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Mechanism for Biological Degradation of H_2S Odour Gas from Livestock Farm

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In this paper, biological removal of H_2S derived from livestock farm was investigated using a self-made biofilter with efficient bioceramics and polyhedral hollow balls. After analyzing the relationship between the mass of the microorganism degrading H_2S and the total mass of input H_2S, it was concluded that, in the process of degradation of H_2S, the concentration of SO_4^{2-} increased with time and sulfate radical could stick to the biofilter firmly. The pH value in the biofilter dropped with degradation of H_2S reaction, the difference between the theoretical value of degradation of S and actual value of degradation of S was increasingly large along with the increase of inlet H_2S concentration. Sulfate ion was the main product in the degradation process. Meanwhile, some of S^{2-} and traces of S element was measured in the biological degradation of H_2S process. Thus, the mechanism of microorganism degrading H_2S could be obtained and it was found that the transformation of H_2S (g) to H_2S (*l*) was a key step in the biodegradation process.

Keywords: Biofilters, Bioreactors, Biokinetics, Kinetic Parameters, H_2S, Degradation mechanism.

INTRODUCTION

In recent years, the livestock and poultry breeding industries have developed rapidly in China and the scale of the livestock industry in general has been continuously enlarged[1,2]. Air pollution derived from the odour of livestock and poultry farming has become a serious problem in the social environmental at present. Odours from livestock operations can not only could cause environmental degradation for humanity, but also has the serious influence on the poultry health of the livestock on the farm. It is a matter of some urgency to eliminate the pollution of odour caused by the livestock farming[2]. In the livestock industry, measurement and control of offensive odour from livestock production facilities are very important because of the requirement of environmental protection[3]. Hydrogen sulfide is a major environment contaminant derived from livestock odour gases. Over 10 ppm of H_2S can affect human health and fatal damage can emerge at higher than 600 ppm[4]. Hence, various odour removal systems have been used to reduce H_2S from livestock farming.

The common methods for removal of H_2S are physical-chemical processes[5]. However, more attention has recently been paid to investigation and application of biological processes due to the high operating costs and unwanted by-products associated with chemical methods[5,6]. However, in the biological degradation of H_2S process many researchers have paid more attentions to the H_2S removal efficiency, such that more than 90 % removal efficiency of H_2S has been obtained in experimental conditions[7,8]. However a few researchers have focused on finding a mechanism for the biological degradation of H_2S. It has been found that S^{2-} transformation into SO_4^{2-} by sulfur microorganisms in the liquid phase can be described[9] as follows: $S^{2-} \rightarrow S^0 \rightarrow S_2O_3^{2-} \rightarrow S_4O_6^{2-} \rightarrow S_3O_6^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-}$. Huang *et al.*[10] have investigated the S^{2-} concentration, the SO_3^{2-} concentration and the SO_4^{2-} concentration with time in biofilter and concluded that at the beginning of the reaction the H_2S concentration in the liquid phase dropped gradually, the SO_3^{2-} concentration hardly changes and on the contrary the SO_4^{2-} concentration increases gradually. The experimental results show that H_2S (g), dissolved in liquid first, then H_2S absorbed and degraded by microorganisms. It is concluded that biodegradation is a control process[10]. At the same time, screening bacteria for removal of H_2S and determination of their desulfurization performance have been reported in the literature[11], but the mechanism for biological degradation of H_2S is relatively sparse[12-14], especially in the term of S mass balance. The aim of this paper is to investigate the relationship between the transformation process of sulfur and different possible forms of sulfur in different experimental conditions to achieve the biodegradation mechanism of H_2S in the biodegradation H_2S process.

EXPERIMENTAL

Experimental apparatus: A self-made biofilter with a 3 L volume made of common organic glass was used in this experiment. The biofilter was filled with the efficient bioceramics

and polyhedral hollow balls as packing materials. The internal diameter of the biofilter was 90 mm and the outside diameter of it was 100 mm, the total height was 900 mm and the packing layer height was 400 mm. The bottom of the biofilter had a sieve plate and enough air and nutrient solution could pass through it smoothly. There was a peristaltic pump between the biofilter and the circular nutrient solution box which made sure that nutrient solution sprayed uniformly into the packing materials from the top of the biofilter. The reactor temperature was controlled by a circulator bath. There was an air flow meter in front of the gas mixer, which was used to measure the flow of H_2S (or air). The schematic diagram of biofilter is shown in Fig. 1 and the experimental set up for the H_2S biodegradation process is shown in Fig. 2.

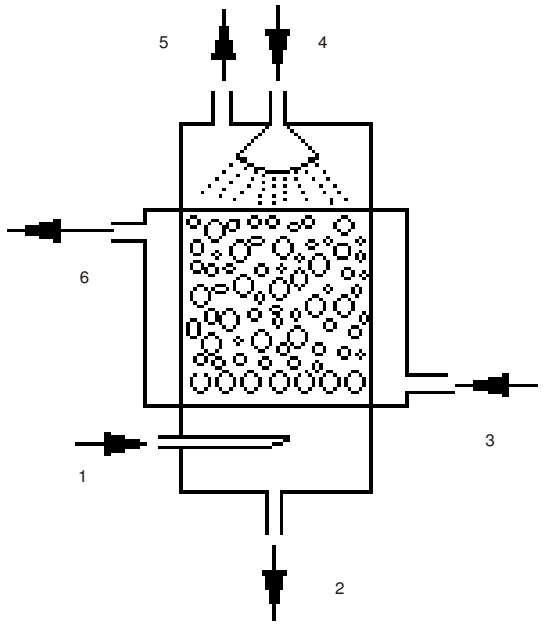


Fig. 1. Schematic diagram of biofilter, 1. Reaction gas inlet; 2. Nutrient solution outlet; 3. Constant temperature water inlet; 4. Nutrient solution inlet; 5. Purified gas outlet; 6. Constant temperature water outlet

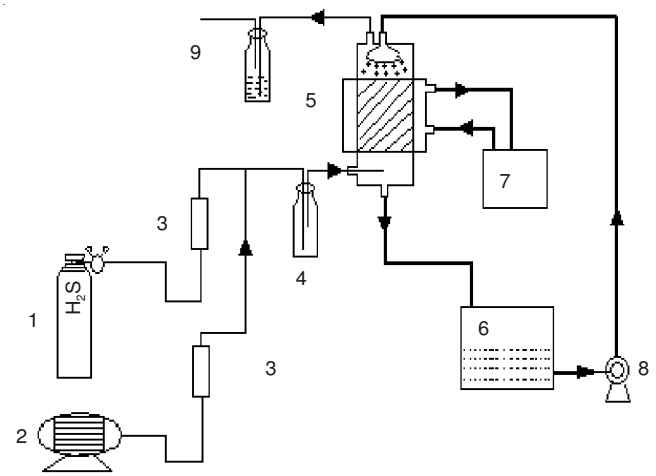


Fig. 2. Experimental set up for H_2S bio-degradation process, 1. H_2S cylinder; 2. Air compressor; 3. Air flowmeter; 4. Gas mixer; 5. Biofilter; 6. Circulation nutrient solution box; 7. Thermostatic water bath; 8. Peristalitic pump; 9. Gas absorption bottle

To start quickly the bioreactor, the way of domesticating active sludge was to add quantitative Na_2S to nutrient solution in fixed time and the value of MLSS and the SO_4^{2-} concentration was regarded as the targets for the effect of domesticating active sludge, which were easier to obtain and more accurate than MLSS value as acclimation targets traditionally. The biofilter was operated by sludge circulation for two days, then the fresh air and the H_2S gas were introduced into the biofilter for 2 weeks and the biomembrane of the reactor was enough to remove the H_2S and H_2S removal efficiency was greater than 99 % at this time. In order to maintain microorganism activity, the nutrient solution was regularly sprayed on the packing materials. The component of the nutrient solution is listed in Table-1. The bioreactor was continuously operated at a temperature range of 15 to 35 ºC.

TABLE-1
COMPONENT OF NUTRIENT SOLUTION

Reagent	Concentration (gL^{-1})
Glucose	0.2
K_2HPO_4	1.2
KH_2PO_4	1.2
$MgCl{\cdot}6H_2O$	0.2
NH_4Cl	0.4
Ferric citrate	0.01

Analysis methods and activity measurements

Analysis methods: In this experiment, the measurement of inlet/outlet H_2S concentration and S^{2-} concentration in nutrient solution were determined according to the standard method (APHA, 1998), the SO_4^{2-} concentration was measured with a 756 spectrophotometer manufactured by the Shanghai Jinghua company through Barium chromate spectrophotometry and the pH value was measured by a pH meter (FE20, Mettler Toledo).

Measurement of S^{2-} concentration: The concentration of S^{2-} in the degradation process was determined by eqn. 1.

$$S^{2-}\,(mg\ L^{-1}) = \frac{(V_0 - V_1)\times C\times 16.03\times 1000}{V} \qquad (1)$$

where V_0 is the volume of standard solution of $Na_2S_2O_3$ in blank test (mL); V_1 is the volume of standard solution of $Na_2S_2O_3$ in titration (mL); V is the volume of nutrient solution (mL); C is the concentration of standard solution of $Na_2S_2O_3$ (mol/L).

Measurement of SO_4^{2-} concentration: The concentration of SO_4^{2-} in nutrient solution was determined by eqn. 2.

$$SO_4^{2-}\,(mg\ L^{-1}) = \frac{m}{V}\times 1000 \qquad (2)$$

where m is the mass of SO_4^{2-} in nutrient solution according to calibration curve (mg); V is the sampling volume of nutrient solution (mL).

Measurement of biodegradation S mass in nutrient solution: The mass of S which was transformed into SO_4^{2-} in nutrient solution can be determined by eqn. 3.

$$M_s \times \frac{(C_T - C_O)\times V\times 32}{96\times 1000} \qquad (3)$$

where M_S is S mass in the final product of SO_4^{2-} (g); C_0 is the concentration of SO_4^{2-} in the initial nutrient solution (mg/L); C_T is the concentration of SO_4^{2-} after running T hours (mg/L); V is the total volume of circular nutrient solution (L).

Measurement of H_2S input: The mass of H_2S input in the biofilter can be determined by eqn. 4.

$$M_{H_2S} = \frac{C_{in} \times Q \times T}{1000} \quad (4)$$

where M_{H_2S} is the mass of H_2S at the inlet of the biofilter (g); Cin is the concentration of H_2S at the inlet (mg/m^3); Q is the air input (m^3/h); T is the time (h).

RESULTS AND DISCUSSION

Concentration of SO_4^{2-} in different height of packing materials: In the condition of pH 5.5, the spray rate 80 mL/min, the temperature 25 °C, the air input 0.2 m^3/h and the concentration of H_2S 300 mg/m^3, after about 30 h of the reactor operation and the H_2S removal efficiency stayed above 99 %. Biofilm samples from the different positions of the biofilter packing layer were taken in order to measure the concentration of SO_4^{2-} in the packing materials. The three positions were located in the top, center and bottom of the biofilter. The concentrations of SO_4^{2-} at different positions are shown in Fig. 3.

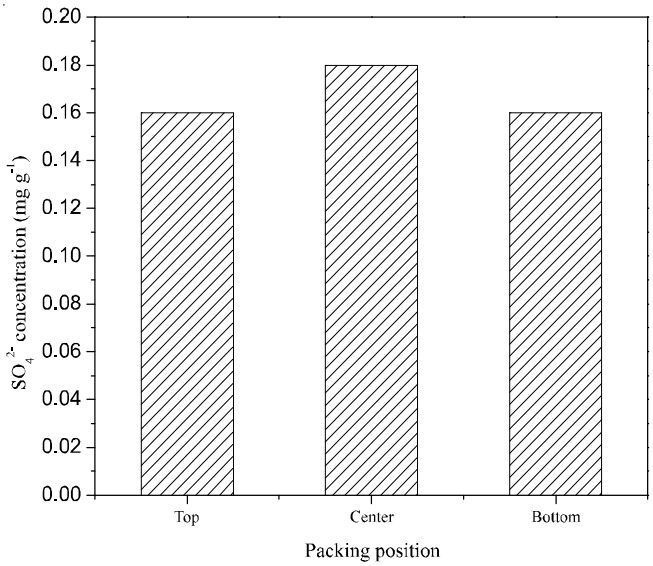


Fig. 3. Concentration of SO_4^{2-} on different positions in packing

As shown in Fig. 3, the concentration of SO_4^{2-} in the center of the packing layer was much higher than that in the top and bottom, but on the whole the SO_4^{2-} concentration was stable in the packing layer. The primary cause was that the biological community in the packing layer distributed uniformly and the H_2S removal efficiency of different positions was basically stable. At the same time, the accumulated SO_4^{2-} in the packing layer could be washed timely by nutrient solution so that the microorganisms in the packing layer could grow well in order to maintain the H_2S degradation process.

Relations of SO_4^{2-} concentration and pH value change in circular nutrient solution: In the condition of pH 6, the spray rate 80 mL/min, the temperature 25 °C, the air input 0.2 m^3/h and the H_2S concentration 100 mg/m^3, the relations of pH value and SO_4^{2-} in nutrient solution are demonstrated in Figs. 4 and 5.

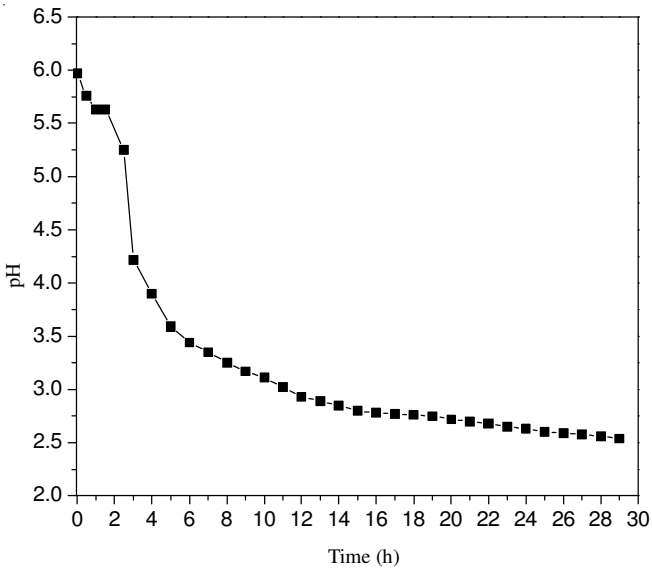


Fig. 4. Change of pH value in nutrient solution with time

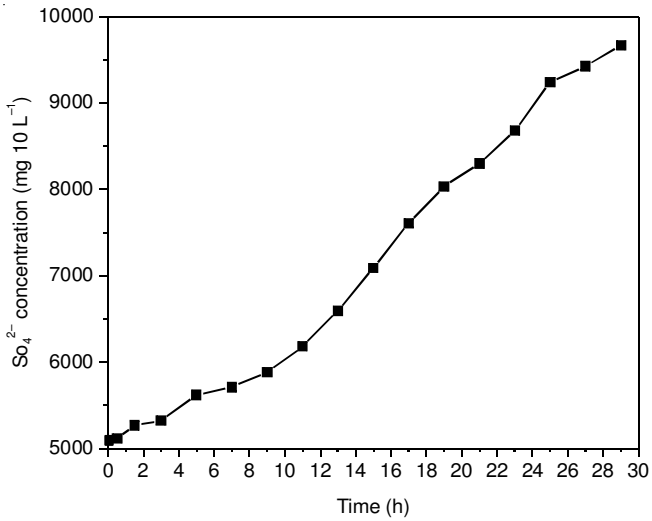


Fig. 5. Change of SO_4^{2-} concentration in circular nutrient solution with time

From Figs. 4 and 5, as the change of the reaction conditions can lead to the inadaptation of desulfurization microorganisms, the SO_4^{2-} concentration and pH value changed slightly at first. After 2 h, the accumulated SO_4^{2-} and H^+ in the packing layer were washed by circular nutrient solution, the concentration of SO_4^{2-} improved greatly while the pH of circular nutrient solution reduced sharply. After 6 h, with the adaptation of microorganisms to the environment in the biofilter, the concentration increment of SO_4^{2-} reached a steady state and the pH value descended slowly. The H_2S re-moval efficiency increased with extension of operation time and reached a steady state, but the relatively low pH value in the circular nutrient solution was unsuitable for the growth of microorganisms. So it was needed to change the nutrient solution immediately in order to maintain the H_2S removal efficiency.

Comparison of the theoretical value of degradation of S and the actual value of degradation of S in the biodegrading H_2S process: As shown in Fig. 6, in the biodegradation H_2S process, the theoretical value and the actual value of S were approximately the same (the errors were less than 3 %) in the condition of the air input 0.2 and 0.25 m^3/h separately and the concentration of H_2S 200 mg/m^3. After 48 h, the theoretical S masses were 1.92 and 2.4 g, while the actual values of S were 1.82 and 2.3 g. However, the theoretical and actual values of S were very different at 0.3 and 0.35 m^3/h air input respectively. The theoretical values of S mass were 2.88 and 3.36 g, while the actual values of S were 2.74 and 3.16 g.

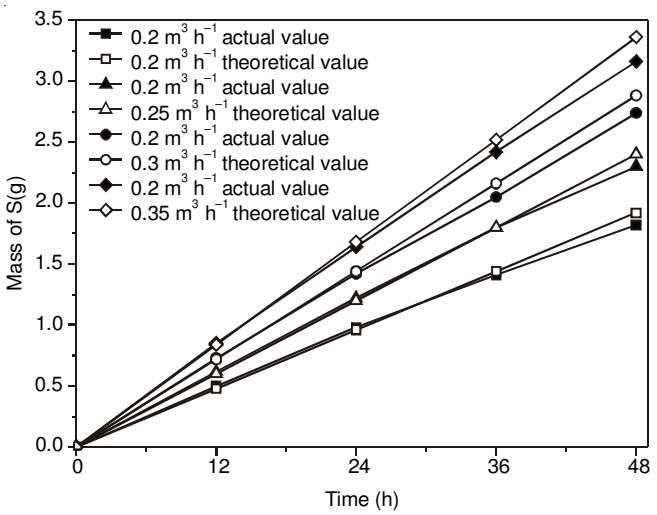


Fig. 6. Change mass of S with time at different air inputs

Fig.7 described the linear regression result of S in the nutrient solution of SO_4^{2-} with time for the actual S mass with different air inputs. In the biodegradation H_2S process, the mass of S which had been transformed into SO_4^{2-} increased linearly and the linear regression coefficients were nearly above 0.99.

In experimental conditions, the mass of S which was transformed into SO_4^{2-} in nutrient solution was larger than the theoretical S mass at the beginning, but with the extended running time, the theoretical S mass was larger than the S mass in nutrient solution reversely. When the theoretical S mass was equal to the actual S mass in nutrient solution in experimental conditions, the running times were 27.1, 29, 14.1 and 12.5 h separately. It was concluded that the low air input could lead to complete H_2S degradation, but the replaced rate of microbial desulfurization was relatively slow. With the increasing air input, the biofilm in packing could be replaced timely, so the actual S mass in nutrient solution was lower than the theoretical S mass.

Biodegradation mechanism for H_2S: Generally, there are three stages in the biodegradation H_2S process Stage I is a physical process, H_2S gas dissolves in liquid phase. Stage II is a mass transfer process, H_2S in liquid phase dissociates and migrates to biofilm surface. Stage III is a bioreaction process, the desulfurization microorganism degrades H_2S on the biofilm.

For Stage I and Stage II, the reaction process can be described as follows:

$$H_2S\ (g) \rightarrow H_2S\ (l) \rightarrow HS^- + H^+ \rightarrow S^{2-} + H^+$$

H^+ and S^{2-} should be in the liquid phase. In order to verify this process, the change of pH value in nutrient solution with time was determined in the condition of H_2S concentration 200 mg/m^3, temperature 20 °C and different air inputs, the results of which are shown in Fig. 8.

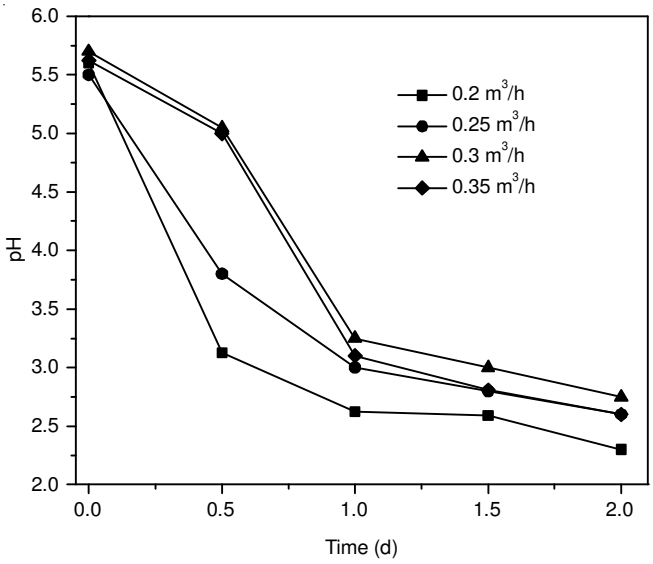
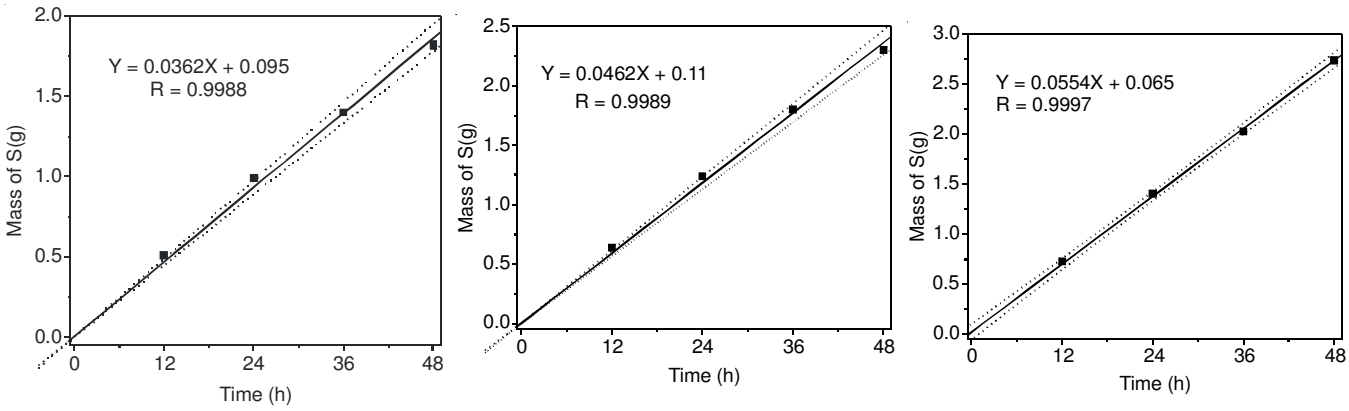


Fig. 8. Change of pH value with time in different air inputs



(a) Linear fitting curve of actual value at 0.2 m^3h^{-1} air input

(b) Linear fitting curve of actual value at 0.25 m^3h^{-1} air input

(c) Linear fitting curve of actual value at 0.3 m^3h^{-1} air input

Fig. 7. Linear fitting curve of the actual S mass with time at different air put

From Fig. 8, after 0.5 day, the pH value in nutrient solution decreased from 5.5 to 3.2 in 0.2 m^3/h air input while it slowly decreased from 5.5 to 5 in 0.35 m^3/h. After 2 days, the pH value in different air input all decreased to about 2.5, thus the H^+ should exist in nutrient solution.

The change of S^{2-} concentration with time had been measured in the condition of temperature 20 °C, air input 0.2 m^3/h, H_2S inlet concentration 200, 300, 400 and 600 mg/m^3. The results shown in Figs. 9 and 10 described the change of pH value with time and Fig. 11 describes the mass of S in nutrient solution with the same conditions.

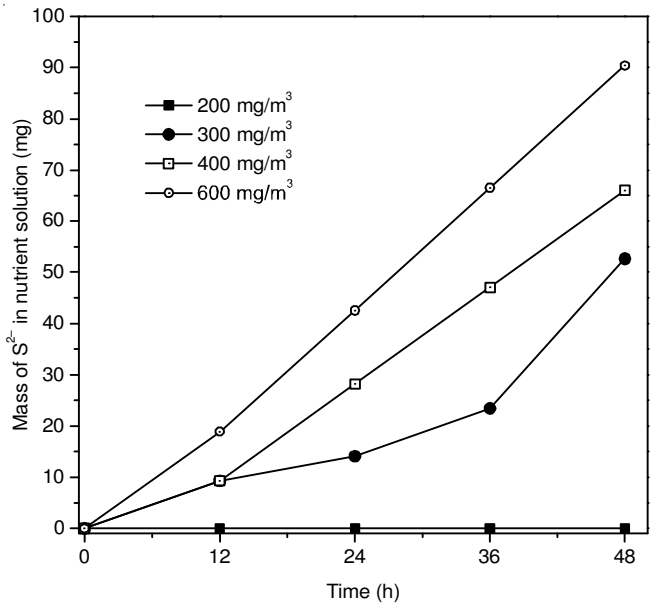


Fig. 9. Change of S^{2-} in circular nutrient solution in different H_2S concentrations

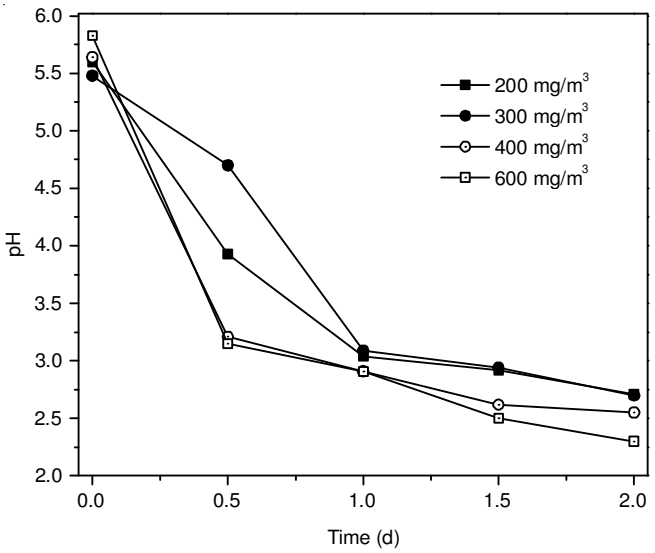


Fig. 10. Change of pH in circular nutrient solution in different H_2S concentrations

From Fig. 9, the concentration of S^{2-} in nutrient solution increased with the increase of the inlet H_2S concentration. There was no S^{2-} in nutrient solution when the inlet H_2S concentration was 200 mg/m^3. However, the mass of S^{2-} separately were 52.7, 66 and 90.4 mg when the inlet H_2S concentration separately were 300, 400 and 600 mg/m^3 and the mass of S^{2-} with time changed little when the inlet H_2S concentration remained stable. This suggests that H_2S could dissolve in liquid film of biofilm surface in low inlet H_2S concentration and migrated from gas phase to liquid phase. The gas phase H_2S could diffuse into biofilm and be degraded by microorganisms. With improving the inlet H_2S concentration, a large amount of H_2S in liquid phase had been degraded into SO_4^{2-}, a few S^{2-} existed in nutrient solution. This showed in the removal process of odour gas, the gas should be dissolved into liquid phase first and then could be degraded by microorganisms.

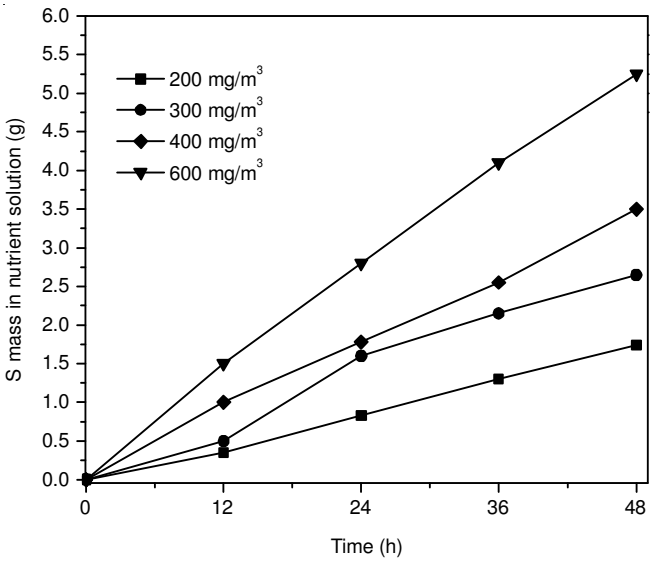


Fig. 11. S mass in the nutrient solution with time in different H_2S concentrations

From Figs. 10 and 11, the pH value in nutrient solution decreased with the increase of inlet H_2S concentration, but the mass of S in the nutrient solution increased. This suggests that H_2S had been finally degraded into SO_4^{2-} by microorganisms, that is a proof for Stage III.

In order to understand S mass change in the H_2S degradation process, the total mass of H_2S at the inlet/outlet, the mass of S in nutrient solution, the mass of S^{2-} and other forms of S in different inlet H_2S concentrations were analyzed, the results of which are shown in Table-2.

As shown in Table-2, in the condition of the inlet H_2S concentration 200 mg/m^3, the H_2S input mass was1.92 g and the mass of S being biodegraded was 1.87 after 48 h. The latter accounted for 97.3 % of the former. This showed that most part of the H_2S had been degraded into SO_4^{2-} by microorganisms and there was no S^{2-} concentration in the nutrient solution. Other forms of S accounted for 2.6 % of the input H_2S mass. This suggests that there existed other S intermediate products. With increasing the inlet H_2S concentration, the mass of S in nutrient solution and undegradation of H_2S also grew slowly. Meanwhile, as shown in Table-2, H_2S input mass was roughly equal to S mass in the final production of SO_4^{2-} and S^{2-} mass in nutrient solution. This suggests that most of inlet H_2S had been degraded into SO_4^{2-} by microorganisms while the undegraded H_2S could be divided into three parts: the first part existed as S^{2-} in nutrient solution, the second part may be other forms of S and the third part had been taken away by outlet gas.

TABLE-2
SULFUR TRANSFORMATION RELATION IN H_2S BIODEGRADATION AT DIFFERENT INLET H_2S CONCENTRATIONS

Inlet H_2S concentration	200 (mg m^{-3})		300 (mg m^{-3})		400 (mg m^{-3})		600 (mg m^{-3})	
Existence form	Mass (g)	Sulfide (%)	Mass (g)	Sulfide (%)	Mass (g)	Sulfide (%)	Mass (g)	Sulfide (%)
Input H_2S	1.92	–	2.88	–	3.84	–	5.76	–
Undegradation H_2S	0.001	0.05	0.05	1.74	0.08	2.1	0.17	3.0
Being degraded H_2S	1.87	97.35	2.77	96.2	3.67	95.6	5.44	94.4
S^{2-} in nutrient solution	0	0	0.05	1.74	0.07	1.8	0.09	1.6
Other forms of S	0.05	2.6	0.01	0.32	0.02	0.5	0.06	1.0

Because H_2S biodegradation is a very complex process and the intermediate product is not very stable, the other forms of S have not been measured carefully in the experimental conditions.

According to the above experimental results, the H_2S biodegradation process can be described as in Fig. 12. On account of Stage II and Stage III proceed rapidly in the whole process, so H_2S (g) → H_2S (l) could be the key step in the degradation process.

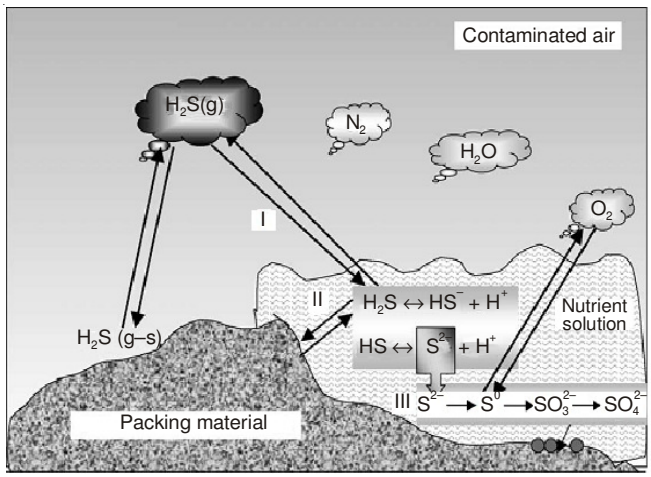


Fig. 12. Biodegradation process of H_2S

Conclusion

In biological removal of H_2S process, biofilm could stay stably on the packing materials in the biofilter in order to maintain the H_2S biodegradation process, while the circular nutrient solution may be acidized with the extended running time. At the same time it may lead to the decrease of pH value and the increase of SO_4^{2-} concentration, with SO_4^{2-} as the main biodegradation product. With increasing inlet H_2S concentration, the mass of S^{2-} in nutrient solution and the undegradation of H_2S, also grew slowly. H_2S input mass was roughly equal to being degraded H_2S mass and S^{2-} mass in nutrient solution. In the whole H_2S biodegradation process, because S^{2-} can be transformed to SO_4^{2-} easily, so the H_2S (g) → H_2S (l) could be the key step.

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