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H_2S removal with an immobilized cell hybrid reactor

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Abstract

When hydrogen sulphide gas was introduced into a single reactor, in which the cells were mixed with iron solution in the absence of the immobilization particles, the cells were damaged by the high concentration of H_2S and the H_2S removal rate was rapidly decreased. Therefore, a hybrid reactor was developed, by combining a chemical reduction reactor and a biological oxidation reactor, to remove the toxic effect of H_2S on the cells and to improve the H_2S removal rate. The microbial cells were immobilized on the surface of curdlan particles, in order to enhance the Fe(II) oxidation rate through repeated fed-batch operation. As a result, the iron oxidation rate was four times faster than that obtained with the free cells. Iron solution, oxidized in an oxidation reactor by *Thiobacillus ferrooxidans*, was fed into the iron reduction reactor, and the reduced iron solution was recycled into the iron oxidation reactor. The X-ray diffractometer (XRD) data indicated that iron was precipitated along with elemental sulphur at the high concentration of H_2S, resulting in the iron oxidation rate being decreased with increasing reaction time.

Keywords: Hybrid reactor; Iron oxidation; H_2S removal; Immobilized cell

1. Introduction

Hydrogen sulphide is a sulphuric compound that is colourless, toxic and has a rotten-egg-like smell. When emitted into the air from various chemical and industrial settings, it becomes the main component of acid rain, giving it a foul smell, while at the same time, being harmful to people and causing water and air pollution. As such, it is one of the major sources of complaint for people living near these chemical and industrial settings and, consequently, studies are urgently needed on methods of efficiently removing this noxious gas [1,2]. The available methods of removing foul smells can be largely divided into physical, chemical and biochemical [3]. Some examples of these methods in the case of the removal of H_2S gas are physical–chemical treatment, cleaning, adsorption on particle surfaces and absorption by liquid solvents. However, various problems exist with the catalysts used in these processes, including the cost of renewing the inactivated catalysts, the generation of secondary substances causing pollution and the high-energy requirement [4]. One method, which is commonly used to overcome the problems associated with the chemical treatment of H_2S, is its oxidation into elemental sulphur, using a metal chelating agent in the form of a liquid catalyst. This method, which was first introduced by Hartley et al., uses the metal, Fe, and various cheating agents, such as EDTA and NTA, which are non-toxic, and therefore, cause no environmental pollution during the removal of H_2S. During this process, H_2S is dissolved in a liquid chelating solution, and the dissolved H_2S then reacts with oxygen to produce elemental sulphur and water. However, most studies on removing H_2S, using these Fe chelating catalysts have focused on the removal rate and mass transfer in the case of an instantaneous reaction, involving low concentrations of H_2S, consequently, information is lacking on the optimal conditions of catalyst dissociation and reaction during long-term continuous reactions [5–8]. Thus, many studies are currently being done on biological treatment, which is inexpensive and offers easy mass removal [9], especially when using microorganisms. One of the more frequently used biological

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treatment methods of removing H_2S involves a combination biological and chemical processes, using a bacteria that oxidize iron from Fe(II) to Fe(III), *Thiobacillus ferrooxidans*. When this bacteria produces oxidized iron, the resulting oxidized iron oxidizes H_2S to elemental sulphur, and then *T. ferrooxidans* turn the Fe(II) into Fe(III). This method is currently attracting the interest of researchers as a new technique of purifying air, because this bacteria is able to treat not only low but also high concentrations of H_2S gas, requires little equipment, is inexpensive and produces only elemental sulphur, thus minimizing the production of pollutants [10–12]. Despite these numerous benefits, the drawback of this immobilization technique is the fact that the overall rate of immobilization is low, due to the relatively low rate of the biological reaction, which is required for the removal of H_2S, using the iron oxidizing microorganisms. Therefore, although many researchers have used cell immobilization supporting media that allow high concentrations of iron oxidizing microorganisms to be maintained, in an attempt to increase the oxidation rate of Fe(II), further progress is needed before these systems can be used in real world applications [13–15].

Thus, in this study, we developed a supporting medium that could maintain high cell concentrations and observed both the iron oxidizing rate and cell growth during H_2S gas removal in an one stage reactor (bubble column reactor). This reactor consisted of several steps, firstly a chemical adsorption process involving the adsorption of H_2S gas in the ferric solution, secondly a biological process in which the biologic action of *T. ferroxidans* oxidized the Fe(II) ion, and a closed reaction process in which H_2S gas was converted to sulphur, using a fixed-bed bioreactor and bubble column absorber. Furthermore, we observed the effects of cell immobilization according to the method of supporting medium cell immobilization, and determined the iron oxidation reaction and removal rate according to the iron oxidation rate and H_2S oxidation in a two-stage reactor. Finally, we examined the iron oxidation in the case where the reduced iron ion solution after H_2S oxidation was reused.

2. Materials and methods

2.1. Strain used and bacteria culture

The strain used was *T. ferrooxidans* (ATCC 19857). Cell culture was done in Silverman's 9 K media [16] with an initial pH adjusted to 1.8. Culturing was done for 3 days by placing 150 mL of this medium in a 300 mL Erlenmeyer flask and inoculating it with 10% (v/v) of inoculum, while maintaining the temperature at 30 °C and stirring the culture solution at 200 rpm. After culturing, the culture medium was filtered twice through a Whatman No. 2 filter paper. The resulting filtrate was centrifuged (6000 rpm, 20 min) to obtain the cell broth, which was suspended in mineral salt solution. After repeating this centrifugation process twice, the filtrate was placed in 9 K medium, containing no $FeSO_4{\cdot}7H_2O$ and used for subsequent inoculations and in the preparation of the supporting medium, while keeping it 4 °C.

2.2. Media

Silverman's 9 K medium was used initially to culture and obtain the bacteria. However, due to the fact that Silverman's 9 K medium has an adverse effect on the reactor's operation, because of its blocking either the reactor itself or the associated (valves) or pipes, due to the formation of jarosite, the cell immobilization medium used was M16 medium (composition: 3 g/L of $(NH_4)_2HPO_4$; 0.2 g/L of $MgSO_4{\cdot}7H_2O$; 0.1 g/L of KCl; and 45 g/L of $FeSO_4{\cdot}7H_2O$) $7H_2O$) developed by Kim [17] with the initial pH adjusted to 1.8.

2.3. Cell immobilization-supporting medium and cell immobilization

The new cell immobilization-supporting medium, prepared in this study, using curdlan and activated carbon, had excellent characteristics. The fact that this supporting medium did not lower the cell growth and did not dissolve in the main media offered a distinct advantage, in that it was possible to change the weight ratio according to the composition ratio. After placing 40 g (100 mL) of supporting medium, containing 200 mL (v/v = 10%) of bacterial solution diluted with 9 K mineral salt solution (pH 1.8), curdlan and activated carbon into the bubble column reactor, M16 medium with pH 1.8 was added, in order to bring the total volume to 2 L. Cell immobilization was done by culturing at 30 °C for 40 h, while supplying air at a rate of 1 vvm. Then, supporting medium was resupplied, and cell immobilization was done while the medium was refluxed into the reactor, containing the supporting medium, using the peristaltic pump in the bubble column reactor.

The immobilized cell reactor was an acryl bubble column with total volume of 2.5 L (inner diameter, 100 mm; outer diameter, 110 mm; and height, 400 mm) and a packed-bed reactor with a volume of 200 mL in which the supporting medium could be refilled (inner diameter, 40 mm; outer diameter, 50 mm; and height, 150 mm). This immobilized cell reactor was placed in a water bath for the purpose of temperature control.

2.4. Iron oxidation rate using batch reaction culture

The supporting medium was isolated from the bubble column reactor and filled to 200 mL. Cells were immobilized, while the medium was refluxed into the reactor, containing supporting medium, using the peristaltic pump. In order to culture high concentrations of cells, new medium was influxed when about 100 mL of medium was left in the bubble column reactor in the case where the Fe(II) was completely oxidized. The batch reaction was repeated, using