

Improving the performance of sequencing batch reactor (SBR) by the addition of zeolite powder

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Abstract

Two types of operation means “SBR reactor alone (control reactor)” and “adding zeolite powder into SBR reactor (test reactor)” were used to treat municipal wastewater. The test results revealed that zeolite powder addition could improve the activity of the activated sludge. It was investigated the specific oxygen utilization rate (SOUR) of the tested zeolite sludge were about double times that of the control activated sludge, and the nitrification rate and settling property of zeolite-activated sludge were both improved. Due to the combination of zeolite adsorption for NH_4^+ -N and enhanced simultaneous nitrification and de-nitrification (SND), a higher nitrogen removal was observed in test reactor compared to the control reactor, and the addition of zeolite powder is helpful to inhibit sludge bulking. In addition, through long-term parallel shock load test, it was found that the zeolite powder addition could enhance the ability of activated sludge in resisting the shock load of organics and ammonium. Compared to the control activated sludge, zeolite powder added activated sludge could remove COD, NH_4^+ -N, TN and TP significantly in a shorter cycle time. At the same operational time period, the test SBR could treat wastewater quantity 1.22 times that treated in control SBR. © 2006 Elsevier B.V. All rights reserved.

Keywords: Sequencing batch reactor (SBR); Zeolite powder; Activated sludge; Shock load; Settling property

1. Introduction

Sequencing batch reactor (SBR) systems have been proven to offer substantial benefits to alternative conventional flow systems for the biological treatment of both domestic and industrial wastewater. The SBR is a wastewater treatment system anomaly, because operationally it is extremely flexible in its ability to meet many different treatment objectives while physically it is very simple.

Natural zeolite is a non-metallic mineral with the characteristics of high porosity and large specific surface area. In addition, it is one ion exchanger with a high affinity for ammonium ion [1–2], which is reported to have a classical aluminosilicate cage like structure and therefore exhibits significant macroporosity [3]. Earlier studies have shown that clinoptilolite, and certain other natural zeolites can be effective in removing ammonia from wastewater [3–5], and has been used to enhance the nitrification

of biofilter and equalize the ammonia peaks from secondary effluent [6–8].

In biological systems of nitrogen removal, the nitrification process generally becomes a limiting step because of the extremely low growth rate of nitrifiers as obligate autotrophic bacteria [9]. Furthermore, wastewater treatment plants employing biological nitrogen removal frequently encounter problems arising from shock loads of organics or nitrogen materials. It is of great importance since nitrifiers are very sensitive to these factors and the deteriorated nitrification process cannot be readily recovered. High loading of organic material results in lower nitrification efficiency because of loss of ammonium by assimilation of heterotrophs and the inhibitory effect of crowded cell of heterotrophs on ammonium oxidation [10], nitrification is therefore inhibited by higher C/N ratio.

To reduce the influence of shock loading on nitrification, many studies of nitrifiers attached onto carriers have been carried out. For example, organic material showing toxicity to nitrifiers can be removed efficiently through adsorption by activated carbon and zeolite [11]. Most of these investigations have been confined to packed-bed type systems. It is quite difficult to

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modify activated sludge treatment works and this increases operation/maintenance costs. Moreover, these modifications involve difficult operational procedures including a backwashing process.

This study was conducted to compare discrepancies in operation efficiency when powdered zeolite was directly added into SBR. The effects of powdered zeolite carrier on nitrification in the SBR under organics and nitrogen shock loading were tested. In this study, two SBRs were run in parallel to treat municipal wastewater, of which one was fed with a certain quantity of natural zeolite powder while the other was run as control system, and the aim of the study was to investigate the effect of zeolite powder addition on the performance of SBR in treating municipal wastewater.

2. Materials and methods

The test sequencing batch reactor was made of polymethyl methacrylate with diameter of 0.3 m, height of 0.6 m and effective volume of 31.1 L. The air was introduced into the reactor with a micro-bubble air diffuser and the air flow rate was controlled with an air flow-meter. There were all two reactors, of which one reactor was run as control reactor, the other reactor fed with zeolite powder as test reactor, and the temperature of the mixed liquid in reactor was maintained at $24 \pm 1^\circ\text{C}$ with a thermostat (XMT-1000, China) submerged into the reactor. In addition, the DO of the reactor was monitored by a dissolved oxygen meter (YSI 550A, USA). A schematic diagram of the process configuration is shown in Fig. 1.

Natural clinoptilolite, a kind of zeolite containing high content of silicon, was used in the form of powder for attached microbial growth as well as the ion exchanger for ammonium ion. The test natural zeolite was obtained from Jinyun, Zhejiang province. Then the zeolite was ground to powder form, and the

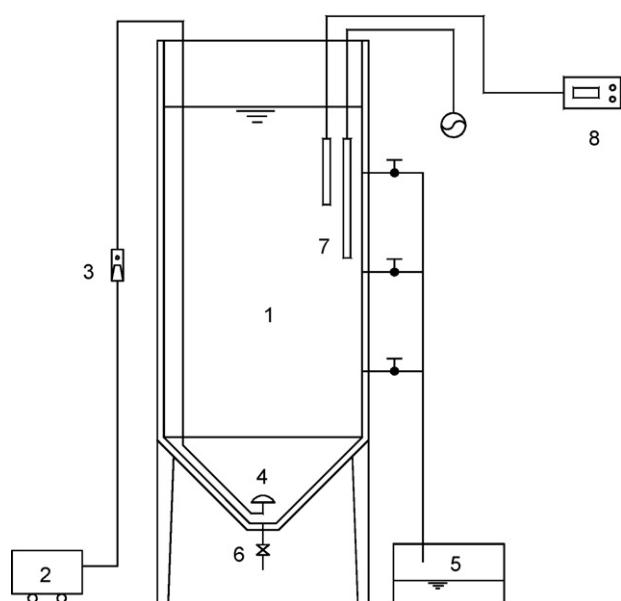


Fig. 1. Schematic illustration of the experimental system. 1, reactor; 2, air compressor; 3, air flow-meter; 4, air diffuser; 5, storage tank; 6, drainage valve; 7, thermostat; 8, dissolved oxygen meter.

Table 1
The characteristics of the test wastewater

Parameter	Range	Mean
pH	6.67–7.86	7.42
SS (mg/L)	94–212	157
COD (mg/L)	274–421	376
NH ₄ ⁺ -N (mg/L)	25.5–44.2	37.2
TN (mg/L)	33.5–68.7	54.4
TP (mg/L)	2.65–4.85	3.42

zeolite powder with a size range of 0.05–0.2 mm was selected for test, and its adsorption capacity for NH₄⁺-N was tested to be 8.95 mg/g. The zeolite powder was added into the test reactor 10 days prior to the steady state. Batch zeolite powder addition was applied to compensate for the loss of zeolite powder through sludge wastage to maintain zeolite powder at 1.0 g/L throughout the test cycle, and the addition of zeolite powder into test reactor was conducted between fill and aeration stage of every cycle.

2.1. Raw water for experiment

The test wastewater was collected from the outlet of grit tank in Shanghai Minhang wastewater treatment plant, and its characteristics are summarized in Table 1.

2.2. Operating conditions and analytical methods

During the test period, the operating conditions of control and test reactors are presented in Table 2. The sludge concentration is maintained by periodic sludge wastage.

2.3. Analytical methods

For components analyses, all samples were filtered through 0.45 μm membranes. TN, NH₄⁺-N, TP, COD, MLSS and MLVSS were measured according to Standard Methods [12]. Nitrite and nitrate were analyzed with an ion chromatograph (Dionex 500, USA).

The measurement of SOUR: a widely used method indicating activity of sludge is the biomass oxygen uptake rate (OUR) which measures the rate of dissolved oxygen (DO) consumption in the aeration bioreactor. The specific oxygen uptake rate (SOUR) is the OUR per unit of dry biomass, and the measurement method is described in literature [13].

2.4. Statistical analysis

In this study, analysis of samples was performed for each parameter using variance. The data from the various water samples were analyzed in duplicate. If an *F*-test proved significant

Table 2
Operating conditions of control and test reactors at steady state

Parameter	Control reactor	Test reactor
MLSS (mg/L)	2500–3000	3500–4000
MLVSS (mg/L)	2000–2500	2000–2500
SRT (day)	20	20

at $P < 0.05$ level, the means of each plot were compared by least significant difference. All values in tables and figures are presented as means.

2.5. SBR's start-up

Seed sludge was inoculated from Shanghai Minhang wastewater treatment plant. These two reactors have the same operation modes, and the time schedule of each mode is as follows: fill is 5 min, aeration is 360 min, settle is 30 min, vacant is 10 min and idle is 15 min.

Two SBRs were run for 6 weeks according to above cycle procedure, and then reached the steady state. After that, the detailed research was conducted.

3. Results and discussion

3.1. Batch experiment

To estimate the adsorption capacity of zeolite for ammonium, a batch test was carried out. Two grams of zeolite powder was mixed with distilled water in a 200 mL-graduated beaker. Together with 4 mL of diluted NH_4Cl , they were put into a closed jar and volume was adjusted to 2L. Stock solutions of NH_4Cl was used as adsorbate and prepared in concentrations of 20 g/L. Temperature and pH were maintained at 24 °C and 7–8, which were the same conditions as in the control and test SBRs, and the mixed solution was kept in suspension by a magnetic stirrer. To measure the residual amounts of adsorbate in solution, 100 mL samples were withdrawn at intervals, immediately filtered through 0.45 μm filter paper, and the detected results is presented in Fig. 2.

As can be seen from Fig. 2 that $\text{NH}_4^+\text{-N}$ decreased from 40 mg/L to 32.5 mg/L in 120 min in a linear way, then kept almost stable, therefore, it demonstrated that the majority of adsorption capacity of zeolite for $\text{NH}_4^+\text{-N}$ was achieved in the first 120 min.

3.2. The characteristics of two SBRs in removing COD, $\text{NH}_4^+\text{-N}$, TN and TP

During the steady operation cycle, the time series samples after aeration were taken for measurement of COD, $\text{NH}_4^+\text{-N}$,

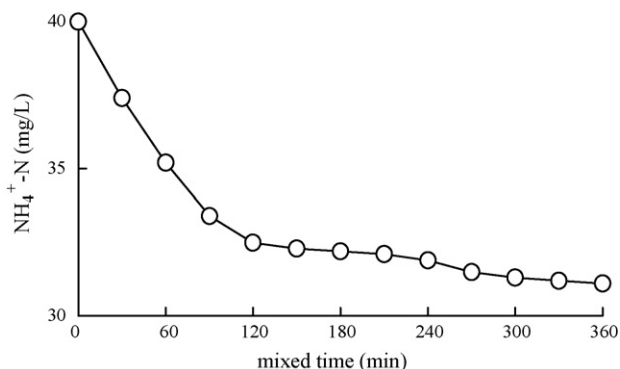


Fig. 2. Variation of $\text{NH}_4^+\text{-N}$ with mixed time in batch experiment.

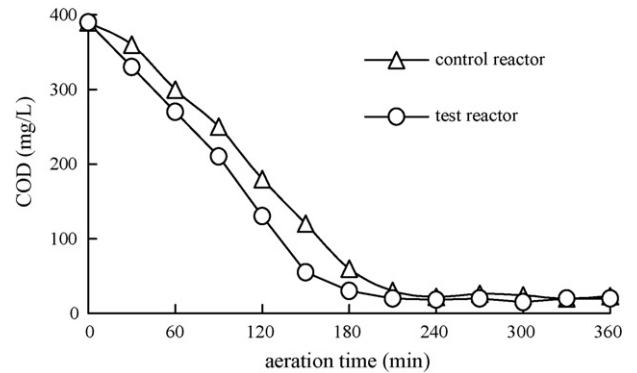


Fig. 3. Variation of COD with aeration time in test and control reactors.

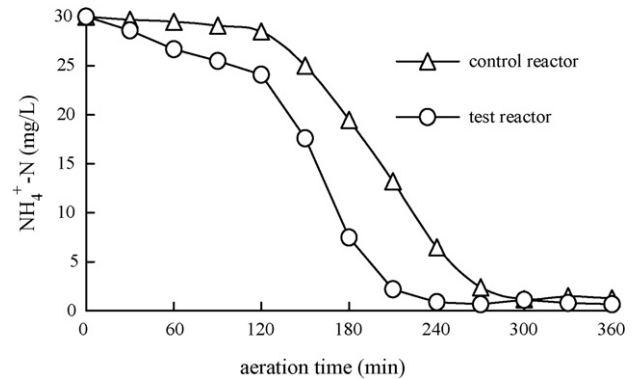


Fig. 4. Variation of $\text{NH}_4^+\text{-N}$ with aeration time in test and control reactors.

($\text{NO}_3^- \text{-N} + \text{NO}_2^- \text{-N}$), TN and TP through the course of the test, and the results are presented in Figs. 3–7.

Fig. 3 shows COD reduced in a linear way at the first 3 h for two SBRs. For control reactor, COD decreased from 390 mg/L to 60 mg/L at a time period of 3 h, while it last 2.5 h for test reactor. For these two SBRs, organic load was calculated to be 0.35 kg COD/(kg MLVSS d^{-1}).

According to Fig. 4, $\text{NH}_4^+\text{-N}$ kept almost stable at first 120 min and then reduced to 2.4 mg/L at the next 150 min in control reactor. For test reactor, $\text{NH}_4^+\text{-N}$ quickly reduced from 30 mg/L to 24.2 mg/L at the first 120 min, while the content of (nitrate + nitrite) increased was negligible at this period. Therefore, the reduction of $\text{NH}_4^+\text{-N}$ should be attributed to the adsorp-

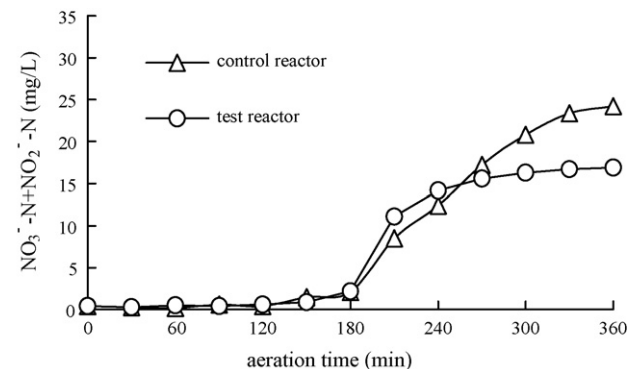


Fig. 5. Variation of ($\text{NO}_3^- \text{-N} + \text{NO}_2^- \text{-N}$) with aeration time in test and control reactors.

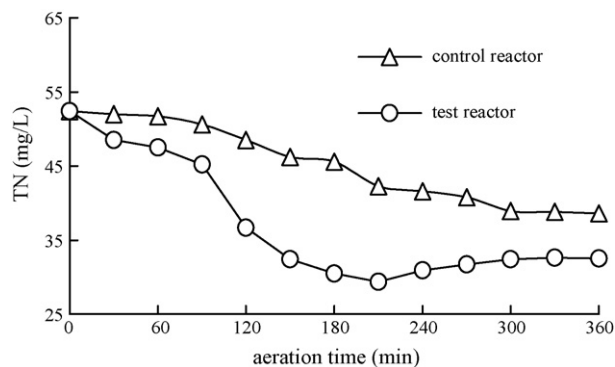


Fig. 6. Variation of TN with aeration time in test and control reactors.

tion and ion exchange of zeolite powder for $\text{NH}_4^+\text{-N}$. After aeration (120 min), COD in the test reactor was decomposed to a low level, and $\text{NH}_4^+\text{-N}$ was then reduced to 0.9 mg/L at a higher speed compared to the control reactor in the next 120 min.

Fig. 5 shows the amount of (nitrite + nitrate) increased significantly after 180 min of aeration. For test reactor, the amount of (nitrite + nitrate) increased from 2.2 mg/L to 14.2 mg/L in 60 min and then kept almost stable, while for control reactor, the amount of (nitrite + nitrate) increased from 2.1 mg/L to 12.4 mg/L during 180–240 min, and then increased to 25.3 mg/L in the next 120 min. Compared to the test reactor, the control reactor has a higher concentration of (nitrite + nitrate) left after 360 min of aeration. During the period of minute 180–240, the amount of $\text{NH}_4^+\text{-N}$ reduction (from 7.5 mg/L to 0.9 mg/L) in test reactor is lower than that (from 19.5 mg/L to 6.5 mg/L) in control reactor, while the amount of (nitrite + nitrate) increased in test reactor is more than that increased in control reactor, and this verified that the nitrification rate is faster in test reactor.

It can be seen from Fig. 6 that TN decreased from 52.4 mg/L to 38.6 mg/L in 360 min in control reactor, while in test reactor TN decreased by 7.2 mg/L which is about equivalent to the amount of $\text{NH}_4^+\text{-N}$ reduction in the first 30 min, and then TN was reduced to 29.4 mg/L at the aeration time point of 210 min. During the period of 210–360 min, it was found that the TN rose to 32.4 mg/L with the extension of aeration, and the amount of (nitrate + nitrite) was detected to have a rise (from 11.1 mg/L to 16.6 mg/L), whereas, it was found there was no $\text{NH}_4^+\text{-N}$ left in the reactor; therefore, it can be concluded that the $\text{NH}_4^+\text{-N}$

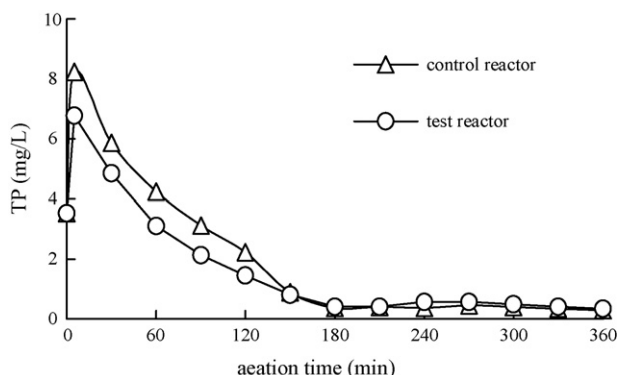


Fig. 7. Variation of TP with aeration time in test and control reactors.

N adsorbed by zeolite powder (about 5.8 mg/L) was nitrified by nitrobacteria. Compared to the control reactor, there has a higher TN removal of 6.2 mg/L in test reactor, which should be attributed to the enhanced simultaneous nitrification and denitrification (SND) took place in test reactor. For the addition of zeolite powder is helpful to the formation of granular sludge with characteristics of bigger size [14–15], which created an appropriate environment for SND.

As shown in Fig. 7, TP in these two reactors rose significantly 5 min after the raw wastewater was fed into both reactors, and increased from 3.54 mg/L to 8.24 mg/L and 6.78 mg/L in control reactor and test reactor, respectively, then decreased to below 1 mg/L at the time point 150 min. The feed of raw water into reactor created a favorably anaerobic condition for phosphorus release, and the phosphorus can then be adsorbed by polyphosphate accumulating bacteria under the subsequent aerobic condition.

3.3. Variation of DO in operation cycle

With the extension of aeration time, DO rise continuously at one reaction cycle in these two reactors, as can be seen from Fig. 8. It was found that DO has a distinct leap at the time point of 160 min and then kept almost stable. In test reactor, another distinct DO leap was observed at time point 210 min while it took place at a late time point 275 min in control reactor.

According to the experimental results illustrated in Figs. 3–6, it was analyzed that time period 0–160 min was the stage of organics degradation. At this stage, supplied oxygen was slightly more than needed oxygen, and DO in reactors rose slowly. After the biodegradable organics was degraded completely, DO leap happened, and then reached a new balance at high level. At the following stage, supplied oxygen was consumed by nitrobacteria for nitrification. At time point minute 205, nitrification stage ended and a second DO leap took place, then DO reached new level 7.0–7.5 mg/L. In control reactor, nitrification stage ended at time point minute 270, and DO jumped at around 7.0 mg/L. Therefore, combining the test result shown in Figs. 4–6, it could be seen that the addition of zeolite powder enhanced the nitrification ability from the view point of DO variation.

During the steady operational period of days 17 and 35, 2 L of sludge was drawn from test and control reactors at the end of settle stage, and the test for two kinds of sludge property was conducted in two separate vessels, then the measured results are summarized in Table 3.

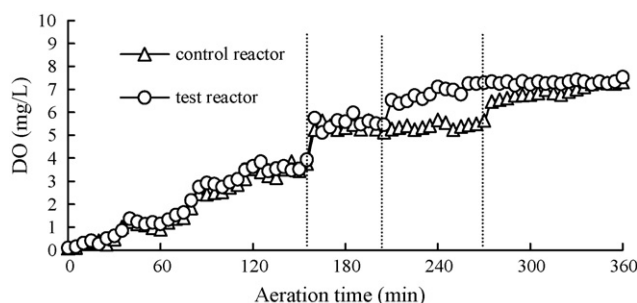


Fig. 8. Variation of DO at one operation cycle.

Table 3
Sludge property in two reactors at steady state

Item	Control reactor	Test reactor
SOUR ($\text{mg O}_2 \text{ g MLVSS h}^{-1}$)	18–25	34–56
SVI (mL/g)	118–124	67–74

It was found that the SOUR of zeolite sludge was about double that of activated sludge in control reactor, and zeolite sludge has a better settling property. Therefore, it can be concluded that the zeolite powder addition is helpful to improve the activated sludge activity and inhibit the sludge bulking.

3.4. Comparison of sludge nitrification performance

At the steady operational period of day 17, and at the end of one operation cycle, two batch reactors with effective volume of 5 L were filled with 2 L mixed liquor obtained from control reactor and test reactor, respectively, and then washed with distilled water repeatedly to remove the organics, ammonium, nitrite and nitrate remained. Thereafter, 5 mL stock solution of NH_4Cl with concentration of 20 g/L were added to the batch reactors, respectively, and kept the initial NH_4Cl at 50 mg/L, then distilled water was added into two batch reactors and kept volume of mixed liquid at 2 L. Following that, aeration was conducted in these two reactors and DO maintained at 1.5–2.0 mg/L, and the time series samples were taken for measurement of $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, $\text{NO}_3^-\text{-N}$ through the course of the test, and the results are presented in Figs. 9 and 10.

It can be seen from Fig. 9 that the $\text{NH}_4^+\text{-N}$ decreased with a higher rate in test reactor. To analyze the difference in $\text{NH}_4^+\text{-N}$ removal of two reactors, the content of nitrite and nitrate in both reactors were also detected. It was found that the amount of $\text{NH}_4^+\text{-N}$ reduction was similar to the amount of (nitrite + nitrate) increase in control reactor, while in test reactor, at time point minute 240, the amount of $\text{NH}_4^+\text{-N}$ reduction is higher than that of (nitrite + nitrate) increase, it is indicated that the $\text{NH}_4^+\text{-N}$ removal was due to the combination of zeolite adsorption and biological nitrification. At time point minute 270, the amount of $\text{NH}_4^+\text{-N}$ reduction was similar to the amount of (nitrite + nitrate) increase, it was indicated that previous $\text{NH}_4^+\text{-N}$ adsorbed by zeolite was nitrified to nitrite and nitrate by nitrobacteria. Com-

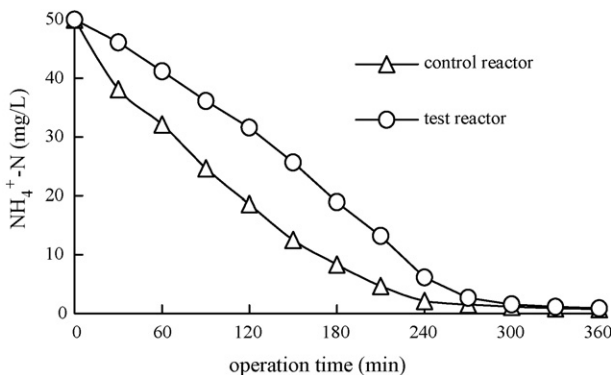


Fig. 9. Variation of $\text{NH}_4^+\text{-N}$ with operation time.

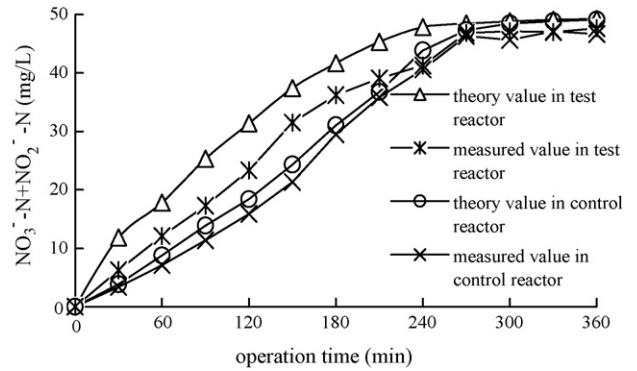


Fig. 10. Variation of ($\text{NO}_2^-\text{-N} + \text{NO}_3^-\text{-N}$) with operation time.

pared the amount of (nitrate + nitrite) in two reactors, it was found there has a higher value of (nitrite + nitrate) in test reactor, and it indicated that the nitrobacteria in test reactor has a better nitrification performance, which should be ascribed to the zeolite powder addition [16].

3.5. Long-term shock load test of two SBRs

In order to exert the advantages of two reactors, the operational parameters were adjusted according to the batch test results and listed as follows: fill is 5 min, aeration is 270 min and 210 min for control and test reactor, respectively; settle is 30 min, vacant is 10 min and idle is 15 min.

Two SBRs were run for 1 week according to above adjusted cycle procedure, and then reached the new steady state. After that, Two SBRs were run for a next continuous period of 60 cycles. At the cycle of 31, 20 mL stock solution of glucose with concentration of 2000 mg/L and 20 mL stock solution of NH_4Cl were mixed together, and then two halves of the mixed liquid were added into two SBRs, respectively, to make the influent COD and $\text{NH}_4^+\text{-N}$ concentration about doubled, and the aim was to compare the ability of these two SBRs in resisting the shock load of COD and $\text{NH}_4^+\text{-N}$, and the operational results are shown in Figs. 11–15.

As shown in Fig. 11, at the first test stage of influent COD about 300 mg/L, the effluent COD of control reactor was in the range of 35–65 mg/L (average of 50 mg/L), and the effluent COD of test reactor was in the range of 26–55 mg/L (average of 41 mg/L). From the cycle 31 on, the influent COD was doubled to about 600 mg/L, and effluent has a slight rise in control

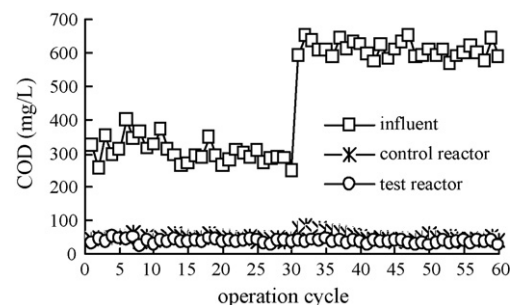


Fig. 11. COD of influent and effluent in control reactor and test reactor.

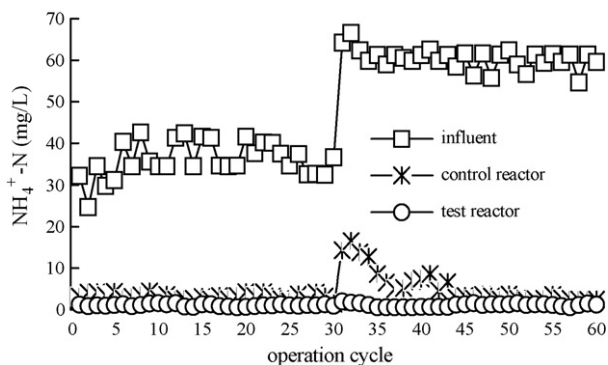


Fig. 12. $\text{NH}_4^+\text{-N}$ of influent and effluent in control reactor and test reactor.

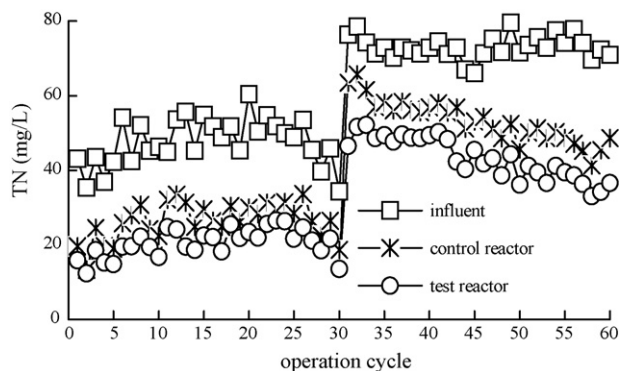


Fig. 13. TN of influent and effluent in control reactor and test reactor.

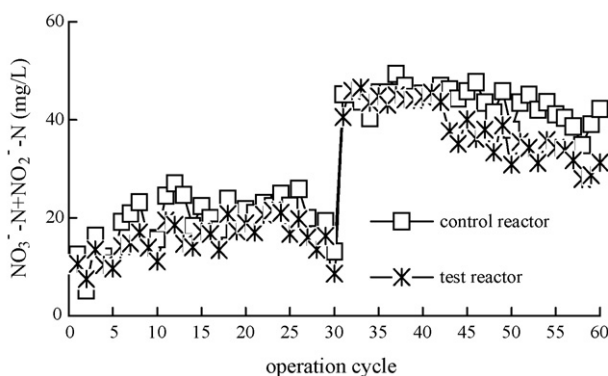


Fig. 14. the amount of ($\text{NO}_2^- \text{-N} + \text{NO}_3^- \text{-N}$) of every cycle in control reactor and test reactor.

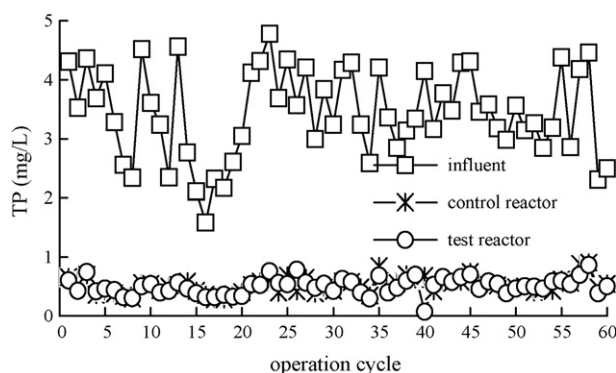


Fig. 15. TP of influent and effluent in control reactor and test reactor.

reactor, while there has no any difference in effluent was observed in test reactor. At this stage, the effluent COD were in the range of 38–85 mg/L (average of 54 mg/L) and 28–55 mg/L (average of 38 mg/L) for control reactor and test reactor, respectively. The organic loads of control reactor are 0.34 kg COD/(kg MLVSS d^{-1}) and 0.68 kg COD/(kg MLVSS d^{-1}), respectively, in these two stages, and test reactor has higher organic loads of 0.41 kg COD/(kg MLVSS d^{-1}) and 0.82 kg COD/(kg MLVSS d^{-1}), respectively.

It can be seen from Fig. 12 that the ammonium removal efficiency in control activated sludge was 83–96% at low ammonium condition, when ammonium loading rate was doubled, the nitrification efficiency was inhibited and ammonium removal efficiency was decreased to 75% and then was restored to around 90% in the following 14 cycles.

Whereas, when zeolite powder added, ammonium removal efficiency was maintained over 95% regardless of the influent nitrogen condition. This suggests that a combination of physical and biological ammonia removal is possible in a zeolite powder added bioreactor. Other workers reported that the enhanced nitrification rates are obtained by the addition of various inorganic media, such as activated carbon [17] and talqueous powder [18], in an activated sludge reactor. The predominant growth form of nitrifying bacteria is the attached form and thus nitrifying bacteria could concentrate on the surface of the particles to accelerate the nitrification.

In the case of control sludge, a higher concentration of ammonia was observed in effluent during the shock-loading period as shown in Fig. 12. On the contrary, the ammonium concentration in effluent was negligible in the zeolite powder added bioreactor. In particular, the amount of (nitrate + nitrite) was increased during that period, suggesting that the exchanged ammonium ions in the zeolite powder were nitrified by the attached microorganisms.

As shown in Fig. 13, at two test stages, it can be seen that control reactor and test reactor have mean TN removals of 44.7%, 27.3% and 56.9%, 40.6%, respectively. It was observed that there has a mean removal difference around 12% between these two reactors, and this phenomenon was attributed to two reasons. One was the adsorption of ammonium ion by zeolite powder, and the other was due to the more effectively simultaneous nitrification and de-nitrification proceeded in the test reactor, which was more easily happened with the addition of zeolite powder due to the formation of aerobic and anoxic environment co-existence [14], and it was also verified by the detection of nitrite and nitrate in effluent in these two reactors shown in Fig. 14.

As shown in Fig. 15, of all 60 operational cycles, influent phosphate was in the range of 1.59–4.78 mg/L, and the effluent phosphate was below 1 mg/L for control reactor and test reactor.

3.6. Comparison of treated wastewater quantity

According to adjusted time schedule, 270 min was one operational cycle for test reactor and control reactor was 330 min. At the same time period, the wastewater quantity treated by test reactor was 1.22 times of that treated by control reactor.

4. Conclusions

Two types of operation means “SBR reactor alone” “adding zeolite powder into SBR reactor” were used to treat municipal wastewater, and the results obtained are as follows:

- (1) The addition of zeolite powder could improve the activity of the activated sludge in SBR reactor, the SOURs of the tested sludge were enhanced significantly, and COD, NH₃-N, TN and TP could be removed in a shorter cycle time.
- (2) The addition of zeolite powder could also improve the nitrification rate and settling property of activated sludge, which is helpful to inhabit the sludge bulking and to enhance the performance of biological nitrogen removal.
- (3) Through long-term parallel shock load test, it was found that the addition of zeolite powder could enhance the ability of activated sludge in resisting the shock load of organics and ammonium, and could treat 1.22 times wastewater quantity compared to the control reactor in the same time period.

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