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Original Research Paper

Effect of pH Value on Denitrification Phosphorus Removal in Sequencing Batch Reactor

Jie Deng, Hongwei Rong, Chaosheng Zhang and Kefang Zhang
Guangzhou University, Key Laboratory for Water Quality Security and Protection in Pearl River Delta, Ministry of Education and Guangdong Province, Guangzhou 510006, China

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ABSTRACT

This paper is aimed to solve the effect of pH value in denitrification and phosphorus removal process, and to determine the best pH value for the treatment. pH value was an important indicator of activated sludge reaction in the water treatment process, and it was necessary to keep the suitable pH value to obtain a good treatment effect. The influence of anaerobic phosphorus release and anoxic phosphorus absorption under pH = 6.0, pH = 7.0 and pH = 8.0 in sequencing batch reactor was studied in this paper. The experiment results showed that, in anaerobic phase, anaerobic phosphorus release increased with the increase of pH value, and no significant change was observed in HRT for anaerobic. In anoxia phase, when pH = 6.0, the activity of denitrifying phosphorus removal bacteria was significantly inhibited and phosphorus absorption was poor. When pH = 7.0 and 8.0, the anoxic phosphorus uptake and denitrification system worked well. In the late stages of anoxic phase pH>8.0, the release and absorption of phosphorus was also very stable.

INTRODUCTION

Traditionally, the mechanism of biological nitrogen and phosphorus removal acknowledged that the progress of denitrification and phosphorus removal were two mutual independence parts, and NO_x-N electron acceptor required for denitrification would inhibit phosphorus anaerobic release, both of them would compete carbon source, and they also needed two different absolutely independent microorganisms (Sanchez et al. 2000, Gilda et al. 2007). However, researchers who studied nitrogen and phosphorus removal system had discovered that some parts of PAOs of activated sludge could use nitrate as electron acceptor to finish denitrification and phosphorus uptake at the same time (Stante et al. 1997, Jeon et al. 2003).

It was easy to gather a species of facultative anaerobic microorganisms which has the function of denitrification and phosphorus removal in the operation of the alternating anaerobic/anoxic conditions; this microorganism could use O_2 or NO_3^- as electron acceptor, and it is based on poly-β-hydroxy butyrate (PHB) and glycogen creature metabolizable action that compared to PAOs of traditional A/O method in phosphorus removal were similar (Kuba et al. 1993, Gaudy et al. 2006). The similar studies creature (Vlekke et al. 1998, Gerber et al. 1987) in laboratory and scale of production of nitrogen and phosphorus removal had also demonstrated that when microorganisms went through anaerobic, anoxic and aerobic three phases, about 50% PAOs could not only utilize O_2 but also use NO_3^- as electron acceptor to accumulate phosphorus, that was the effect of DPB phosphorus removal amount to about half of total PAOs. And compared with traditional crafts of creature nitrogen and phosphorus removal, the craft of denitrification phosphorus removal could save 50% COD, 30% oxygen consumption volume, and reduce 50% volume of excess sludge and the volume of CO_2 released into the atmosphere (WAN et al. 2008, Lee et al. 2001, Third et al. 2003). The above findings have shown the possibility of the craft of denitrification phosphorus removal, and on the other hand it could confirm that the craft of denitrification phosphorus removal was a sustainable craft.

The research and actual reaction had showed that pH value was a key factor influencing the treatment. Every biochemical reaction could lead pH value up or down, biological nitrification could consume alkalinity to decrease pH value and the process of denitrification would produce alkalinity to increase pH value (Kishda et al. 2006, Spangni et al. 2001, Peng et al. 2002). As introduced by Smolders et al. (1994), the effect of pH value between DPB denitrification phosphorus removal system and traditional phosphorus removal system were similar. This research applied SBR reactor, investigated the effect of pH value influencing the anaerobic phosphorus release and anoxic phosphorus uptake under faintly acid (pH=6.0), neutral (pH=7.0) and faintly alkali (pH=8.0) conditions.

MATERIALS AND METHODS

Test device: Three Sequencing Batch Reactors (SBR) were performed, which were made of organic glass with a total volume of 13 L (including 12 L the effective volume), as shown in Fig. 1.

Sample connections were set up at the different heights of the reactor wall, and inflow pipe and delivery pipe were also set up at the bottom of the reactor. In the anaerobic/anoxic phase, in order to keep the mud mixing, it needed to install a motor stirrer inside the reactor. Air pump was used to blow air, rotameter to adjust air, and adhering sand block as microporous aerator. DO, ORP and pH instruments were set up in the reactor to on-line monitor the changes in the reaction process.

Test method: Simulated domestic wastewater was applied in this study, which was sodium acetate, ammonium chloride, potassium dihydrogen phosphate, some calcium chloride, magnesium sulphate, ferric sulphate and tap water. The concentrations of TP and COD were about 7.0mg/L and 180 mg/L in the three SBR reactors. By adding the hydrochloric acid and sodium hydroxide the pH value was adjusted. The stable denitrifying phosphorus sludge was equally distributed to three SBR reactors. The MLSS was approximately 3500 mg/L in the three SBR reactors.

RESULTS AND DISCUSSION

The effect of pH on the anaerobic phosphorus release: In the anaerobic phase, the pH of the three reactors was controlled at about 6.0, 7.0, 8.0 at the beginning of the reaction, anaerobic time was 60min. The effect of different pH values on the anaerobic phosphorus release is shown in Fig. 2. It can be seen that anaerobic phosphorus release increased with the increase of pH value, but the rate of increase gradually decreased. After anaerobic reaction of one hour, the phase of anaerobic phosphorus release was over. The changes of pH affected the amount of total phosphorus, but did not change the phosphorus release time.

Fig. 3 shows the COD uptake in anaerobic phase under the different pH value conditions. From the Figs. 2 and 3, the release quantity of phosphorus, when sludge system consumed unit mass of acetic acid (P/C), can be found. The P/C were 0.16, 0.20, 0.21 at pH value of 6.0, 7.0, 8.0. The increase of pH value made phosphorus sludge enhance the ability to release phosphorus acetate when consumed the same amount of acetic acid.

The reason why the sludge phosphorus release ability increased with the increased pH can be explained by the anaerobic phosphorus biochemical model (Smolders et al. 1995) An electric potential difference and acetic acid concentration gradient existed in the process of PAOs absorbed acetic acid and across the cell membrane and it need to provide the energy for coupling to achieve the absorption of acetic acid. The energy needed, which absorb acetic acid, can be used (1) to represent.

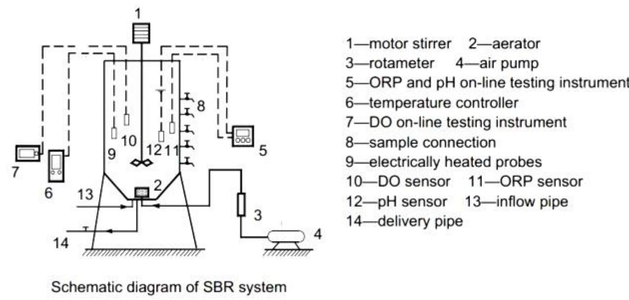

Fig. 1: Schematic diagram of SBR system.

$$\Delta G = n\Delta\psi + 2.3nRT\log\left(C_{in}/C_{out}\right) \quad ...(1)$$

ΔG - the energy needed to absorb a mole acetic acid, kJ/mol; $\Delta\Psi$ - electric potential difference, kJ/mol; n - transfer the acetic acid load per mole; C_{in} - inside of the cell concentration of acetic acid, mol; C_{out} - outside of the cell concentration of acetic acid, mol; R - gas constant, kJ/(K·mol); T - the water temperature, K.

Electric potential difference is the proton motive force and internal alkaline pH gradient generated by joint action, it can be represented as (2).

$$\Delta\psi = \Delta p + 2.3RT\left(pH_{in} - pH_{out}\right) = \Delta p + 2.3RT\Delta pH \quad ...(2)$$

Δp - proton motive force, kJ/mol; pH_{in} - the pH inside the cell; pH_{out} - the pH outside the cell.

So the energy needed which absorb acetic acid can be used (3) to represent.

$$\Delta G = n\left(\Delta p + 2.3RT\Delta pH\right) + 2.3nRT\log\left(C_{in}/C_{out}\right) \quad ...(3)$$

It is assumed that the pH and Δp inside the cell remained constant. As the pH increases, the potential difference $\Delta\Psi$ increases, so the energy required ΔG, which absorb the acetic acid, is also increased. In the case of absorbing the same acetic acid, PAOs need to break down a larger number of phosphorus granules to produce energy, which meet the needs for absorbing the acetic acid. Therefore, as the pH rose much phosphorus would be released in the anaerobic environment.

The effect of pH on phosphorus uptake in anoxic phase: In the anoxic phase, denitrifying activated sludge was divided equally into three SBR reactors after sufficient anaerobic

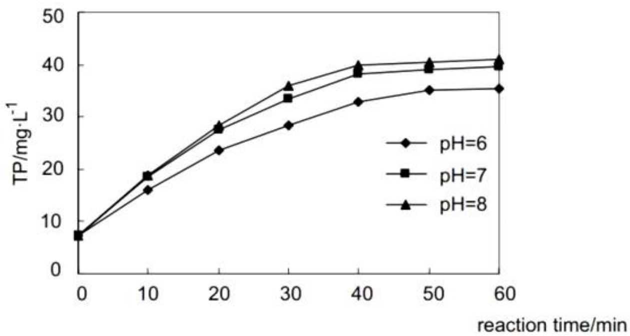

Fig. 2: Effect of pH on phosphorus release in anaerobic phase.

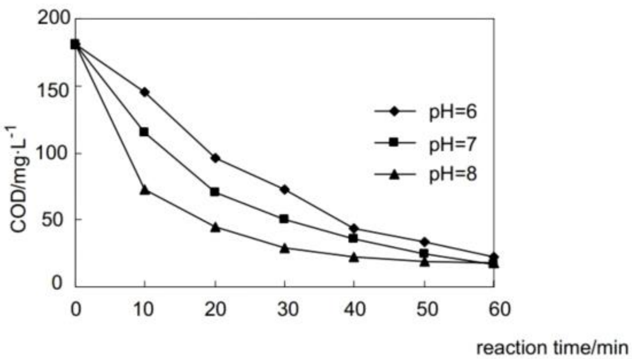

Fig. 3: Effect of pH on COD uptake in anaerobic phase.

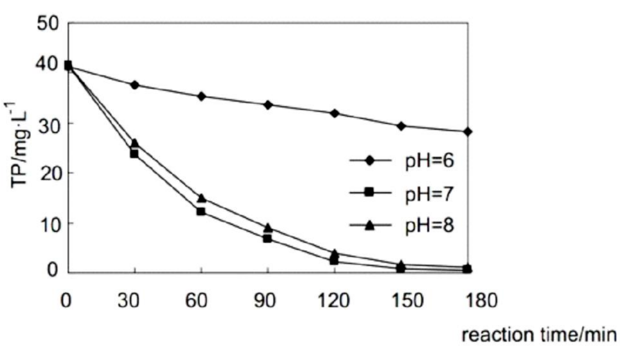

Fig. 4: TP variation curve in anoxic phase.

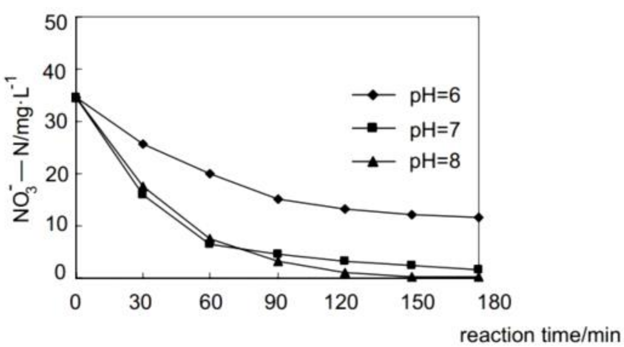

Fig. 5: NO_3-N variation curve in anoxic phase.

phosphorus release. The concentration of MLSS was about 3500mg/L. In order to control the NO_3-N concentration of the three reactors at about 35mg/L, the water, which contained the same amount of potassium dihydrogen phosphate and potassium nitrate, was put into the three reactors. Dilute hydrochloric acid and sodium hydroxide were added into mixture to control the pH at 6.0, 7.0, 8.0 in the beginning of the anoxic phase. Then the effect of different pH on anoxic phosphorus uptake of denitrification were investigated. Figs. 4, 5 and 6 show the results.

Evolution of the effluent of pH on phosphorus uptake in anoxic phase is presented in Fig. 4. Under the condition of pH = 6.0 in the initial stage of the anoxic phase, the system was still in weak acid environment (the pH changed between 6.0 and 6.3) throughout the anoxic phase. In this process, both anoxic phosphorus uptake rate and denitrification rate were very slow. It showed that when the reaction process of the whole system was in acid environment, the destruction of the denitrifying phosphorus removal system was obvious, the activity of denitrifying phosphorus removal bacteria has also been significantly inhibited, and the effluent effect was poor. By analysing the conditions of the acidic oxygen environment, we found that it would damage a part of the phosphorus removing bacteria, and reduce the content of DPB. So in the actual process, it needed to avoid anoxic phase under the weak acid in the process of operation, and ensure the smooth progress of anoxic phosphorus absorption. Effect of anoxic phosphorus absorption was very good when pH values were at 7.0 and 8.0. Normally, the operation situation of the initial pH 7.0 was the most frequently applied throughout the experimental study, the oxygen and denitrifying phosphorus absorption effect was the best, the phosphorus content in system was decreased to 0.72 mg/L after running 2.5h. Under the condition of the pH 7.0, pH would rise following the anoxic denitrification, and phosphorus absorption at the end of the anoxic phosphorus absorption will appear bottlenecks, this trend was monitored in line with the monitoring process frequently. When the initial pH was 8.0, the system pH had an upward trend, and rose to above 8.5 quickly due to denitrification and phosphorus absorption. Under the condition of the pH, the rate of anoxic phosphorus removal can reached 94%. Meanwhile, the nitrate was reduced constantly in the system, and it illustrated that the system was performing the role of denitrifying phosphorus removal effectively. In normal circumstances, there will be a chemical phosphate precipitation when the pH > 8.0. But in the process of phosphorus uptake in anoxic phase of denitrifying phosphorus removal, the system was still on denitrification

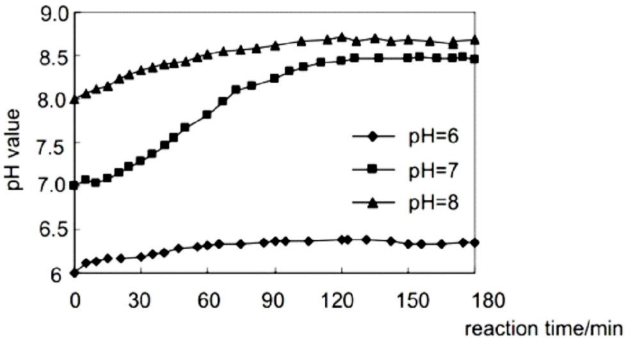

Fig. 6: pH value variation curve in anoxic phase.

and phosphorus absorption normally at pH > 8.0. During the experiment in the long run, the pH value between 8.0-8.5 in most time was in late anoxic phase, but the effect of the release of phosphorus and absorption was stable. It confirmed that the denitrifying phosphorus removal can still be stable in condition of pH > 8.0 in anoxic phase.

CONCLUSIONS

1. In the anaerobic phase, anaerobic phosphorus release increased with the increased of pH value, but the rate of increase gradually decreased. Meanwhile, the changes of pH value affected the amount of total phosphorus, without changing the phosphorus release time.
2. In the anoxic phase, under the condition of pH 6.0, the denitrifying phosphorus removal systems were significantly damaged and the activity of denitrifying phosphorus removal bacteria was inhibited; when pH = 7.0 and 8.0, the anoxic phosphorus uptake and denitrification system worked well. In the late stages of anoxic phase pH > 8.0, the release and absorption of phosphorus was also very stable.

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