Characteristics of Sulfite Reduction by SRB Using Sodium Lactate and Formic Acid as Carbon Resource

Xiaoye Liu*, Yang Yang, Lin Yue, Shanzhi Xin, Fang Huang, Zhen Lu, Minghua Hu, Hui Zhang

Hubei Key Laboratory of Industrial Fume and Dust Pollution Control, School of Chemical and Environmental Engineering, Jianghan University, Wuhan, Hubei, China

* Corresponding author, Email: 1024xiaoye@163.com

Keywords: Sulfate-reducing bacteria, Sodium lactate, potassium formate, sulfite reduction

Abstract: Nowadays flue gas desulfurization (FGD) by limestone gypsum was still the most effective and world widest method to solve the problem of SO_2 emission. But the by-product wouldn't be used easily. Biological fume gas desulfurization (BFGD) has been concerned on more and more widely for its characteristics of low investment and operation cost, low energy input and no secondary pollution. The selection of its carbon resource would be a key problem. Sodium lactate and potassium formate as carbon resource were applied to reduce sulfite to discuss the commonality and characteristics of this two types of carbon resource in this paper. The results show that the best COD/SO_3^{2-} (calculated as SO_2) ratio is around 3.0 in both cases. Sulfite reduction ratio could reach nearly 90% when enough sodium lactate is applied while potassium formate was used, the best COD/SO_3^{2-} was around 2.74-4.11, and sulfite reduction ratio could reach nearly 80%. Sodium lactate would be more fiTable for such SRB to use as carbon resource. The results would apply some theoretic bases for realizing BFGD by SRB using different carbon resources.

1. Introduction

SO_2 is still the core pollutant around the world, because it would cause acid rain, corrode the buildings and hazard the people. However SO_2 mostly comes from flue emission of coal-fired power plant. Nowadays, FGD by limestone gypsum was still the most effective and word widest method to solve the problem. However there is some deficiencies according to the method that the by-product couldn't be reused easily because the sulfate couldn't be separated from sulfite conveniently and treated as waste finally [1-3].As the development of biotechnology, BFGD process has been becoming hotspot of this area because of its superior characters of low investment and operation cost, low energy input and no secondary pollution [4]. As sulfate reducing bacteria (SRB) plays an important part in sulfur cycle in nature world, its features of removal and reuse of sulfur compounds off gases make the BFGD become the most potential technology around the word [5]. Carbon resource also plays a key role in forming sulfide by SRB, so which one and what concentration would be more fiTable for SRB would be the questions to explore. Wang A. et. al. [6] found that the removal efficiency of sulfate is not more than 80% until COD/SO_4^{2-} is more than 2.0, and load rate is lower than 7.5 kg $SO_4^{2-}/m^3 \cdot d$. Li Q. X. et. al. [7] indicates that COD/SO_4^{2-} is the key index to assess the competition of SRB and methane producing bacteria (MPB), and competing with MPB the lower the COD/SO_4^{2-} is, the stronger the ability of SRB using carbon resource is in the condition of COD/SO_4^{2-} around 2.5~16.7. Silva A. J. et. al. [8] and Mizuno O. [9] also show that the higher the COD/SO_4^{2-} is, the more the removal of sulfate is. As for the type of carbon resource, According to Cao J. et. al.'s research [10] SRB tends to use Low molecular organic acids preferentially, such as formic acid, Li T. et. al. [11] founds that the removal ratio sequence of carbon resource and sulfate is formic acid, sodium lactate, glycerin, glucose from high to low. However, in BFGD, sulfur oxides are dissolved into liquid as sulfite mostly, so whether different type of carbon resource used by SRB follows the same law would be an problem that we have to investigate in order to find out which one is used by SRB easily and what ratio of COD/SO_3^{2-}

would be fit for the process. In this paper formic acid and sodium lactate were served as the carbon resource used to investigate which one and what ratio of COD/SO_3^{2-} are more fiTable for sulfite reduced by SRB.

2. Methods and Materials

2.1 Culture Medium.

1/4 Postgate's C medium [12] was prepared except carbon resource and sulfate. Then $CaSO_4$ was replaced by $CaCl_2$ to keeping the same quality of Ca. Carbon resource was applied by sodium lactate and potassium formate. And set different concentrations to compared with each other. Sulfate was chanced into sulfite and its concentration reduced to the half of the sulfate in Postgate's C medium. So it contains 0.125 $g \cdot L^{-1}$ KH_2PO_4, 0.25 $g \cdot L^{-1}$ NH_4Cl, 0.015 $g \cdot L^{-1}$ $MgSO_4 \cdot 7H_2O$, 0.0025 $g \cdot L^{-1}$ $FeSO_4 \cdot 7H_2O$, 0.2175 $g \cdot L^{-1}$ $CaCl_2$, 2.5 $g \cdot L^{-1}$ Na_2SO_3, 0.25 $g \cdot L^{-1}$ yeast extract, 0.075 $g \cdot L^{-1}$ sodium citrate, and different concentrations of potassium formate or sodium lactate, which were prepared with distilled water. In the process of preparation, the Na_2SO_3, sodium citrate and $FeSO_4 \cdot 7H_2O$ were added later, after other matters dissolved into the distilled water and bottled in 250 mL anaerobic bottle with N_2 aerating for 5-10 min. After that the medium were adjusted to pH=7 ± 0.02 by a pH meter (PHS-3C, INESA, Shanghai, China) with hydrochloric acid 1:1 (V/V) . At last, it was again aerated by N_2 for 10 min and sealed tightly. Then it was put into the shaking Table (HNY-2102C, Honour, Tianjin, China) at 35℃ to preheating for 1 hour.

2.2 Inoculation and SRB material.

SRB used in the process was extract from the black mud at the bottom of the drain near the refuse transfer station in Wuhan China. And 3 g mud was taken to cultivate at least 6 times. After that 20 mL cultured bacterium mixture was inoculated into each test bottle and the pressure was balanced to atmosphere. All the related reagents were applied by Sinopharm Chemical Reagent Co., Ltd.

2.3 Tests and Analytical methods.

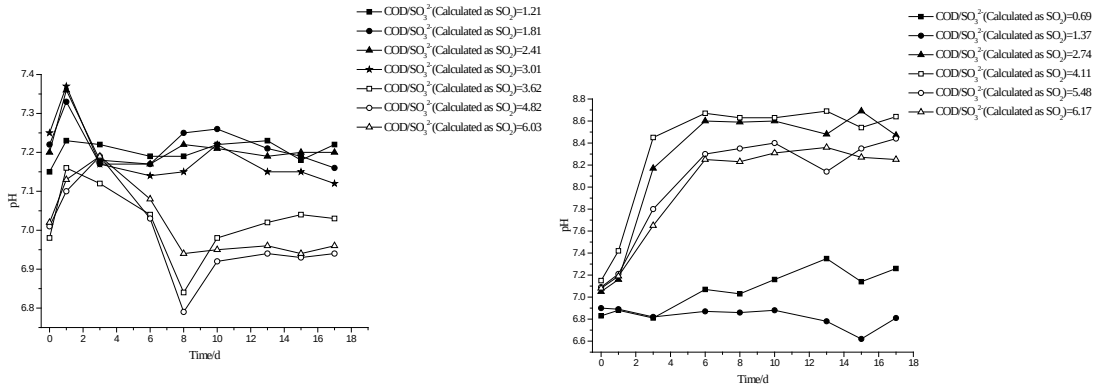
Various initial concentrations of potassium formate and sodium lactate calculated as COD/SO32-(Calculated as SO2) ratio from 0.5 to 6, was set to investigate the characteristics of sulfite reduced by SRB. The COD was calculated as the consumption of O2 oxidizing the organics completely. 5 mL bacteria solution samples was taken out to test its pH and concentration of SO32- and sulfide after it was centrifuged (TDZ4A-WS, Xiangli, Hunan, China) every 2-3 day. Sulfite was determined by Formaldehyde absorbed, pararosaniline hydrochloride spectrophotometric methods at 577 nm [13].Sulfide was determined by methylene blue hydrochloride spectrophotometric methods at 665 nm [14].

3. Results and discussion

3.1 pH variation in the courses cause of the competition of SRB and MPB

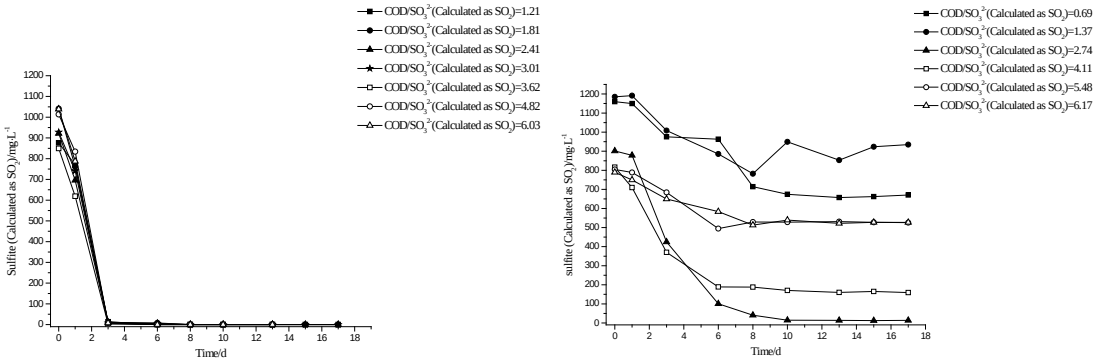
When sulfite was reduced by SRB using potassium formate as carbon resource at the condition that COD/SO_3^{2-}(Calculated as SO_2) was less than 2.74, pH in the process was much lower than the ratio that was more than 2.74, and pH was around 6.7-7.1 in the end of the process in the Fig. 1 (b). To the opposite, While sodium lactate was set as carbon resource at the ratio that was less than 3.01, pH in the process was much more than the ratio that was more than 3.01, and finally the pH was around 6.8-7.1 in the Fig. 1 (a). It indicates that when COD/SO_3^{2-} is at a low level, potassium formate was mostly used by other bacteria such MPB and so on not SRB in the medium, and sulfide produced little in fig. 3 (b). As a result, pH at the condition wasn't raised too much. On the other hand, sodium lactate couldn't used directly by the bacteria like MPB. After inoculation, SRB used sodium lactate and produced sulfide fig. 3 (a), which inhibit other bacteria strongly, and the pH was raised. While COD/SO_3^{2-} is at a high level, potassium formate was used by SRB to reduced sulfite

little, it seems that the higher the COD/SO_3^{2-} is, the lower the sulfite is reduced in Fig. 2 (b) and sulfide produced in the condition of its COD/SO_3^{2-} more than 4.11 is also lower than that is among 2.74-4.11. Potassium formate as one of the low molecular organic acids, was easily used by MPB and other bacteria. Although some sulfide was produced, MPB was little inhibited and used more potassium formate competed with SRB. So SRB produced a little sulfite and at a disadvantage in the competition. Hence the pH was raised a little.



(a) pH variation of sodium lactate (b) pH variation of potassium formate

Fig. 1 pH variation in the process of formic acid and sodium lactate used by SRB



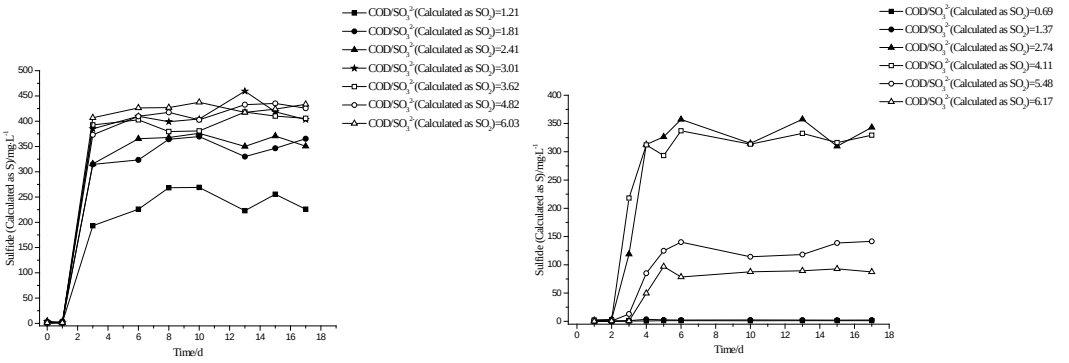
(a) Sulfite variation of sodium lactate (b) Sulfite variation of potassium formate

Fig. 2 sulfite removal in the process of formic acid and sodium lactate used by SRB

3.2 Comparation of two carbon resources in the reduction ratio of sulfite by SRB

when COD/SO_3^{2-} was more than 3.01 in the case of sodium lactate as carbon resource in Fig.3 (a), it seems that the sulfide was produced to the most around 400-450 mg/L. And the amount of sulfide produced by SRB was nearly changed little as the raising of COD/SO_3^{2-}, and the pH was also changed little in Fig.1 (a), which shows that once SRB won the competition during the fighting for sodium lactate as carbon resource, SRB would try its best to produce sulfite and produce sulfide, keeping sodium lactate not used by other bacteria for the inhibition of sulfide. And when the initial concentration of SO_3^{2-} (Calculated as SO_2) is around 1000 mg/L, sulfide (Calculated as S) would be produced around 450 mg/L in Fig. 3 (a), and the reduction ratio is around 90% in about 3 days. So the enough sodium lactate as carbon resourse would reduced the vast majority of sulfite to sulfide.

When COD/SO_3^{2-} was among 2.74-4.11 which is the best ratio for potassium formate as carbon resource used by SRB, sulfide was produced about 350 mg/L to the most in Fig. 3 (b). So the reduction ratio is nearly reach 80% in about 6 days.



(a) Sulfide variation of sodium lactate (b) Sulfide variation of potassium formate

Fig. 3 sulfide formation in the process of formic acid and sodium lactate used by SRB

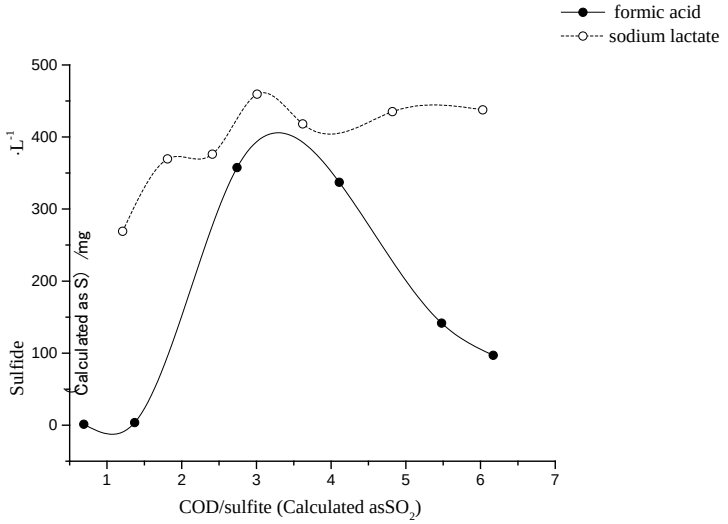


Fig. 4 Sulfide formation tendencies in the condition of different COD/SO_3^{2-} (calculated as SO_2) in the process of potassium formate and sodium lactate used by SRB

3.3 Characteristics of sulfide production by SRB based on COD/SO_3^{2-}

According to the process of sulfite reduced by SRB using sodium lactate and potassium formate as carbon resource, it seems that the best COD/SO_3^{2-} (calculated as SO_2) ratio is around 3.0 in both cases in Fig. 4. That is to say when SO_3^{2-} (Calculated as SO_2) is around 1000 mg/L, 3000 mg/L carbon resource would be enough to reduce most of the sulfite. While too much or too little potassium formate would not be fit for SRB to reduce sulfite. So both of sodium lactate and potassium formate could be used for SRB as carbon resources. However, sodium lactate would be more fiTable to take this part for such SRB.

4. Conclusion

Sodium lactate and potassium formate was applied as carbon resource for SRB to reduce sulfite. The results show that the best COD/SO_3^{2-} (calculated as SO_2) ratio is around 3.0 in both cases. When sodium lactate was used, sulfite reduction ratio is around 90% in 3 days at its COD/SO_3^{2-} more than 3.01, and the amount of sulfide produced by SRB was nearly changed little in this case. While potassium formate was used and COD/SO_3^{2-} was among 2.74-4.11, the sulfite reduction ratio is nearly reach 80% in about 6 days, and more or less than this value, the reduction ratio of sulfite by SRB would be shorten strongly. Sodium lactate would be more fiTable for such SRB to use as carbon resource.

Acknowledgement

The authors are all grateful for the support of Science and Technology Research Project of Education Department of Hubei (B2016282).

References

[1] Yang L.. Status of wet flue gas desulfurization technology [J]. Chenmical Intermediate, 2017, (11): 104-105. (In Chinese)

[2] Wang L.,Huo D.,Zhong M.,et.al.. Research on wet flue gas desulphurization [J]. Chemical Engineering Design Communications, 2018, 44(08): 68. (In Chinese)

[3] Jin X., Liu Y.. Summary of wet flue gas desulfurization technology [J]. Chenmical Intermediate, 2017, (6): 5-6. (In Chinese)

[4] Huang, X., Cai, X.. Applied research on fume gas desulfurization by microbe [J]. Light Industry Science and Technology, 2014, (6):105-106. (In Chinese)

[5] Muyzer G, Stams A J. The ecology and biotechnology of sulphate-reducing bacteria[J]. Nature Reviews Microbiology, 2008, 6(6):441-454.

[6] Wang A., Ren N., Liu W., et. al.. The role of sulfate reducing bacteria population in acidogenic-desulfate bioreactor [J]. China Environmental Science, 2001, 21(2): 119-123. (In Chinese)

[7] Li Q., Fan C., Li L., et. al.. Performance of anaerobic baffled reactor for treatment of high-strength sulfate wastewater [J].China Water＆Wastewater, 2007, 23(15): 47-50. (In Chinese)

[8] Silva A. J., Varesche M. B., Foresti E., et. al.. Sulphate removal from industrial wastewater using a packed-bed anaerobic reactor [J]. Process Biochemistry, 2002, 37(9): 927-935.

[9] Mizuno O., Yu-You L. I., Noike T.. Effect of sulfate reduction on the acidogenesis of sucrose [J]. Journal of Japan Society on Water Environment, 1995, 18(11): 894-900.

[10] Cao J., Zhang G., Mao Z., et. al.. Availability of sulfate reducing bacteria on carbon sources [J]. The Chinese Journal of Nonferrous Metals, 2008, 18(s1): 96-100. (In Chinese)

[11] Wang T.,Zhou J.,Xu W., et. al.. Research on the effect of growth factors on the treatment of wastewater containing sulfate by SRB [J]. Industrial Water Treatment, 2016, 36(6): 38-42. (In Chinese)

[12] Atlas R. M.. Handbook of Media for Environmental Microbiology (Second Edition) [M]. Boca Raton: CRC Press, 2005: 453

[13] HJ 482-2009.Ambient air-Determination of sulfur dioxide -Formaldehyde absorbing-pararosaniline spectrophotometry [S]. Beijing: China Environmental Science Press,2009.

[14] GB/T 16489-1996.Water quality - Determination of sulfide - Methylene blue spectrophotometric method [S]. Beijing: Standards Press of China, 1997.