–149.
- [18] H.Q. Duan, R. Yan, L.C.C. Koe, X.L. Wang, Combined effect of adsorption and biodegradation of biological activated carbon on H<sub>2</sub>S biotrickling filtration, *Chemosphere* 66 (2007) 1684–1691.
- [19] C.L. Qiu, J.X. Liu, M.L. Peng, Amendment method for sulfide content of soil, *Chinese J. Public Health* 8 (1992) 549–550 (in Chinese).
- [20] M.C. Delhoménie, L. Bibeau, M. Heitz, A study of the impact of particle size and adsorption phenomena in a compost-based biological filter, *Chem. Eng. Sci.* 57 (2002) 4999–5010.
- [21] A. Bagreev, F. Adib, T.J. Bandosz, pH of the activated carbon surface as an indication for its suitability of H<sub>2</sub>S removal from moist air streams, *Carbon* 39 (2001) 1897–1905.
- [22] W.X. Yuan, T.J. Bandosz, Removal of hydrogen sulfide from biogas on sludge-derived adsorbents, *Fuel* 86 (2007) 2736–2746.
- [23] N. Haimour, R. El-Bishtawi, A. Ail-Wahbi, Equilibrium adsorption of hydrogen sulfide onto CuO and ZnO, *Desalination* 181 (2005) 145–152.
- [24] F. Adib, A. Bagreev, T.J. Bandosz, Analysis of the relationship between H<sub>2</sub>S removal capacity and surface properties of unimpregnated activated carbons, *Environ. Sci. Technol.* 34 (2000) 686–692.
- [25] C. Yongsiri, J. Vollertsen, T. Hvitved-Jacobsen, Effect of temperature on air–water transfer of hydrogen sulfide, *J. Environ. Eng.* 130 (2004) 104–109.
- [26] S. Pipatmanomai, S. Kaewluan, T. Vitidsant, Economic assessment of biogas-to-electricity generation system with H<sub>2</sub>S removal by activated carbon in small pig farm, *Appl. Energ.* 86 (2009) 669–674.
- [27] C.C. Huang, C.H. Chen, S.M. Chu, Effect of moisture on H<sub>2</sub>S adsorption by copper impregnated activated carbon, *J. Hazard. Mater.* 136 (2006) 866–873.
- [28] H. Schack-Kirchner, E.E. Hildebrand, Changes in soil structure and aeration due to liming and acid irrigation, *Plant Soil* 199 (1998) 167–176.
- [29] S. Fall, S. Nazaret, J.L. Chotte, A. Brauman, Bacterial density and community structure associated with aggregate size fractions of soil-feeding termite mounds, *Microb. Ecol.* 48 (2004) 191–199.
- [30] V. Meeyoo, D.L. Trimm, N.W. Cant, Adsorption-reaction processes for the removal of hydrogen sulphide from gas streams, *J. Chem. Tech. Biotechnol.* 68 (1997) 411–416.
- [31] T. Nakamura, S. Tanada, N. Kawasaki, T. Hara, J. Fujisawa, K. Shibata, Hydrogen sulfide removal by iron containing activated carbon, *Toxicol. Environ. Chem.* 55 (1996) 279–283.
- [32] D. McNeven, J. Barford, J. Hage, Adsorption and biological degradation of ammonium and sulfide on peat, *Water Res.* 33 (1999) 1449–1459.
- [33] F. Adib, A. Bagreev, T.J. Bandosz, Effect of surface characteristics of wood-based activated carbons on adsorption of hydrogen sulfide, *J. Colloid Interface Sci.* 214 (1999) 407–415.
- [34] R. Yan, D.T. Liang, L. Tsen, J.H. Tay, Kinetics and mechanisms of H<sub>2</sub>S adsorption by alkaline activated carbon, *Environ. Sci. Technol.* 36 (2002) 4460–4466.
- [35] D. Nguyen-Thanh, T.J. Bandosz, Activated carbons with metal containing bentonite binders as adsorbents of hydrogen sulfide, *Carbon* 43 (2005) 359–367.
- [36] I.A.A.C. Esteves, M.S.S. Lopes, P.M.C. Nunes, J.P.B. Mota, Adsorption of natural gas and biogas components on activated carbon, *Separ. Purif. Technol.* 62 (2008) 281–296.
- [37] D. Kim, Z.L. Cai, G.A. Sorial, Determination of gas phase adsorption isotherms—a simple constant volume method, *Chemosphere* 64 (2006) 1362–1368.
- [38] O.A. Pinto, A.J. Ramirez-Pastor, F. Nieto, Adsorption thermodynamics of a lattice-gas model with non-additive lateral interactions, *Surf. Sci.* 602 (2008) 1763–1769.
- [39] J.U. Keller, R. Staudt, *Gas Adsorption Equilibria: Experimental Methods and Adsorptive Isotherms*, Springer, Heidelberg, 2004, pp. 361–362.