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RESEARCH ARTICLE

Optimum Tuning for the High-efficiency Removal of Malodorous Gas Containing Hydrogen Sulphide Using Biological Treatment

Rabia Sultana[1], Shizhong Yan[2], Lu Bai[3], Xingyu Jiang[4], Xue Yuan[5], Xin Zhang[1], Yinghui Han[1*]

[1] College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 101408, China

[2] China Energy Engineering Group Shanxi Electric Power Engineering Co., LTD, Taiyuan 030001, China

[3] State Grid Shanxi Electric Power Research Institute, Taiyuan 030024, China

[4] College of Materials Science and Engineering, Nanjing Tech University, Nanjing 211816, China

[5] College of New Energy, North China Electric Power University, Beijing, 102206, China

ABSTRACT

Hydrogen sulfide, as the main pollutant causing stench, has always been one of the main problems in environmental protection. In order to promote the practical application, a pilot study was carried out in this work on the biological treatment of hydrogen sulfide malodorous gas by the combined process of biological drip filtration on the basis of our previous laboratory-scale experiments. After enlarging the reactor in pilot experiment, various factors affecting the deodorization efficiency are compared in pilot scale and laboratory scale, and the optimum pilot condition are obtained. Furthermore, the mechanism of biological deodorization is analyzed. Based on the results of the comparison between the previous laboratory-scale and the pilot-scale of this work, possible bottlenecks and challenges of biological deodorization technology from pilot to industrial application are discussed. The technical approach proposed in this work provides an economical and efficient feasible scheme for biological deodorization in the industrial practice.

Keywords: Biological deodorization; Optimum control; Hydrogen sulfide; Malodorous gas; Padding

*CORRESPONDING AUTHOR:
Yinghui Han, College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 101408, China; Email: hanyinghui@ucas.ac.cn

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1. Introduction

Hydrogen sulfide, a colorless, highly toxic, acidic gas with a special rotten egg smell, heavier than air, can spread to a considerable distance at a lower place [1]. Its production in nature is mainly related to the chemical reaction of sulfur-containing substances. In industrial production, hydrogen sulfide mainly comes from natural gas purification and petroleum refining tail gas and so on. The highest concentration of hydrogen sulfide often occurs in natural gas purification, petroleum refining. Hydrogen sulfide is also produced in chemical industry, such as sulfur dyes, synthetic fibers, carbon disulfide, etc., as well as in light industry production process, such as the pharmaceutical, papermaking, pesticides, leather, etc., even though they produce small amount of hydrogen sulfide, for environmental pollution is still serious, also harm human health [2], so attention must be paid to governance.

As a typical malodorous atmospheric pollutant, hydrogen sulfide affects the human body through the respiratory system using air as a transmission medium. However, it has its uniqueness, that is the olfactory concentration of odorous gases is relatively low, and the concentration of odorous substances required in the treated gas is even lower or almost zero (extremely low odor threshold of 0.05 ppm), which makes the control of odor pollution different from that of general air pollution.

Currently, deodorizing technologies, such as masking method, dilution diffusion method, thermal (catalytic) combustion method, absorption method, adsorption method, biological method, aeration method, catalytic oxidation method, low temperature plasma method, etc., have been vigorously developed [3]. In every treatment method, biological deodorization has been the darling of industry and academia because of its many advantages, such as high deodorization efficiency, simplified device, and low treatment cost [4]. The biological method involves using microbial metabolic activities to degrade odorous substances, oxidizing them into final products, thereby achieving deodorization and harmlessness. Since the 1980s, many microbial deodorization devices and equipment have been used in the metallurgy industry, petroleum industry, chemical industry, and slaughter and wastewater treatment, and some effects have been achieved [5]. Cho et al. used three different samples of porous lava as a carrier of Thiobacillus thiooxidans in a laboratory-scale biofilter for deodorization of hydrogen sulfide and found that natural, porous lava is a promising candidate as a carrier of microorganisms in biofiltration[6]. Jiang et al. proved that H_2S was improved by a bio-trickling filter with the optimal substrate acclimation strategy using H_2S-exhausted carbon as packing material. They also found that PCR–DGGE (polymerase chain reaction denaturing gradient gel electrophoresis) was employed to produce genetic fingerprints that could provide information on the temporal and spatial difference in the microbial communities of H_2S degrading biofilm in a horizontal bio-trickling filter (HBTF) [7]. Shinabe studied the quantitative relationship between the basic characteristics of carriers (such as shape, porosity, and presence of macro pores) and H_2S removal and found that the best carrier was cylindrical and the surface and inside of the carrier had macro pores (about 1 mm in diameter) [8]. The main types of biological reactors are bio-filter, bio-scrubber, and bio-trickling filters[9]. There is an experimental demonstration that combining bacteria and fungi would be a better choice for inoculation into a bio-trickling filter because of the quick degradation of H_2S and rapid recovery under shut-down experiments [10]. We developed the three-stage bio-trickling deodorization technique, and obtained good deodorization effect with laboratory scale in the early stage [11]. However, at present, it is still a technical difficulty to use bio-trickling method to treat odor at industrial scale, which is either too low efficiency or too high cost [12].

In this study, a pilot-scale study is conducted on the removal of odorous gas containing hydrogen sulfide by a three-stage biological trickling filter based on our previous laboratory-scale research experience [11]. After the reactor is scaled up, our packing is revolutionized. In order to be suitable for industrial applications, we use the ceramic particles made of solid waste coal gangue as a filler, which greatly reduces the process cost, and this is more advantageous than the fiber balls we used in the laboratory scale before, its specific surface area is larger, conducive to adsorption with odor, and increases the reaction time of microorganisms and odor. The purpose of this study is to help the industrialization of this technology.

2. Experiment

2.1 Chemicals and reagents

Coal gangue ceramic packing with industrial grade from Xianghuan recycling Co., LTD., Shanxi province, China. Beef extract peptone medium with a total nitrogen content of 13.2% from Wuhan Jiyesheng Chemical Co., LTD., China. All other chemical agents and reagents, including dipotassium phosphate (K_2HPO_4), potassium dihydrogen phosphate (KH_2PO_4), ammonium sulfate ($(NH_4)_2SO_4$), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), sodium sulfate ($Na_2SO_4 \cdot 2H_2O$), calcium dichloride ($CaCl_2 \cdot 2H_2O$), manganese chloride ($MnCl_2 \cdot 4H_2O$), iron vitriol ($FeSO_4 \cdot 7H_2O$), sodium sulfide (Na_2S), concentrated sulfuric acid, etc., are analytically pure grades, and are sourced from CASMART third party B2B e-commerce platform (casmart.com.cn).

2.2 Setup and apparatus

The pilot test system consists of several parts: a workshop odor unit, biological bacteria culture unit, a drip filtration deodorizing biological reacting unit, a gas analysis unit, and a tail gas absorption unit, etc. The core setup and apparatus of the system is shown in **Figure 1**. The three-stage bio-trickling filter apparatus has dimensions of 7.10m × 2.30m × 2.50m and blowing rate of 10000 m^3/h. The biofilter has a standby time of 16 hours per day. The spray rate of microbial nutrient solution is 6 L per hour. The entire system is fully automated, with a computer micro-control switch managing the water spray system and spray frequency. The bio-trickling filter process system consists of three parts: the waste gas collection system, the spraying device, and the main body of the trickling filter. The flow chart of the pilot test system is shown in **Figure 1**.

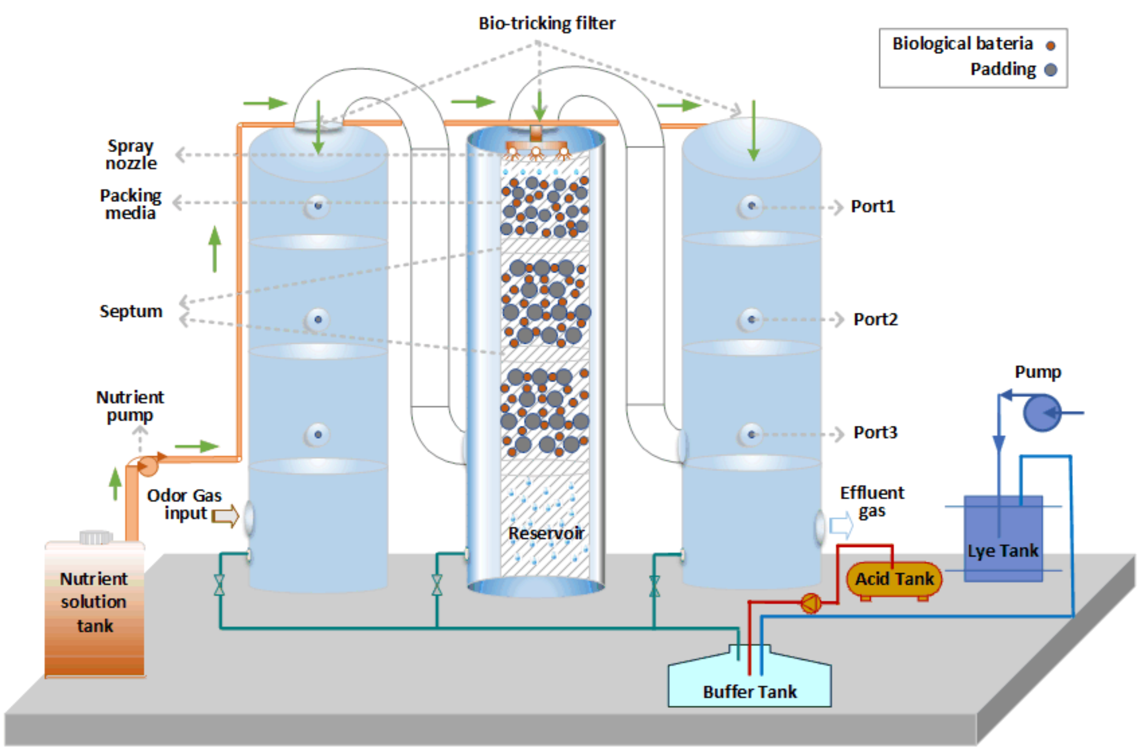

Figure 1. Flow chart of pilot-scale biological deodorization.

2.3 Methods

In this pilot study, a three-stage bio-trickling filter is used to remove hydrogen sulfide gas. The height of the reactor was expanded from 2 meters at the original lab-scale to 7 meters at the pilot-scale. The filter is updated from the original fiber ball packing, and a mixture of multifaceted (polyhedron) and a small amount of fiber ball packing to coal gangue ceramic particles, which is more economical, and has a large specific surface area and developed pores. The nutrient solution tank is used for microbial culture and domestication. The buffer tank is used to mediate pH, because the results of lab-scale experiments show that biological deodorization is greatly affected by pH, and this time we will also examine its impact on deodorization efficiency. We will focus on comparing the differences and similarities between lab-scale tests and pilot-scale tests, such as import concentration, filler height, pH and temperature, and their effects on hydrogen sulfide removal, so as to find out the deodorization mechanism of biological trickling filter under metastable conditions, laying a theoretical foundation for the industrial application of biological trickling filter.

3. Results and analysis

3.1 Effect of concentrations on deodorization efficiencies

The inlet odor concentration has great influence on the removal efficiency. We study the hydrogen sulfide with high-concentration and low-concentration respectively. The system ran for 60 days. The pilot-scale results are divided into five categories according to minimum value, lower quantile, middle quantile, upper quantile and maximum value. The inlet concentration, outlet concentration and deodorization efficiency were compared. The results are shown in **Figure 2.** The results show that the pilot test has achieved optimal deodorization efficiencies, whether with low concentration and high concentration, especially for hydrogen sulfide gas with high concentrations. The microorganisms in the reactor are well adapted and the operation is relatively stable. The strategy of three-stage cyclic drip filtration is conductive to replenishing the carbon source required by microorganisms at any time.

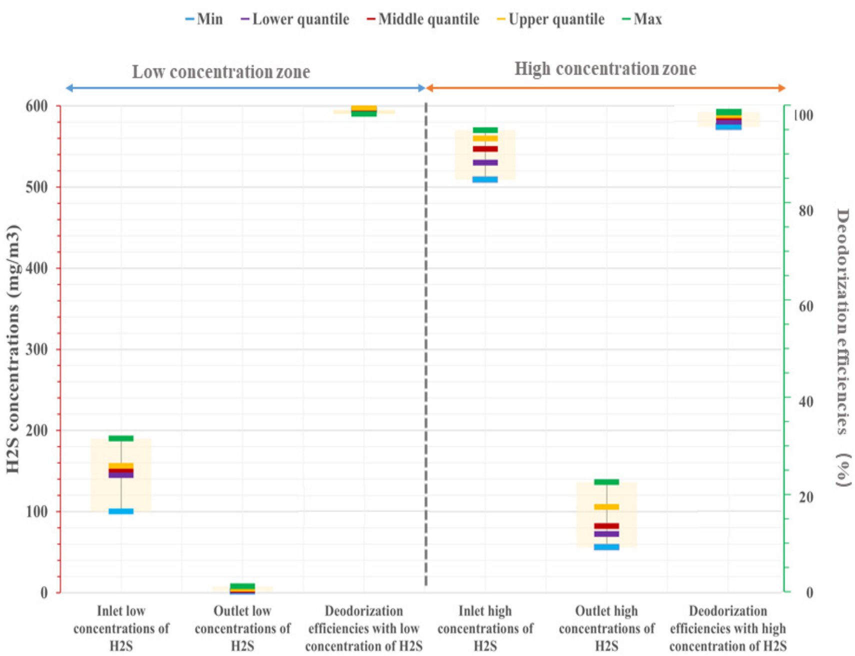

Figure 2. The comparison of deodorization efficiency of low concentrations (< 200mg/m^3) and high concentrations (> 220mg/m^3) of hydrogen sulfide with both low concentration and high concentration in inlet workshops, which was conducted in a pilot test for 60 days. The lowest, lower, median, upper and maximum quantiles of inlet concentration, outlet concentration and deodorization efficiencies were represented by blue, purple, red, orange and green respectively.

3.2 Effect of packing layer height on deodorization efficiency

Figure 3 compares the relationship between the height of packing layer and deodorization efficiency in lab-scale and pilot scale. As can be seen from **Figure 3**, both at laboratory and pilot scale, it is found that the removal rate of hydrogen sulfide gradually increases with the increase of the height of the packing layer. Therefore, the deodorization efficiency at the pilot scale is significantly higher than that at the lab-scale. Although increasing the height of the packing layer inevitably increases the gas resistance and energy consumption, the multi-tower series strategy increases the residence time of gas-liquid mass transfer. Therefore, the deodorization efficiency in pilot experiment has better efficiency than that in lab-scale.

From the padding material, we have also made updates. In the laboratory, we use a mixture of fiber spheres and polyhedral materials (1:2 ratio). In laboratory experiments, the height of packing decreases with the increase of inlet gas concentration. However, in terms of effectiveness, the performance of fiber ball packing is obviously better than that of mixed packing. In this pilot test, we boldly tried to make the industrial waste coal gangue into ceramic particles as fillers. Coal gangue ceramide has a large specific surface area, which makes it easier to be loaded by microorganisms, and its high-water content promotes microbial growth, resulting in better degassing effect. The porous structure allows it to hold more microorganisms, thus improving the deodorization effect.

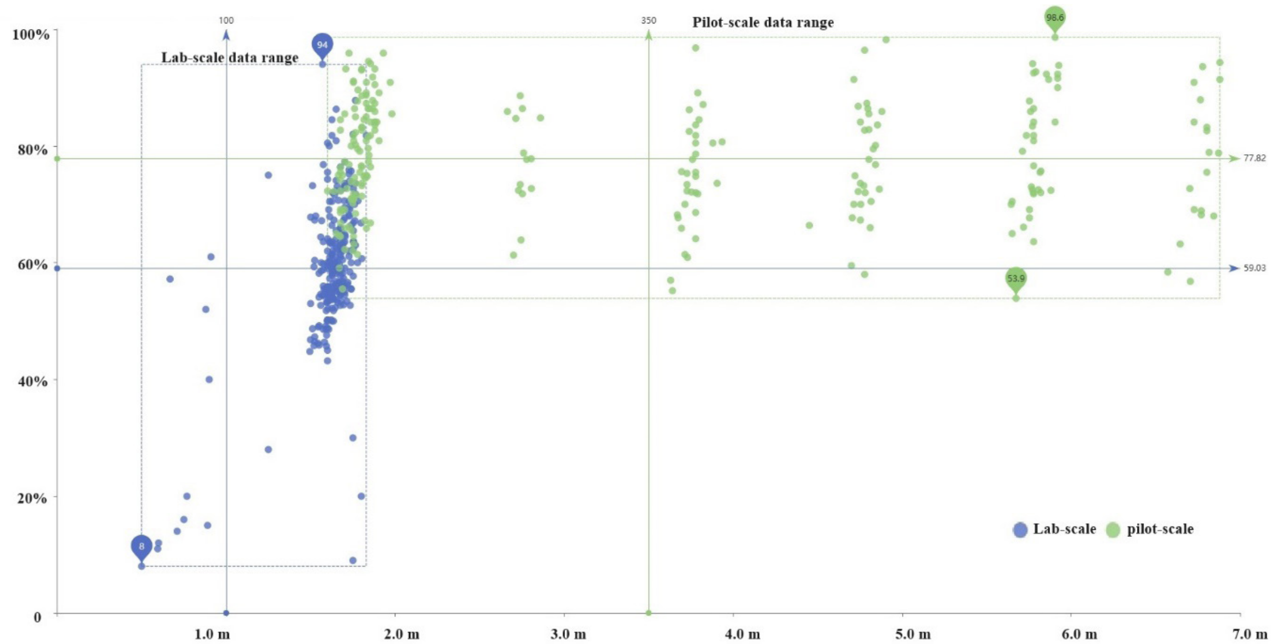

Figure 3. Pilot-scale and lab-scale packing height and deodorization efficiencies distribution.

3.3 Synergistic effect of pH and temperature on deodorization efficiencies

In view of the fact that the purification process in the biological trickling filter is mainly completed by the life activities of microorganisms, the level of microbial activity directly affects the purification efficiency of the biological trickling filter. Both pH and temperature are important factors affecting biological activity. The majority of previous studies have only considered the effect of pH or temperature as a standalone variable. In the pilot test, we comprehensively considered the synergistic effect of both factors, as shown in **Figure 4.** The pH value decreases rapidly with the increase in inlet load. When the pH is relatively low, the removal effect of hydrogen sulfide is very effective. However, as the pH value increases, the removal rate decreases but starts to increase again around a pH of 1.5, before showing a downward trend once more. When the pH exceeds 5, the deodorization efficiency decreases significantly. Although the lower the pH, the better the deodorization effect, while emphasizing efficiency, meanwhile, it is necessary to consider that the corrosive effect of a strong acidic environment at lower pH levels on equipment in practical application. Moreover, extreme pH value may lead to the destruction of membrane structure, affecting the normal physiological function of microorganisms. The change of pH value will affect the solubility and ionization of substances , which will affect the absorption and utilization of nutrients by microorganisms. According to the pilot test results, the optimal deodorization effect can be achieved by controlling the pH in the weak acid environment at normal temperature. The reason is that the change of pH value will affect the permeability of the plasma membrane, which will affect the absorption of nutrients and the expulsion of metabolites, and thus tuning the deodorization efficiency.

Temperature also has an important impact on microorganisms, which is mainly reflected in affecting enzyme activity, the fluidity of the plasma membrane of cells, and the solubility of affected substances. Specifically, with the increase of temperature, the intracellular chemical and enzyme reactions of were carried out at a faster rate, and the growth rate of was accelerated; When the temperature decreased, the intracellular chemical and enzyme reactions took place at a slower rate, and the growth rate slowed down. When the temperature is high, the fluidity is large, is conducive to material transport; low temperature reduces fluidity, is not conducive to material transport, affects the absorption of nutrients and secretion of metabolites. Temperature changes directly affect the solubility of substances, and then affect the absorption and utilization of nutrients by microorganisms. As can be seen from **Figure 4**, the deodorization efficiency of the biological trickling filter is the highest in the temperature range of 25°C~35°C during the pilot operation. When the temperature drops below 25 °C, the efficiency begins to decline, and it drops rapidly below 10°C. This is because most microbes have relatively low biological activity at lower temperatures. Considering the cost and efficiency comprehensively, the best temperature for deodorization by biological method is room temperature. When running in winter, increase the temperature appropriately. In this way, the biological activity can be ensured without increasing the operating cost due to energy consumption.

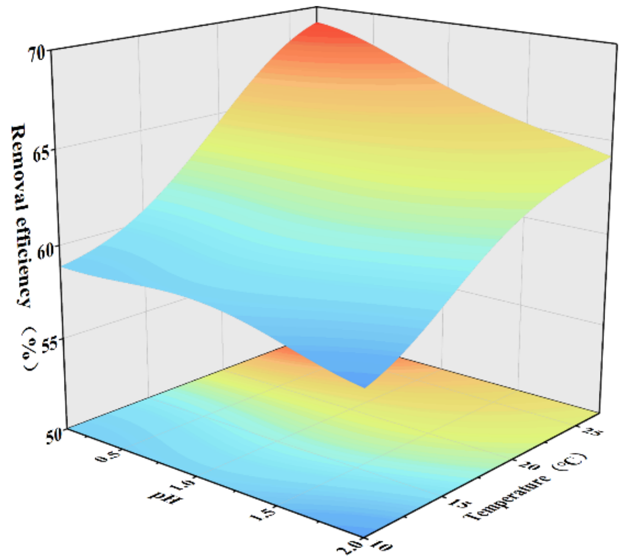

Figure 4. Changes in purification efficiency of purification tower with pH and temperature.

3.4 Mechanism of odor removal by biological drip filtration

In this study, beef paste is used as microbial medium and coal gangue ceramide as filler. The mechanism of the biological process to remove the odor of hydrogen sulfide mainly involves the use of microbial metabolic process to degrade the malodorous gas. Beef paste is a kind of brown paste obtained from fresh beef after removing fat, digestion, filtration and concentration. It is rich in a large number of probiotics and a variety of beneficial bacteria, these microorganisms can quickly decompose and transform the odor source, degrade the organic matter in the odor source, reduce the content of ammonia and nitrogen, and have excellent odor removal effect, and can effectively inhibit the recurrence of odor. This biological deodorant improves air quality by converting the foul-smelling components of hydrogen sulfide into elemental sulfur and sulfate. The method is non-toxic, no secondary pollution, the required equipment is simple, easy to operate, low operating cost, high processing efficiency and convenient management and maintenance. The mechanism of biological deodorization is shown in **Figure 5**. The main processes are as follows: the mass transfer process of hydrogen sulfide malodorous gas from gas phase to liquid phase through biological drip filtration; the odor dissolved in drops is absorbed by microorganisms through cell wall and membrane, while the odor insoluble in water is decomposed into soluble substances by extracellular enzymes secreted by microorganisms and then infiltrates into cells. After the odor enters the cell, it is decomposed and utilized by microorganisms as nutrients in the body, so that the odor can be removed. The metabolites produced by the digestion and absorption of odorous substances by microorganisms can be used as metabolic substrates of other microorganisms to continue to decompose and utilize, so as to achieve the purpose of gradually degrading odorous substances. Compared with our previous lab-scale experiments, this study replaced a new coal gangue padding, which on the one hand is conducive to promoting odor adsorption through the excellent pore characteristics of coal gangue ceramics and increasing the microbial reaction time, on the other hand, the use of waste coal gangue also greatly reduces the cost of biological deodorization. At the same time, the microbial culture process has been further optimized in this work. Through the separation, screening and domestication of specific bacteria, the dominant bacterial community is formed, so as to improve the deodorization efficiency, and achieve an important breakthrough in industrial application. This method can not only effectively remove the malodorous gas such as hydrogen sulfide, but also fundamentally degrade the substance that produces the malodorous gas, which has environmental protection and economic advantages.

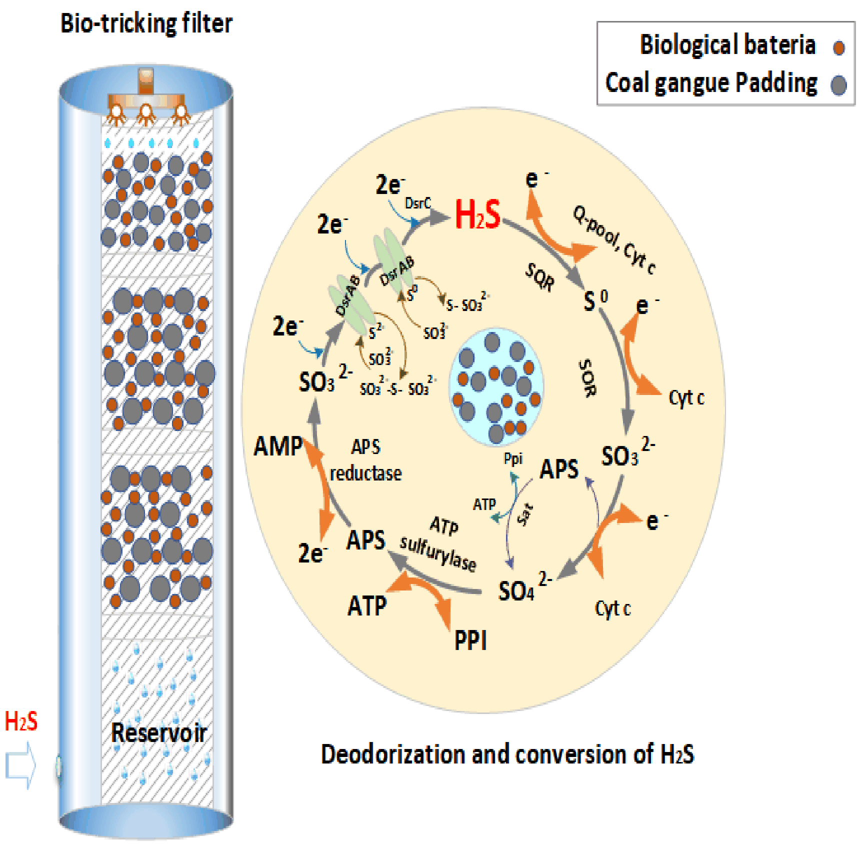

Figure 5. Mechanism of biological trickling to remove malodorous gas containing H_2S.

4. Conclusions

On the basis of the original laboratory experiment, a pilot scale scale-up experiment was carried out in this work. The optimum ecological conditions for the purification of odorous gas containing hydrogen sulfide by pilot-grade biological trickling filter were optimized. The effects of inlet/outlet concentration, filler height, pH and temperature on the deodorization efficiency of hydrogen sulfide were studied. In the pilot experiment, solid waste coal gangue is innovatively used as filler to treat waste and promote the sustainable development of circulation. The work aims to provide reference for industrial and commercial application of biological deodorization technology.

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Conflict of Interest

All authors declare no conflict of interest.

Funding

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