

Study of enhancing excess sludge broken walls by alkali coupling organic solvents

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Targeted at excess sludge, this paper studies the influence of different organic solvents, different addition ways and different processing time on the broken walls of excess sludge. With SCOD and SCFAs representing the effects of broken walls, the result shows that under the temperature condition of 30 °C, compared with the blank control, the pretreatment by methanol - alkali, alkali - methanol, acetone - alkali, alkali - acetone can increase the production of SCOD and SCFAs greatly, which affects the percentage composition of each monomer acid in SCFA. If the methanol treatment follows the alkali treatment (pH=10.0), the production of acetic acid reaches 90mgCOD/gVSS and it accounts for 50% of the total SCFAs, whose effect is better than that when the alkali treatment follows the methanol treatment and the propanol treatment follows the alkali treatment. Thus, when carrying out the wall-breaking on the excess sludge, the method of the methanol treatment after the alkali treatment should be adopted.

Key words: excess sludge; cell disruption; organic solvents

INTRODUCTION

Activated sludge process is widely used in the field of wastewater treatment in china, which has caused a large number of excess sludge. The problem of dealing with excess sludge has become a hot topic with much attention currently [1, 2]. It is found in the study that the protective effect of cell walls of the microorganisms in the sludge hinders the release and utilization of organics in the sludge. The pretreatment on the sludge can damage the structure of cell membranes, which releases the intracellular substance and improves the hydrolysis rate. The pretreatment mainly includes ultrasonic, pyrolysis, microwave, supercritical oxidation, adding alkaline, etc. [3-5]. This study adopts the alkali coupling organic solvents to break cell walls and uses SCOD and SCFAs to represent the effect of wall-breaking.

EXPERIMENTAL

Instrument and reagents

The dichromic acid at reference level, ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), ammonium ferrous sulfate [$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$], concentrated sulfuric acid, concentrated hydrochloric acid, silver sulfate powder, phenanthroline, mercury sulfate, yeast extract, tetrahydrofuran, acetone, methanol, ethyl alcohol, petroleum ether, COD constant temperature heater, drying oven, COD digestion apparatus, ultraviolet and visible spectrophotometer, 1 gas chromatograph (Shanghai Tianmei Scientific Instruments Co., Ltd.)

and 1 constant temperature shaking table.

Experimental methods

The experiment makes use of 7 reaction bulbs (suction flasks) with an effective volume of 500 mL and the number is set as R0, R1, R2, R3, R4, R5, R6 respectively. There is a parallel experiment for all 4 different pretreatment. R0 is the blank control and the pH of the excess sludge will not be regulated artificially. For R1, methanol (1%) will first be added into the excess sludge and then add sodium hydroxide for alkaline (pH = 10.0) with each maintaining 4d. For R2, the excess sludge will first be changed to alkaline (pH = 10.0) and then add methanol (1%) with each maintaining 4d. For R3, methanol (1%) is added to the excess sludge and then maintains alkaline (pH=10.0). After 8d, acetone (1%) will be added to the excess sludge of R4 firstly and then add sodium hydroxide for alkaline (pH=10.0) with each maintaining 4d. The excess sludge of R5 will first be changed to alkaline (pH=10.0) and then add acetone (1%) with each maintaining 4d. For R6, the excess sludge will maintain alkaline (pH = 10.0) for 8d after being added acetone (1%).

Pretreatment conditions: Add 250 ml of sludge to each reaction bulb and regulate the pH of sludge with 4.0 mg L⁻¹ of NaOH and 4.0 mg L⁻¹ of HCl. The blank control will not be adjusted. During the regulation process, the pH meter will be used to evaluate the pH of the sludge. Before pH is no stable, it will be measured every 2 hours for the first day. Adjust after one measurement in order to keep the pH in the range of requirements.

Using 500 mL of the suction flask as reactor, the cork of the suction flask links the latex tubing and

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directly connects water-sealed equipment to make the fermentation system in the anaerobic situation, which can be shown in figure 1. The suction flask is placed in the water-bath constant temperature shaking table at 30 °C with the rotating speed of 180r/min. Shaking can make the mixture inside the bottle fully contacted. The schematic diagram of the experimental device is as follows:

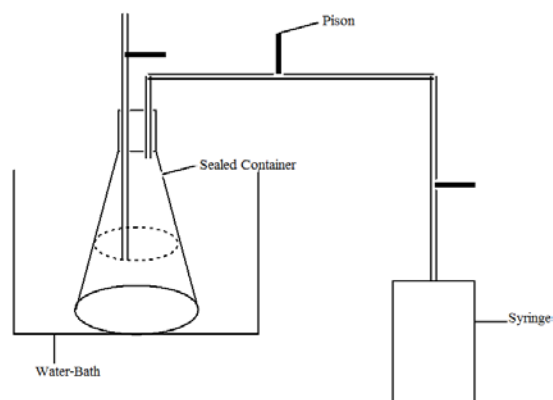


Fig. 1. Experimental device

Representation and measurement

National standard method is used to measure pH, TSS, VSS, SCOD, TCOD, PO₄³⁻-P and total nitrogen(SEPAC, 2006). Gas chromatograph GC7890II is used to measure the components of SCFAs. The carrier gas is nitrogen and the detector is FID. The chromatographic column is 30m×0.32mm×0.5mmTM-FFAP and the temperature of sample injector and detector is set at 200°C and 220°C respectively. The furnace temperature will run for 5 min at 110°C and then rise to 220°C at a speed of 5°C /min and the sample is injected 1.0 μL per time [6].

RESULTS AND DISCUSSION

Influence of different processing methods on the SCOD dissolution of excess sludge

Figure 2 reflects the SCOD concentration in each reaction bulb with the change of fermentation time when the excess sludge is under different pretreatment conditions. It can be seen from figure 2 that after 4d, it is adjusted to alkaline (PH=10.0). During the fermentation time in the first 2d, the SCOD of the excess sludge in the reaction bulb R2 and R5 grows fastest, probably because the alkaline environment leads to the rapid wall-breaking by biological microorganism extra-membrane substances and the rapid increase of SCOD concentration. It reaches around 3985 mg L⁻¹ in the 8th day. Two days ago, except the blank control of R0, the release intensity of other treatment methods is relatively bigger. The intensity of R1, R3 and R5

is basically same and then the slow-down is almost the same. The reason is that both the organic solvents and alkaline environment can lead to the rupture of membranes of biological bacteria and in the 4th day, the intensity increase of R1, R2, R3, R4, R5 and R6 is almost the same, because under different environmental conditions with alkaline sequence, the microbial cell walls in the sludge is more easily broken to release SCOD.

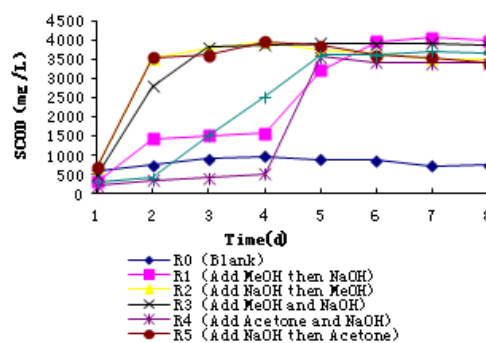


Fig. 2. Changes of dealing with SCOD by different methods

Influence of different processing methods on the content of SCFAs in the excess sludge

After the acid or alkali treatment, the SCFAs produced by the excess sludge mainly consist of fatty acids linearly chained or branched chained with 2 to 5 carbon atoms, such as acetic acid, propionic acid, isobutyric acid, n-butyric acid, isovaleric acid and n-valeric acid, etc. [7]. After being dealt with for 4d and 8d by different methods, the situation of SCFAs in the fermentation system of the sludge in the reaction bulb can be seen in figure 3 and figure 4.

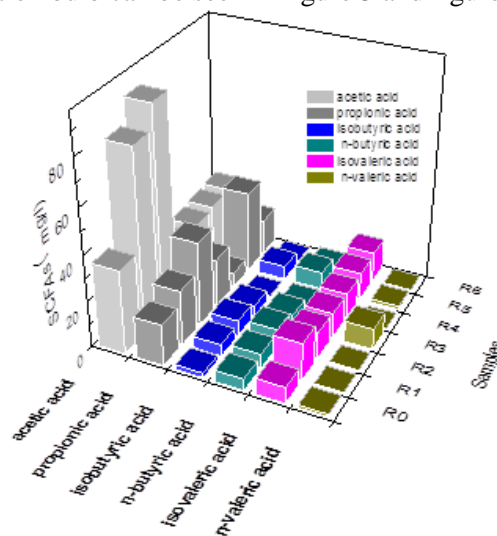


Fig. 3. Influence of different processing methods on the content of SCFAs after 4d.

As shown in figure 3, R1 and R2 produces the largest amount of acetic acid and propionic acid in the first 4d. But the rapid of breaking the microbial

cell membrane is not fast, probably because the influence of the chemical action time leads to the differences of acid production by biological fermentation.

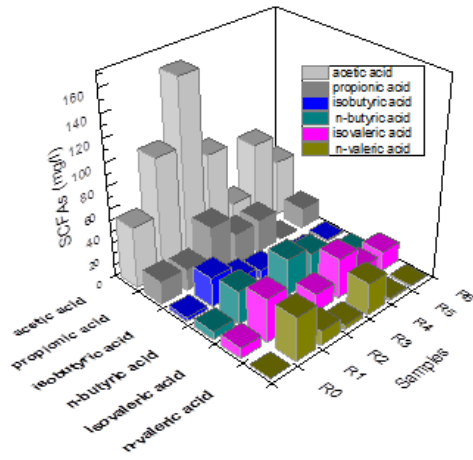


Fig. 4. Influence of different processing methods on the content of SCFAs after 8d

It can be seen from figure 4 that the production of acetic acid and propionic acid by 6 different processing methods is much bigger compared with the blank control. The productivity of acetic acid of R1 and R2 is relatively larger. In the 8th day of fermentation, the production of acetic acid of R2 reaches 160 mg L⁻¹, accounting for 67% of total acid while that of other groups has few difference. In addition, R5 and R6 hardly produce propionic acid and isobutyric acid. Obviously, within a certain period of time, adding alkali first and followed by organic solvents is more advantageous to produce acid.

Content of nitrogen and phosphorus release

During the hydrolytic acidification process of the excess sludge, the nitrogenous substances such as protein and amino acid will hydrolyze and carry out ammoniation, which generates the corresponding organic acids and release ammonia [8]. Figure 5 reflects NH⁴⁺-N concentration with the changes of hydrolysis acidification time under different processing conditions. It can be seen from figure 5 that under anaerobic conditions, in the fermentation time of 8d, the accumulated concentration of NH⁴⁺-N all increases with the time by three processing methods and blank control. By all processing methods, the NH⁴⁺-N concentration increases quickly in the first 4d and the release intensity reaches 155 mg L⁻¹ in the 6th day. It is because that both the alkaline environment and organic solvents are conducive to the biological organisms to break cell membranes and then the release amount becomes gentle. During the hydrolytic acidification

process of excess sludge, as the microbial substances of main ingredients of excess sludge, the polyphosphates in and outside its cell matrix break up and constantly release orthophosphate [9].

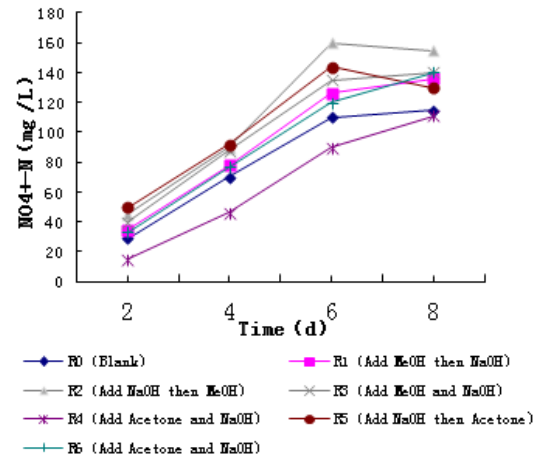


Fig. 5. Change of NH⁴⁺-N concentration with hydrolytic acidification time under different processing conditions

Figure 6 respectively reflects the PO₄³⁻-P concentration and release intensity with the change of time under different processing conditions. PO₄³⁻-P concentration in the sludge mixture by several processing methods all shows a trend of increasing over time and it is particularly significant in the first 2 days. Without the regulation of pH (blank control), the change of release intensity of phosphate is not significant.

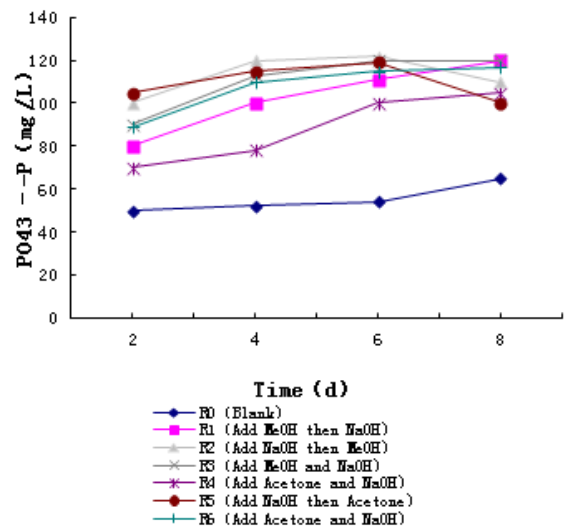


Fig. 6. Change of PO₄³⁻-P concentration with hydrolytic acidification time by different processing methods.

CONCLUSION

Under the condition of temperature 30 °C, compared with the blank control, the pretreatment by

MeOH-NaOH, NaOH-MeOH, acetone-NaOH, NaOH-acetone can increase the production of SCOD and SCFAs greatly, which affects the percentage of each monomer acid in SCFA. If the MeOH treatment follows the NaOH treatment (pH=10.0), the production of acetic acid reaches 90mg COD/gVSS and it accounts for 50% of the total SCFAs, whose effect is better than that when the NaOH treatment follows the MeOH treatment and the acetone treatment follows the NaOH treatment. Thus, when carrying out the wall-breaking on the excess sludge, the method of the MeOH treatment after the NaOH treatment should be adopted.

After 8d of pretreatment, the NH_4^+ -N and PO_4^{3-} -P concentration dissolved by NaOH-MeOH processing method is higher than that by the blank control, NaOH-acetone and MeOH-NaOH processing methods. Using magnesium ammonium phosphate (MAP) can be helpful to recycle more struvite with economic application value.

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