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Simultaneous removal of sulfide, nitrate and acetate: Kinetic modeling

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ABSTRACT

Biological removal of sulfide, nitrate and chemical oxygen demand (COD) simultaneously from industrial wastewaters to elementary sulfur (S^0), N_2, and CO_2, or named the denitrifying sulfide (DSR) process, is a cost effective and environmentally friendly treatment process for high strength sulfide and nitrate laden organic wastewater. Kinetic model for the DSR process was established for the first time on the basis of Activated Sludge Model No. 1 (ASM1). The DSR experiments were conducted at influent sulfide concentrations of 200–800 mg/L, whose results calibrate the model parameters. The model correlates well with the DSR process dynamics. By introducing the switch function and the inhibition function, the competition between autotrophic and heterotrophic denitrifiers is quantitatively described and the degree of inhibition of sulfide on heterotrophic denitrifiers is realized. The model output indicates that the DSR reactor can work well at $0.5 < C/S < 3.0$ with influent sulfide concentration of 400–1000 mg/L. At >1000 mg/L influent sulfide, however, the DSR system will break down.

1. Introduction

Biological removal of sulfide, nitrate and chemical oxygen demand (COD) simultaneously from industrial wastewaters is a cost effective and environmentally friendly process. Autotrophic denitrifiers convert sulfide to S^0 with available nitrate [1]. Wang et al. [2] developed a simultaneous de-sulfurization and denitrification (SDD) process utilizing a single autotrophic strain, *Thiobacillus denitrificans*, in a CSTR. Reyes-Avila et al. [3] achieved maximum removal rates for nitrogen, sulfide, and COD from a single CSTR of 0.209 kg-N/(m^3 d), 0.294 kg-S/(m^3 d), and 0.303 kg-C/(m^3 d), respectively. Chen et al. [4] utilized an expanded granular sludge bed (EGSB) reactor for simultaneous removal of sulfide, nitrate, and organic carbon at 3.0 kg-S m^{-3} d^{-1}, 1.78 kg-N/(m^3 d), and 1.13 kg-C/(m^3 d), respectively. A compromising balance between autotrophic and heterotrophic denitrifiers presents the prerequisite of success of the denitrifying sulfide removal (DSR) process. Competition between the autotrophic and heterotrophic denitrifiers under mixotrophic environment complicates system dynamics and appropriate control system design [3,5].

Biological models, such as Activated Sludge Model (ASM) or anaerobic digestion model (ADM) developed by International Water Association (IWA) [6–8], were developed to quantitatively describe the substrate degradation rates and the microbial growth rates in wastewater treatment processes [9,10]. However, the models for DSR process are still lacking to the authors' best knowledge.

This paper aims at developing the biological model on the basis of ASM1 model for DSR tests conducted in an EGSB reactor operated at C/S ratio of 0.75–1.26 and at influent sulfide concentration of 200–800 mg/L. Then the calibrated model was utilized to quantitatively study the effects of C/S ratio and influent sulfide concentrations on DSR performance.

2. Materials and methods

2.1. The EGSB reactor

The bench-scale EGSB reactor used in this study was refined from that used in Chen et al. [4] (Fig. 1). The EGSB reactor was made up of a plexiglass column with an internal diameter of 6 cm and a height of 180 cm. The working volume was 4.0 l (excluding head space). The bottom of the column, with a height of 5 cm, was the influent distributor. The middle part with a height of 140 cm and a height-per-diameter ratio of 23.33 was the DSR reaction zone filled with biological granules collected from an upflow anaerobic sludge blanket (UASB) reactor treating brewage wastewater of 70.6 mg/L suspended solids (SS) and 52.3 mg/L volatile suspended solids (VSS). The top, with a height of 35 cm, was the three-phase separator. An inverted funnel shaped gas separator was used to collect the produced biogas. A liquid upflow of 5 m/h was maintained for internal circulation. The EGSB reactor was kept at 30 °C. For the granules, the specific gravity was 1.065; the physical strength, expressed as integrity coefficient (the ratio of residual granules to

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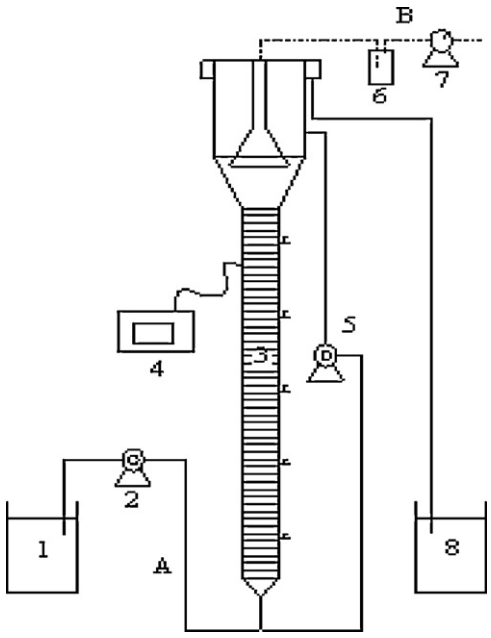

Fig. 1. The schematic of experimental reactor (1) feed tank, (2) influent pump, (3) EGSB reactor, (4) thermostat, (5) recycling pump, (6) gas sampler, (7) wet gas meter, (8) effluent water metering tank. A. water pipe, B: gas tube.

the total weight of the granular sludge after 5 min of shaking at 200 rpm on a platform shaker, expressed as percent), is higher than 95%. The reactor was set-up under mixotrophic conditions and during the whole process all sludge was stabilized. The influent sulfide and the ratio of C/S/N were 200 mg S/L and 1/1/1, respectively. The influent pH and hydraulic retention time maintained were 7.5 and (HRT) 10 h.

2.2. Tests

Experiments were conducted to study the effects of C/S and influent sulfide concentrations on the performance of the DSR-EGSB process. The effects of the ratios of C/S (0.75 mol/mol, 1.0 mol/mol and 1.26 mol/mol) were investigated with influent sulfide and nitrate concentrations of 400 mg S^{2-}/L and 175 mg NO_3^-N/L (giving the S/N ratio of 1.0) at pH 7.5 controlled by hydrochloric acid and hydraulic retention time (HRT) 10 h. With prescribed C/S ratio, effects of sulfide concentrations on DSR process performance were studied at concentration of 200–800 mg/L for model calibration. During the study sodium sulfide, sodium nitrate and sodium acetate acted as sulfide, nitrate, and acetate, respectively. And the headspace above the medium was flushed with N_2 to exclude oxygen to prevent the chemical oxidation of sulfide supply.

2.3. Chemical analysis

An ion chromatography (Dionex ICS-3000, USA) measured the concentrations of acetate, nitrate, nitrite, sulfate, and thiosulfate in the collected liquor samples following 0.45-μm filtration. Sample separation and elution were performed using an IonPac AG4A AS4A-SC 4 mm analytical column (Dionex, USA) with carbonate/bicarbonate eluent (1.8 mmol/dm^3 Na_2CO_3/1.7 mmol/L $NaHCO_3$ at 1 cm^3/min) and a sulfuric regeneration (H_2SO_4, 25 mmol/L at 5 cm^3/min). The sulfide concentration was determined by potential titration using Sure-Flow™ Combination Silver/Sulfide Electrodes (Tianli Biochem, China). The solution alkalinity was measured via titration using diluted hydrochloric acid (HCl). A pH/ORP meter (pHS-25) determined the pH/ORP of the liquid samples. The compositions in the gas phase were measured by a gas chromatography (Agilent 4980 DGC, USA). S^0 was qualitatively analyzed with hexahydropyridine and quantitative analyzed by sulfur balance analysis (defined as the percent of S^0 produced in the influent total sulfur).

3. Experimental results

3.1. Effects of C/S ratio

The reactor was under anaerobic conditions as indicated of −300 mV ORP. Fig. 2 shows the sulfide, nitrate and acetate removal degree at C/S ratio 0.75–1.26 (stages I–III). At C/S = 1.0, the sulfide, nitrate and acetate were completely removed. At C/S = 0.75, the organic carbon was insufficient for nitrate removal via heterotrophic denitrification. Hence, a 90% (about 0.38 kg-N/(m^3 d)) nitrate-N removal rate was noted. At C/S = 1.26, the heterotrophic denitrifiers overcompeted the autotrophic denitrifiers, yielding a 92%(about 0.89 kg-S/(m^3 d)) removal rate of sulfide-S. The last observation correlates with those by Oh et al. [11] and Lee et al. [12] that the presence of organic compounds enhances the nitrate removal under mixotrophic condition in a sulfur-utilizing autotrophic denitrification system.

In the present test N_2O and nitrite accumulation were not noticeable, all nitrate reduced were converted to N_2. There is no CH_4 produced, the organic substrate removal may mostly convert to CO_2. And this result was conforming to the study of Chen et al. [4]. Additionally, the S^0 conversion rate was maintained at around 80% (0.77 kg-S/(m^3 d)). About 20% (0.19 kg-S/(m^3 d)) influent sulfides were converted to sulfate.

3.2. Effects of influent sulfide concentration

Fig. 3 shows the sulfide, nitrate and acetate removal degree with influent sulfide concentration of 200–800 mg/L. The C/S ratio was fixed at 1.0 and influent pH 7.5.

After the startup period, the EGSB reactor removed completely the sulfide-S, the acetate–COD, and the nitrate-N. Further increase in loading rates of sulfide, nitrate and acetate to 1.96 kg-S/(m^3 d), 0.84 kg-N/(m^3 d) and 0.72 kg-C/(m^3 d), did not reduce the removal rates. In most cases the sulfide was nearly completely converted to S^0 (Fig. 2a).

4. Kinetic model

4.1. Model development

The mathematical model for describing the reactor performance is implemented in the well-established AQUASIM simulation software [13]. The biological conversion processes were modeled using a modified ASM1 with a consideration of carbon removal and denitrification [7]. The established model is calibrated and used to simulate the biological reactions that occur in the DSR system, and the simulation results are compared with the experimental data obtained.

4.1.1. Biological reactions

The present DSR model adopted modified ASM1 reaction scheme to account for the simultaneous COD oxidation and SDD processes using nitrifier, denitrifier and aerobic carbon removal bacteria. The denitrifiers, including autotrophic and heterotrophic counterparts, were active only under anaerobic condition. Autotrophic denitrifier conducted denitrification not ammonification reaction. The heterotrophic denitrifiers completed denitrification and carbon removal. A switch function was intro-