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Influence of transient pH and substrate shocks on simultaneous anaerobic sulfide and nitrate removal

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ABSTRACT

The influence of pH and substrate shocks was investigated on the performance of anaerobic reactor for simultaneous sulfide and nitrate removal. The performance was noticeably affected by the transient pH or substrate shocks. Unlike substrate shocks, the reactor was more sensitive to pH shocks. The effluent sulfide concentration was a sensitive parameter, which increased up to 31 times of that at steady state, so it could be used as an indicator of the reactor performance. The performance recovered from the disturbances during all the shocks applied. The recovering velocity was relatively stable, which did not increase with the increasing intensity of the shocks. The reactor was easier to recover from pH shocks than substrate shocks.

1. Introduction

A number of industries such as petrochemical plants, tanneries, viscose rayon, etc. generate sulfides containing waste streams. The sulfides cause a number of deleterious effects including corrosion of sewer infrastructure, noxious odor, and human health problems [1,2]. The physicochemical and biological processes may be applied for the treatment of sulfides [3]. Physicochemical processes are costly and generally require high energy input. In contrast, biological processes operate at prevailing environmental conditions without any requirement for expensive chemicals and catalysts [4].

Oxygen injection is an attractive option to control sulfide emissions which requires energy. As an alternative to oxygen, nitrate or nitrite can be used to control sulfide generation while treating the S-containing wastewaters [5]. Nitrate and nitrite are usual constituents of many wastewaters, or can be generated separately in a nitrification reactor [6]. Compared to oxygen, nitrate and nitrite have the added advantage of being highly soluble in water. Thus the use of nitrate or nitrite does not require the application of an external gas flow; consequently, there will be less stripping of gaseous sulfide. The feasibility of using nitrate and nitrite as electron acceptors for sulfide oxidation has been successfully demonstrated in several reactor studies [7–14].

Wastewater treatment processes are vulnerable to variations in one or more operational parameters (such as pH and fluctuating loads) which affect the overall performance of the reactor. Even some of these variations can be predicted or controlled; the reactor's performance would still be deteriorated due to extreme disturbances in these operational parameters. If the shock lasts for a longer time, acclimation may be observed. In most cases the performance would revive in the end. The transient shocks are very common in the industrial operations, such as mechanical problems. Literature review suggested that a few reports highlighted the role of pH and transient shocks in affecting the hydrogen sulfide oxidation [15,16]. Thus the present study was designed to elucidate the effect of transient substrates and pH shocks on the simultaneous sulfide and nitrate removal in anaerobic reactor.

2. Materials and methods

2.1. Inoculum and enrichment of microbial communities

Inoculum was taken from the anaerobic methanogenic reactor of Dengta wastewater treatment plant (WWTP) located in Hangzhou City of China. Its total solids (TS) and volatile suspended solids (VSS) were 95.03 g/L and 68.68 g/L, respectively, with VSS/TS ratio of 0.72. The anoxic sulfide oxidizing reactor was operated under lithoautotrophic conditions where sulfide was used as electron donor and nitrate as electron acceptor to accomplish denitrification. For the initial 1 month the reactor was fed with synthetic

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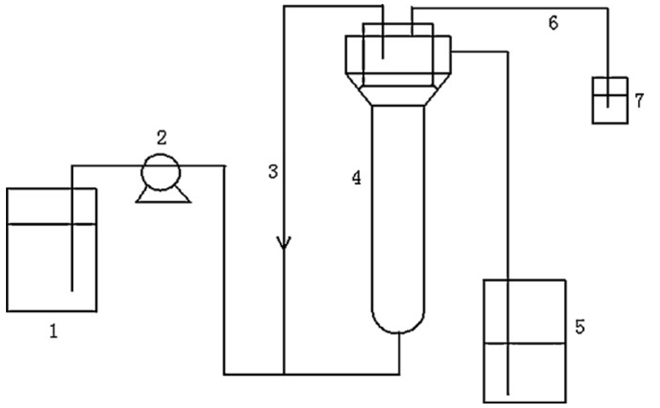

Fig. 1. Flow chart of anaerobic sulfide and nitrate removal process. ((1) influent tank, (2) pump, (3) recycle stream, (4) UASB reactor, (5) effluent tank, (6) gas outlet and (7) water seal).

wastewater in order to acclimatize the bacteria to the new substrates and sludge enrichment.

2.2. Synthetic wastewater

The reactor was fed with synthetic influent containing $NaHCO_3$, $MgCl_2$, KH_2PO_4, (1 g/L each), $(NH_4)_2SO_4$ (0.24 g/L) and trace element solution (1 mL/L). The composition of trace element solution was used according to Mahmood et al. [14]. The nitrate-nitrogen and sulfide-sulfur concentrations were added in the form of sodium sulfide ($Na_2S{\cdot}9H_2O$) and potassium nitrate (KNO_3), respectively, with their concentrations varying according to the type of experiment conducted. 0.1 M HCl solution was used to adjust pH value.

2.3. Reactor

The anaerobic sulfide oxidation (ASO) reactor was an upflow reactor with biomass retention in a continuous operational mode (Fig. 1). The reactor was made of perspex with a working volume of 1.3 L. The synthetic influent was pumped through a peristaltic pump from a 10 L influent vessel to the reactor. A recycling pump was employed to mix the influent (substrate) and sludge (biocatalyst) well and hence to decrease possible substrate inhibition. The ratio of recycling flow to the influent flow was set to about 2.5–3. The temperature of the reactor was controlled between 29 °C and 31 °C.

2.4. Experimental design

The anaerobic reactor for simultaneous sulfide and nitrate removal was operated stably for more than 4 months before conducting shock loading tests. When the influent pH was about 7.0 at hydraulic residence time (HRT) of 4 h, the sulfide-sulfur and nitrate-nitrogen concentrations in the influent were 520 mg/L and 95.5 mg/L, respectively; the removal rates of sulfide-sulfur and nitrate-nitrogen were 6.23 kg/(m^3 d) and 1.04 kg/(m^3 d), respectively. While the effluent sulfide-sulfur and nitrate-nitrogen concentrations were 0.51 mg/L and 8.92 mg/L, respectively. Under these circumstances, nitrite was not detected in the effluent.

Keeping other operational parameters at constant level, a way of simulating shock loading was to increase the influent substrate concentrations or pH values abruptly. Based on the range of safe factors, the substrate shock load intensities were set at 2.0, 2.5 and 3.5 times of the original influent concentrations, while the pH shock loads intensities included the rise in the influent pH from 7.0 to 8.0, 9.0 and 10.0. We did not choose pH value higher than 10 because it was harmful to the performance of the reactor. Each shock load lasted for 2 h. After shock loadings, the influent substrate concentrations were decreased to the original level. The pH and the substrate concentrations were determined every 30 min until the reactor performance recovered completely.

2.5. Analytical procedures

Influent and effluent ammonium-nitrogen, nitrite-nitrogen, nitrate-nitrogen, pH, sulfide and sulfate were analyzed during the operation of ASO reactor. Ammonium-nitrogen (NH_4^+-N) was measured by phenate method [17], nitrite-nitrogen (NO_2^--N) through colorimetric method and nitrate-nitrogen (NO_3^--N) was analyzed through ultraviolet spectrophotometric screening method [17] on daily basis using spectrophotometer (Unico UV-2102 PC and 722S, China). The sulfide was determined by iodometric method and sulfate was measured through turbimetric method [17]. Sulfide-sulfur and nitrogen were calculated according to principle of mass conservation. The pH was determined following standard method [17]. A three-point calibration of pH meter was performed daily. Total solids (TS) concentration was determined according to gravimetric method at 103 °C [17] and volatile solids were analyzed through gravimetric method at 550 °C [17].

3. Results

3.1. The performance of reactor under shock loads

When the influent sulfide and nitrate concentrations were increased from 520 mg/L and 91 mg/L to 1040 mg/L and 182 mg/L (2.0 times), respectively, the reactor showed an immediate rigorous response: the effluent pH increased rapidly and reached 8.94 which persisted even after an hour of the shock load. The effluent sulfide and nitrate concentrations increased from less than 1 mg/L and 8.90 mg/L to 6.78 mg/L and 20.97 mg/L, respectively. Upon increasing the influent sulfide and nitrate concentrations to 2.5 and 3.5 times over the original one, the responsive curves for pH and the substrates concentrations to the high intensity of shock loads were similar to one when exposed to the low intensities, and the responsive strength increased with the increasing shock load intensity (Figs. 2A–4A

When the influent pH was increased from 7.0 to 8.0 abrup).

When the influent pH was increased from 7.0 to 8.0 abruptly, the reactor pH escalated from 7.50 to 7.96 within half an hour, then stabilized. Until an hour after the shock load, the reactor pH reached at the highest value 8.57 whereby the effluent sulfide and nitrate concentrations increased from less than 1 mg/L and 7.60 mg/L to 7.46 mg/L and 15.94 mg/L, respectively. In the situation when the influent pH was increased to 9.0 and 10.0, the responsive curves of pH and the substrate concentrations to the high intensity shock loads were similar to ones exposed to low ones, and the responsive strength went high with the increasing shock load intensity (Figs. 2B–4B).

Sensitivity can be used to indicate the effect of operational conditions on the performance of the reactor [18]. Table 1 showed that the effluent sulfide concentration was a more sensitive parameter in response to pH and substrate shocks than the nitrate. Compared with the substrate shock loads, the pH shock loads had more adverse effects on the effluent sulfide. When the reactor was run under the pH 10.0 shock load, the effluent sulfide concentration was 31 times over the stable concentration. Thus, it could be used as performance indicator parameter.

3.2. The performance of reactor after shock loads

The application of the substrate shock load of 2.0 times over the original one, the reactor pH started to decrease slowly, and

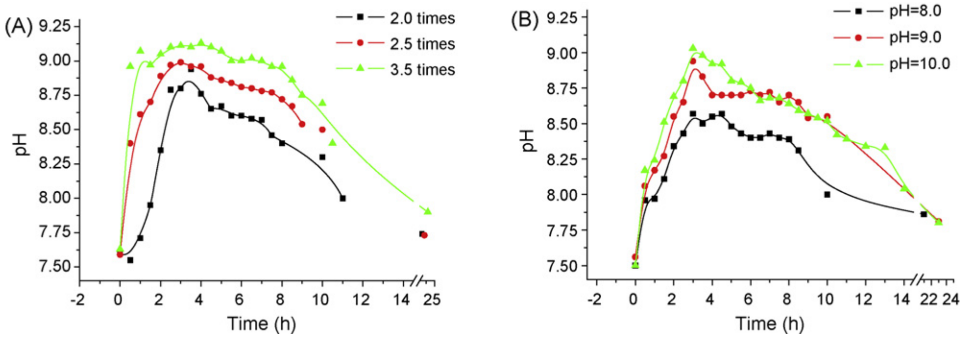

Fig. 2. The response of effluent pH to different shocks.

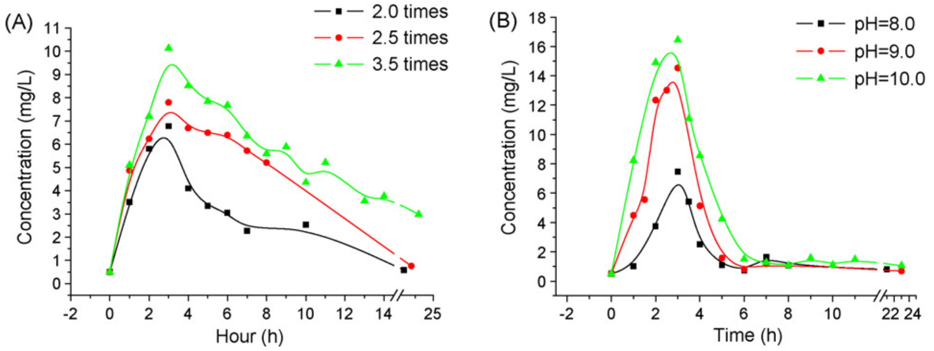

Fig. 3. The response of effluent sulfide concentration to different shocks.

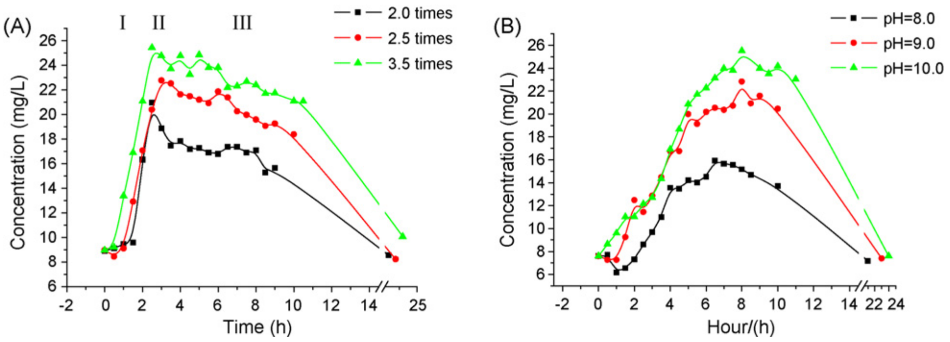

Fig. 4. The response of effluent nitrate concentration to different shocks.

it returned to 7.74 after 21 h. The sulfide and nitrate concentrations in the effluent decreased to 0.59 mg/L and 8.56 mg/L, respectively. When the influent sulfide and nitrate concentrations were increased to 2.5 and 3.5 times over the original one, pH and the substrates concentrations could recover to the normal stable condition, however, the recovery time increased with the increasing shock load intensity. It took 22 h and 30 h to recover 2.5 and 3.5 times of shock load, respectively (Figs. 2A–4A).

When exposed to the pH shock load of pH 8.0, the reactor pH continued to increase which returned to 7.86 after 21 h. The effluent sulfide decreased rapidly, and it recovered to stable state after 6 h (less than 1 mg/L). The effluent nitrate decreased slowly, and it

Table 1
Effects of different shock loads on the responsive index.

Intensity		Max response			Sensitive index (SI)		
		Effluent pH	Effluent sulfide (mg/L)	Effluent nitrate (mg/L)	Effluent pH	Effluent sulfide	Effluent nitrate
Substrate shock loads	2.0 times	8.94	6.78	20.97	0.17	12.29	1.35
	2.5 times	8.99	7.80	22.77	0.18	16.06	1.55
	3.5 times	9.13	10.13	25.43	0.19	18.86	1.85
pH shock loads	pH 8.0	8.57	7.46	15.94	0.13	13.63	0.79
	pH 9.0	8.94	14.53	22.83	0.18	27.49	1.56
	pH 10.0	9.03	16.44	25.52	0.19	31.24	1.86

$S_I = (O_{max} - O_n)/O_n$.
S_I, selectivity index; O_{max}, the maximum substrate concentration in the effluent; O_n, the normal substrate concentration in the effluent.

Table 2
Effects of different shock loads on the recovery indices.

Intensity		Recovery time		Recovery velocity					
		Absolute value (h)	Relative value (HRT)	pH value (1/h)	R^2	Sulfide (mg/(L h))	R^2	Nitrate (mg/(L h))	R^2
Substrate shock loads	2.0 times	21	5.25	0.06	0.9882	0.18	0.8775	0.54	0.9428
	2.5 times	22	5.50	0.07	0.9865	0.33	0.9943	0.76	0.9740
	3.5 times	30	7.50	0.07	0.9203	0.31	0.7737	0.75	0.9538
pH shock loads	pH 8.0	21	5.25	0.04	0.9660	3.20	0.9135	0.61	0.9987
	pH 9.0	23	5.75	0.05	0.9405	6.48	0.9366	0.99	0.9929
	pH 10.0	24	6.00	0.06	0.9525	6.10	0.9724	0.98	0.9199

returned to stable state after 22 h (7.18 mg/L). When the influent pH values were increased to 9.0 and 10.0 times over the original one, both pH and the substrates concentrations could recover to the normal and stable condition, although the recovery period increased with the increasing shock load intensity. The recovery process took about 24 h (Figs. 2B–4B).

Recovery time is an important index to evaluate the recoverability of the reactor [19,20]. Table 2 shows that the greater was the intensity of shock load, the longer was the required recovery period. The reactor performance could be recovered by allowing sufficient recovery time. But it was just suitable up to a limited extent. Once the intensity of shock load exceeded the tolerable range (such as the substrate shock load of 3.5 times), the performance was hard to recover.

Recovery velocity is negatively correlated with recovery time, which can also indicate the recovery process of the reactor's performance. Origin software was used to linear fit the curve, in which the ordinate was the performance indices of the reactor (effluent pH values, sulfide and nitrate concentrations) and the abscissa was the recovery time. The slope of the curve was the recovery velocity (Table 2). When the reactor was exposed to the substrate shock loads, the maximum recovery velocities for the pH, sulfide and nitrate were $0.07\,h^{-1}$, 0.33 mg/(L h) and 0.76 mg/(L h), respectively. During the pH shock loads, the maximum recovery velocities of the pH value, sulfide and nitrate were $0.06\,h^{-1}$, 6.48 mg/(L h) and 0.99 mg/(L h), respectively. It implied that the reactor had a stronger aptitude to recover from pH shock loads than substrate shock loads.

However, when the shock load intensities were 2.5 and 3.5 times, the recovery velocities of these indices were not significantly different (keeping confidence interval of 95%). The situation of pH shock loads was similar to that of substrate shock loads. When the intensities of pH shocks were 9.0 and 10.0, the recovery velocities of the indices were not significantly different also (at confidence interval of 95%). It implied that the recoverability of the reactor was limited, which did not increase with the increasing intensity. The reason of such limited recoverability under increasing shock intensities needs further investigations.

4. Discussion

Usually, shock load is regarded as an important motive that would cause the performance instability of a reactor [18]. It seems that shock load overloads the reactor that results in the performance deterioration [21]. Usually, the overloads are abrupt and instantaneous; consequently the reactor performance cannot be synchronized. In order to avoid the instability under shock loads, the operational conditions should be controlled stably along with timely eliminating the fluctuations of environmental factors. On the other hand, the "carrying capacity" of the reactor should also be considered. If the reactor suffers from the shock loads, the extra "carrying capacity" of the reactor can take up the overload part to tolerate the negative effects caused by the fluctuations.

The microorganisms are the essential part of the biological wastewater treatment processes. The stability of the reactor depends on the stabilized microbial growth and metabolism [22], which needs proper growth conditions, such as environmental conditions and nutrient demands. Any change in the prevailing conditions may influence the microbial metabolism, which would affect the performance of the reactor. The interactions among the conditions are very complex; any change in one condition may induce some undesirable changes. In this way, the shock load is "the fuse". Any abrupt change in one condition may result in the whole change of the reactor's performance, finally leading to the deterioration of the reactor's performance.

According to Jin et al. [18], there are two aspects of the stability of a bioreactor. One is resistibility which means the ability to resist any disturbance; the other is resilience, i.e. the ability to recover from the disturbance. It is an abstract concept, which cannot be considered as judgment index. In the present paper, the authors used two specific indices to make the concrete concept. The sensitivity index and the recovery velocity were used to estimate the ability of the reactor to maintain the general stability. These parameters represent the response of the reactor to the shock loads and the recovery process.

The effluent pH is an important parameter used to the judge stability of a reactor [23]. The sensitivity indices showed that, the effects caused by pH shock on the performance of the reactor were greater than the substrate shock loads. The reason behind such behavior might be that simultaneous sulfide and nitrate removal was an alkalinity-producing process (Eq. (1)). A high reactor pH will have adverse effects on the overall performance of the reactor. The reactor performance did not start to recover just after the substrate shock loads, but continued to deteriorate resulting from the pH value outside the optimum range for the microbial metabolism:

$$5HS^{-}+2NO_3^{-}+7H^{+} \rightarrow 5S^{0}+N_2+6H_2O \qquad \Delta G_m^{\theta}=-1264\,kJ/mol \tag{1}$$

The recovery velocity is the function of substrate concentrations or pH in the reactor and the recovery time, which can be used to induce resilience. The recovery velocities showed that the reactor performance recovered faster from the pH shock loads than the substrate shock loads. After applying a pH shock of 10.0, pH decreased below 8.75 in 6 h, while the reactor suffering from 3.5 times shock loads took 11 h for its recovery (Fig. 2). When pH shock loads decreased, the microbial biomass would return to their optimum growth condition quickly.

It is interesting to note that though pH shock load caused significantly larger effects on the reactor performance than shock loading, it easily recovered from it. It means that the microorganisms that simultaneously removed sulfide and nitrate were very sensitive to environmental conditions, particularly pH variations. The change of pH can immediately affect the microbial metabolism through inactivation of enzymes and the dissociation states of the substrates. So pH shock had serious and significant effects on the performance of the reactor. Once the pH shock load was over, the inhibition caused by pH was relieved quickly. According to Lettinga et al. [24], the process efficiency recovers almost immediately from pH shock loads when the influent pH is returned to the optimal range. The same was observed during the pH shock investigation in our study.

Substrate shock load is different from pH shock. Increased substrate concentration does not affect the microbial activities directly. Although the substrate concentration increased in the reactor, the cell membranes acted as physical protection barriers preventing the entry of excess substrate into the cell for a while, thus relieving the substrate shock loads. That is why substrate shock load had less significant effects than pH shocks. With the continued substrate shock loads, the reactor pH increased. It would aggravate the intensity of substrate shock loads. So the reactor was hard to recover from the substrate shock loads.

5. Conclusion

(1) When the reactor suffered from substrate or pH shock loads, the reactor performance fluctuated considerably. The pH values aggravate the intensity of substrate shock loads. The performance of the reactor was more sensitive to pH shock loads than substrate shock loads. Among pH values and substrate concentrations, sulfide was the most sensitive index, whose effluent concentration was 31 times higher than the stable concentration. Thus, effluent sulfide can be used as indicative parameter of the reactor performance.

(2) The reactor could recover from substrate or pH shock loads in the tested range. After applying substrate shock loads of 2.0–3.5 times and pH shock loads of 8.0–10.0, pH and substrate concentrations could return to the original state, and the recovery time was less than 30 h. The recovery velocities of the pH values and substrate concentrations were constant after the shock loads. The performance recovery of the reactor after pH shock was faster than that after the substrate shock loads.

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