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Experimental study on pressurized activated sludge process for high concentration pesticide wastewater

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Abstract

Pressurized biochemical process derived from traditional activated sludge processes is an innovative technology for wastewater treatment. The main advantage of the pressurized process is that the oxygen transfer barrier can be overcome by increasing the dissolved oxygen level. In this study, high concentration pesticide wastewater was treated by pressurized activated sludge process. It was found that the removal of chemical oxygen demand (COD) increased steadily with the increase of operating pressure, aeration time, and sludge concentration. When the operation pressure was 0.30 MPa and the aeration time was 6 hr, 85.0%–92.5% COD, corresponding to an effluent COD of 230–370 mg/L, was removed from an influent COD of 2500–5000 mg/L. The obtained outlet COD concentration was lower than 350–450 mg/L for the identical process operated under the atmospheric pressure. In addition, pressurized biochemical process could produce a higher COD volumetric loading rate at 5.8–7.6 kg COD/(m^3·day), compared with 2.0–2.8 kg COD/(m^3·day) using the same equipment at the atmospheric pressure. The COD concentration followed a modified Monod model with V_{max} 2.31 day^{-1} and K_S 487 mg/L.

Key words: pressurized biochemical process; pesticide wastewater; activated sludge; kinetics

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Introduction

Activated sludge processes are the main technology used to treat organic wastewater. However, it is difficult to increase the removal rate and the volumetric loading rate of chemical oxygen demand (COD), because of the limited oxygen solubility in wastewater at atmospheric pressure. In addition, the operation cost is high, especially for large volume reactors. Through the pressurized activated sludge process, the solubility of oxygen in wastewater can be enhanced by increasing total air pressure and thus the oxygen transfer rate can be promoted (Ellis et al., 1997; Krauth and Staab, 1993; Lei et al., 2008). Ho and Tan (1988) applied the pressurized activated sludge process to a secondary treatment of palm oil mill effluent and their results showed that the high efficiency of the process was related to the high oxygen transfer rate at elevated pressure in the bioreactor, and that, with a dissolved oxygen level of 10–14 mg/L in the bioreactor, filamentous microbe growth and sludge bulking were prevented. Lin and Huang (1994) studied the efficiency of cyclic pressurized aeration in the activated sludge process and observed that the COD removal increased steadily with increasing operating pressure, aeration time and decreasing wastewater/sludge ratio. In pressurized activated sludge process, the oxygen transfer barrier was overcome by the rise of dissolved oxygen level in the system, such that high loadings, effective COD removal, high oxygenation efficiencies, and low sludge yield coefficients can be achieved (Ellis et al., 1997; Krauth and Staab, 1993; Guo et al., 2001). It was also found that the microorganism in the activated sludge process had tolerance to pressure (Guo et al., 2001).

Compared with other approaches, the pressurized activated sludge process has the following advantages: (1) it has high volumetric organic loading rate and high operating flexibility; (2) it occupies small land area and the associated cost is low; and (3) the most important, it results in a little residual sludge (Huang et al., 2004). Organic wastewaters from dyeing (Ming and Gao, 1996; Huang et al., 2004; Pan et al., 2004; Zhang et al., 2004; Fang et al., 2006), chemical industry (Liu, 1997; Cheng and Bai, 2000; Li et al., 2002; Ma, 2002; Liu and Meng, 2004), food industry (Hu and Kong, 1995; Su et al., 2000; Yan et al., 2003; Zhao et al., 2008) have been treated by pressurized activated sludge in lab-scale. Liu and Meng (2004) found that high-efficiency of removing COD and phosphorus from spray paint wastewater could be achieved by using coagulation-pressurized bio-oxidation process. Fang et al. (2006) reported that more than 70% COD could be removed and less than 600 mg/L of effluent COD could be obtained when the organic intermediate wastewater was

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treated by the pressurized activated sludge process.

Due to high toxicity, high concentration and complicated composition of wastewater from manufacturing agrochemicals, its treatment and purification have become one of the biggest challenges. In this article, we described the treatment of high concentration pesticide wastewater by the pressurized activated sludge process, gave an explanation for the improvement of the COD removal rate achieved, and reported the kinetics parameters obtained, which can be used for bioreactor simulation, design and optimization in wastewater treatment.

1 Materials and methods

1.1 Experimental materials

The wastewater was supplied by a pesticide factory, which produced insecticides (omethoate, parathion-methyl methamidophos, colofentezine acephate, fenvalerate, omethoate-fenvalerate etc.), herbicides (butachlor, acetochlor, metolachlor, fenclorim ect.), and fungicide (prochloraz). The characteristics of the raw wastewater from pesticide factory were: COD_{Cr} 2500–5000 mg/L; BOD_5 750–1200 mg/L; suspended solid (SS) 40–50 mg/L, NH_3-N 40–50 mg/L, total phosphorus (TP) 300–400 mg/L, pH 4–5. We denoted the pesticide by COD_{Cr} and BOD_5. Activated sludge was obtained from a wastewater treatment station of the same pesticide factory, and was acclimatized for two weeks before experiment. Most of the chemicals used were AR grade.

1.2 Bioreactor setup

A schematic diagram of the process is shown in Fig. 1. The bioreactor is a polypropylene column with 150 mm

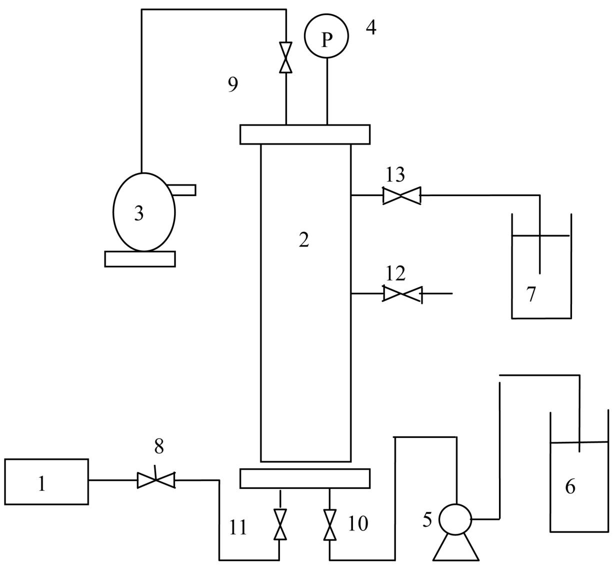

Fig. 1 Schematic flow diagram of the pressurized activated sludge process. (1) compressor; (2) pressurized bioreactor; (3) flow mater; (4) pressure gauge; (5) pump; (6) influent tank; (7) effluent tank; (8) redactor; (9) outlet air valve; (10) inlet water valve; (11) inlet air valve; (12) sampling valve; (13) effluent valve.

in diameter, 1000 mm in height and 12 L in its effective volume. Porous grit stone diffusers with a diameter of 20 mm were used to aerate the sludge. Wastewater was pumped into the bioreactor from the raw wastewater tank, while the compressed air entered the bioreactor through an inlet air valve at the bottom. The pressure in the bioreactor and the air flow were controlled by the inlet air valve and the outlet valve. The system was operated at absolute pressures from 0.1 up to 0.4 MPa and the influent COD was 2500–5000 mg/L under semibatch operation conditions. At the end of the treatment, the supernatant was vented from the effluent valve. The operation temperature was controlled at 25°C.

1.3 Analysis

Wastewater samples were collected every two hours from the reactor and assayed for COD, pH and mixed liquor suspended solids (MLSS). Three replicates for each sample were obtained. COD, pH and MLSS were assayed according to the Standard Methods (SEPAC, 1989).

2 Results and discussion

2.1 Effect of pressure on COD removal

Maintaining the appropriate concentration of dissolved oxygen in the bioreactor is important for efficient operation of a bioreactor. Oxygen can affect the activity of microorganisms, which in turn affect the COD removal rate. The pressurized aeration increases the concentration of dissolved oxygen (DO) in mixed liquor in reactor and speeds up the biodegradation rate of organic matter in wastewater. To this end, COD removal was investigated at different pressures ranging from 0.10 to 0.40 MPa, while the aeration rate (aeration air volume/ effective volume of bioreactor/ aeration time), the MLSS concentration and the aeration time were fixed. Aeration air volume was calculated at 25°C and 0.10 MPa.

Figure 2 shows the COD removal with respect to the aeration time at different pressures with MLSS of 2 or 6 g/L and the aeration rate of 25 $m^3/(m^3 \cdot hr)$. Figure 3 shows the COD removal with respect to different pressures with MLSS of 2 or 6 g/L at the aeration time 6 hr. The COD removal increased rapidly at low pressure. Once a certain pressure reached, however, the increase of COD removal became slowly but steadily at high pressures. A certain pressure was defined as a critical pressure. As shown in Fig. 3, the critical pressure increased from 0.15 to 0.30 MPa as the MLSS concentration increased from 2 to 6 g/L.

This is consistent with a biochemical reaction with a control step from oxygen transfer, improving that the oxygen transferring rate could increase the biochemical reaction rate. However, the oxygen transferring rate could not affect the biochemical reaction significantly when the oxygen transferring rate increased to a high enough level. At that level, the oxygen transferring rate was not a limiting factor in the biochemical reaction. A high DO concentration can be maintained in the mixed liquor with pressurized aeration. High DO was associated with high

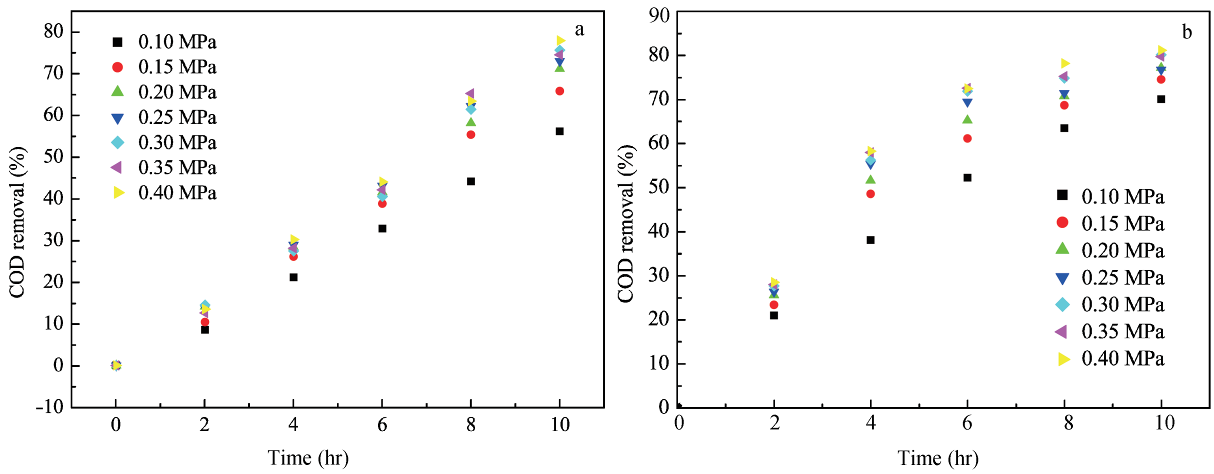

Fig. 2 COD removal vs. the aeration time at different pressures and MLSS. (a) aeration rate 25 $m^3/(m^3 \cdot hr)$, MLSS 2 g/L; (b) aeration rate 25 $m^3/(m^3 \cdot hr)$, MLSS 6 g/L.

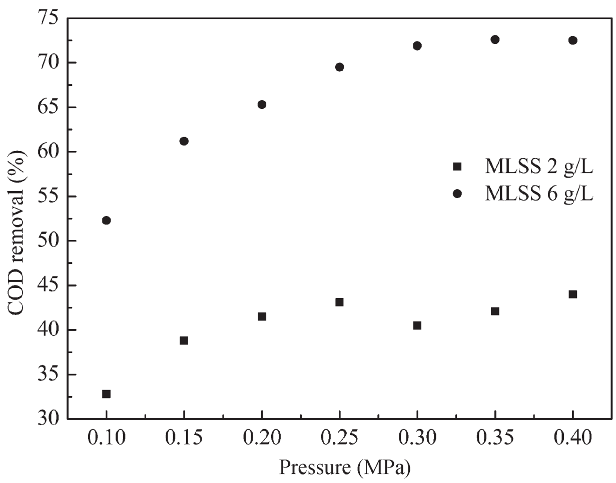

Fig. 3 COD removal vs. pressures at the aeration time 6 hr and aeration rate 25 $m^3/(m^3 \cdot hr)$.

MLSS concentrations. Different activated sludge concentrations result in different oxygen demands while the COD removal can not be improved with significantly high DO concentration at certain MLSS concentration. The COD removal was increased with the aeration time at a fixed experimental pressure, indicating that the pressure used in our experiment does not have a negative effect on the activities of microorganisms.

2.2 Effect of aeration rate on COD removal

Aeration not only supplies oxygen to bio-reaction but also stirs the wastewater. Although high aeration rate can provide more oxygen to the system, but the energy consumption will increase also by using air pressure pump. An appropriate aeration rate is important for bio-reactor to achieve the high COD removal rate and economic energy consumption. The effect of aeration rate on COD removal was tested. When the aeration rate was less than 15 $m^3/(m^3 \cdot hr)$ and at pressure 0.30 MPa, the wastewater could not be agitated fully and a part of the sludge settled down, yielding relatively low efficiency of COD removal. To ensure the reaction the aeration rate was controlled at 20, 25, 30, 40, and 50 $m^3/(m^3 \cdot hr)$, respectively.

It can be seen in Fig. 4 that COD removal increased rapidly with the increase of the aeration rate. Once a critical aeration rate was reached, the increase of COD removal became slower but steadily even at substantially high aeration rates. The experimental result indicted that COD removal can reach the satisfactory level at the optimal aeration rate 25 $m^3/(m^3 \cdot hr)$ with influent COD 2500–5000 mg/L, pressure 0.30 MPa, MLSS concentration 4 g/L, and aeration time 6 hr.

2.3 Effect of aeration time on COD removal

Aeration time has close relationship with the quality of the treated wastewater and other operation parameters. To determine the optimal aeration time of the pressurized activated sludge process in the lab-scale bioreactor, the effect of aeration time on COD removal was investigated at pressure of 0.3 MPa, aeration rate of 25 $m^3/(m^3 \cdot hr)$, and MLSS concentration of 6 g/L with different influent COD loadings (670, 1086, 1765, 2118 mg/L). As shown in Fig. 5, COD removal increased with the aeration time rapidly at beginning and then became saturated after a certain time

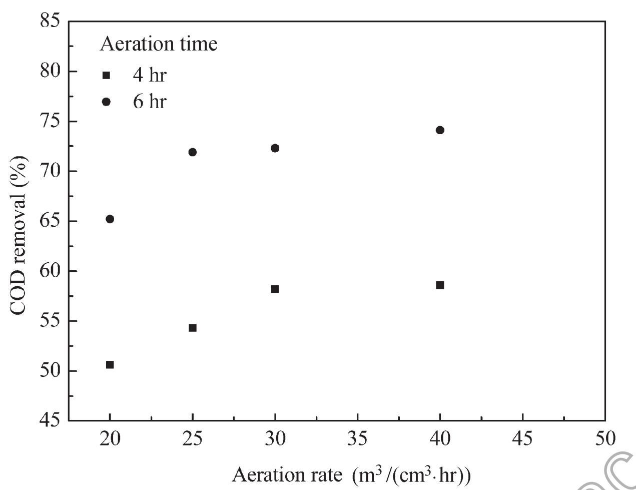

Fig. 4 COD removal during the aeration process for different aeration rates at pressure 0.30 MPa, MLSS 4 g/L.

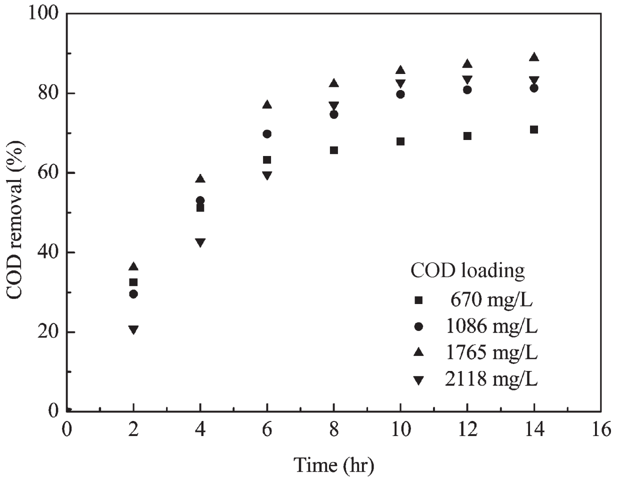

Fig. 5 COD removal during the aeration time under different COD loadings at pressure 0.30 MPa, aeration rate 25 $m^3/(m^3{\cdot}hr)$, MLSS 6 g/L.

point. This point is referred to as the optimal aeration time.

Figure 5 shows that the optimal aeration time extended with the increase of the influent loads. It was about 10 hr at COD loading of 2118 mg/L, while shortened to 6 hr at COD loading 1756 mg/L. The optimal aeration time was 6–8 hr at the pressure of 0.30 MPa.

2.4 Effect of MLSS concentration on COD removal

The influence of MLSS concentration on COD removal was studied by changing MLSS concentration at pressure 0.30 MPa, aeration rate 25 $m^3/(m^3{\cdot}hr)$, and aeration time 6 hr. The results are shown in Fig. 6.

COD removal increased at low MLSS concentrations and reached a maximum value when MLSS was around 6 g/L. With further increase in the MLSS, the COD removal decreased. However, it was difficult to separate sludge from wastewater when the MLSS concentration was higher than 8 g/L because of the effluent turbid and high COD. It was reported that the microorganism in the activated sludge process had tolerance to pressure (Fang et al., 2006). Therefore, it was reasonable to control the MLSS concentrations between 4 and 6 g/L at 0.30 MPa.

2.5 System operation under optimum conditions

Under the optimal conditions (0.30 MPa operating pressure, aeration rate of 25 $m^3/(m^3{\cdot}hr)$, 6 g/L of the MLSS concentration, and 6 hr of aeration time) the pressurized activated sludge bioreactor system can be operated steadily and efficiently. For the purpose of comparison, non-pressurized activated sludge test at atmosphere pressure, aeration rate of 25 $m^3/(m^3{\cdot}hr)$, MLSS concentration of 3 g/L, and aeration time 12 hr was also conducted.

As shown in Fig. 7, COD removal in pressurized activated sludge bioreactor was much higher than that in non-pressurized one because the former had higher activity and sludge concentration. With the pressurized approach at influent COD 2500–5000 mg/L, 85.0%–92.5% COD removal and less than 300 mg/L effluent was achieved. Moreover, the pressurized process had substantially large loading capacity. With a volumetric organic loading rate of 5.8–7.6 kg $COD/(m^3{\cdot}day)$ compared to only 2.0–2.8 kg $COD/(m^3{\cdot}day)$ in non-pressurized one. The pressurized process had a higher COD removal rate because a high dissolved oxygen (DO) concentration can be maintained in the mixed liquor with pressurized aeration.

2.6 Kinetics

The empirical Monod model is frequently used to describe the kinetics of biological substrate removal for activated sludge. A modified Monod model is used to describe the kinetics of non degradable dissolved COD in pesticide wastewater treatment. It can be expressed as Eq. (1):

$$V = -\frac{1}{X}\frac{dS}{dt} = V_{max}\frac{(S - S_n)}{K_S + (S - S_n)} \qquad (1)$$

where, dS/dt is organic degradation rate, V_{max}, K_s, and S_n represent the maximum substrate utilization rate, half velocity coefficient, and no degradation substrate COD, respectively.

Equation (1) is a convenient mathematical representation for a smooth transition from a first-order relation at low concentration to a zero-order relation at high

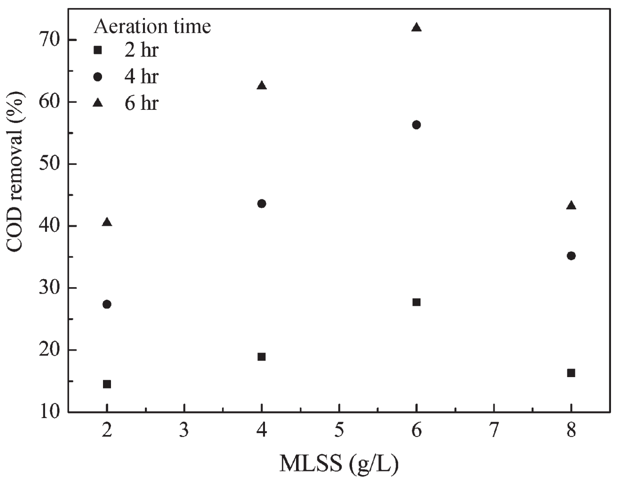

Fig. 6 COD removal change with MLSS at pressure 0.30 MPa, aeration rate 25 $m^3/(m^3{\cdot}hr)$.

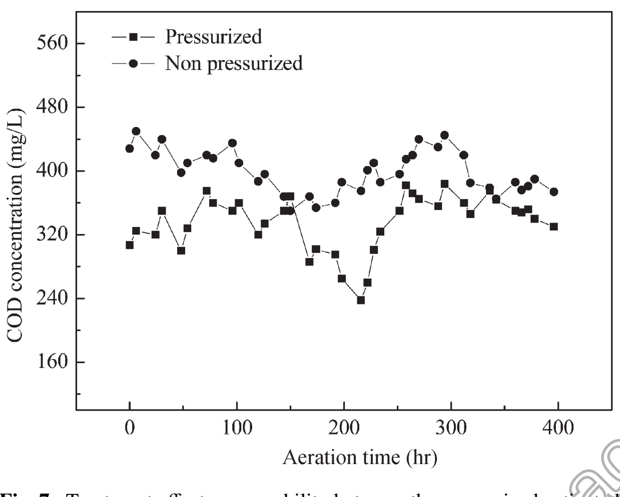

Fig. 7 Treatment effect comparability between the pressurized activated sludge and non-pressurized actived sludge.

concentration, where, S_n should be determined to capture such a transition. The trend of COD removal is shown in Fig. 8 at the influent COD of 2500–5000 mg/L (mixed liquid COD 1200–1600 mg/L), operating pressure of 0.30 MPa, MLSS concentration of 4.12 g/L, aeration time of 6 hr, and aeration rate of 25 $m^3/(m^3 \cdot hr)$.

It can be seen from the curve in Fig. 8 that the residual COD concentration in bioreactor decreases slightly after 6 hr, indicating the existence of difficulty of pollutants degradation. From the experimental data after 6 hr, a first-order relationship can be obtained, as shown in Figs. 9 and 10.

$$V = 7.3568 \times 10^{-5} S - 0.009 \tag{2}$$

S_n of 122 mg/L can in turn be obtained from Eq. (2). Meanwhile, K_S and V_{max} can be calculated from the same experimental data by using the following Eq. (3):

$$\frac{1}{V} = \frac{K_S}{V_{max}} \cdot \frac{1}{(S - S_n)} + \frac{1}{V_{max}} \tag{3}$$

A linear regression of our experimental data gives $1/V_{max}$ = 10.39 hr and K_S/V_{max} = 5057 mg/(L·hr). This gives the V_{max} = 2.31 day^{-1} and K_S = 487 mg/L.

From the above calculations, the kinetics equation of pressurized activated sludge process can be described as the following Eq. (4):

$$-\frac{dS}{dt} = \frac{2.31 \times X(S - 122)}{487 + (S - 122)} \tag{4}$$

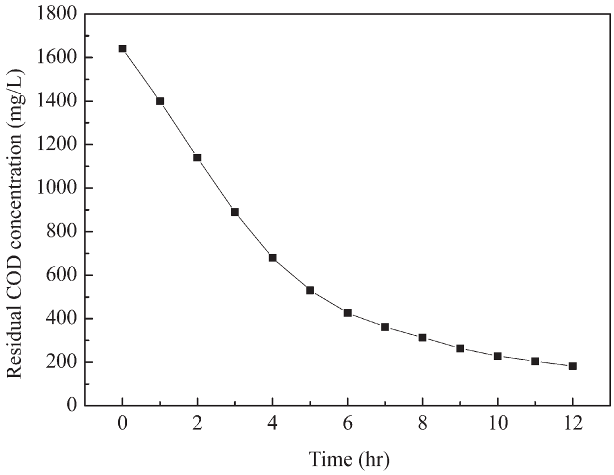

Fig. 8 Mixed liquor COD removal during the aeration process. Operation condition: influent COD: 2500–5000 mg/L; 0.30 MPa; MLSS: 4.12 g/L; aeration time: 6 hr; aeration rate: 25 $m^3/(m^3 \cdot hr)$.

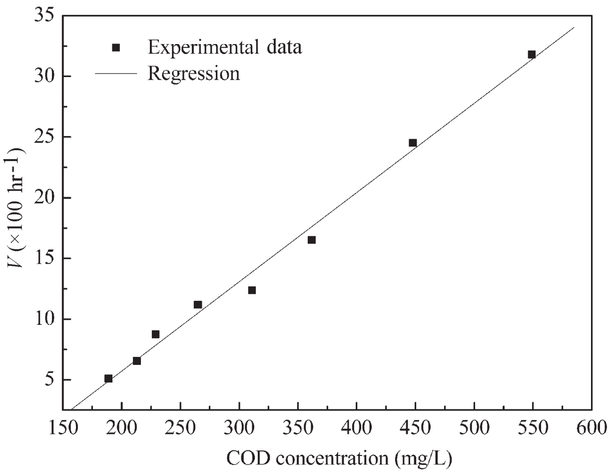

Fig. 9 *S*-*V* experiment datum and regression.

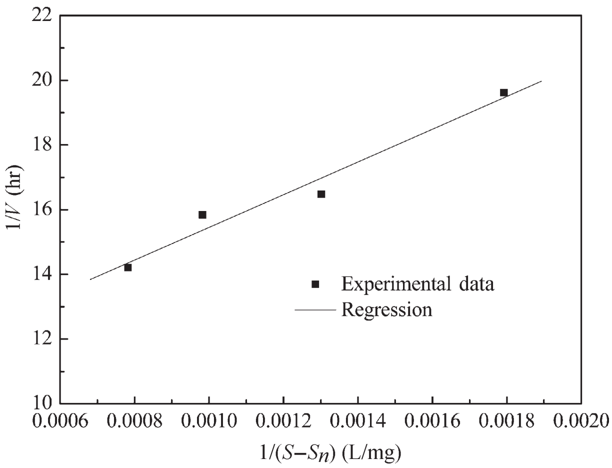

Fig. 10 $1/V$ vs. $1/(S–S_n)$ experiment datum and regression.

3 Conclusions

High concentration pesticide wastewater was treated in this work by pressurized activated sludge process. It was found that COD removal increased steadily with the increase operating pressure. Once a critical pressure was reached, the increase of COD removal became slower but steadily at high pressures. It was observed that the critical pressure increased with the increase MLSS concentration and the COD removal increased with the increase aeration rate. However, after reaching a critical aeration rate, the increase of COD removal became slower but steadily even at high aeration rates; the critical aeration rate was 25 $m^3/(m^3 \cdot hr)$ if aeration time was 6 hr. Extending the aeration time could increase the COD removal. The optimal aeration time was 6–8 hr at the pressure of 0.30 MPa. The COD removal increased at low MLSS concentrations and decreased at high MLSS concentrations, and it was optimal to control the MLSS concentrations between 4 to 6 g/L at 0.30 MPa. The results were compared with those of an identical bioreactor operating at atmospheric pressure. The COD volumetric organic loading rate in the pressurized system was 5.8–7.6 kg COD/(m^3·day), while it was 2.0–2.8 kg COD/(m^3·day) in the system operated under the atmospheric pressure. The COD removal could be described by a modified Monod model in pressurized system, with the biochemical kinetics parameters of S_n =122 mg/L, V_{max} = 2.31 day^{-1}, and K_S = 487 mg/L.

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