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Study on zeolite enhanced contact–adsorption regeneration–stabilization process for nitrogen removal

Zhichao Wu[a], Ying An[a,*], Zhiwei Wang[a], Shuang Yang[a], Heqian Chen[a], Zhen Zhou[a], Suihai Mai[b]

[a] *State Key Laboratory of Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Tongji University, Shanghai 200092, People's Republic of China*

[b] *Operation and Management of Wastewater of South Shanghai Municipality Co., Ltd., Shanghai 201203, People's Republic of China*

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Abstract

Utilizing preferential ion exchange of zeolite to ammonium, the conventional contact stabilization activated sludge process (CS) can be upgraded to a new type nitrogen removal process, zeolite enhanced contact–adsorption regeneration–stabilization process (ZCS). For municipal wastewater, the effluent ammonium concentration of the ZCS process was around 6.83 mg/L, indicating that ammonium removal efficiency was enhanced over 27% when the influent ammonium concentration was between 24.7 and 50.5 mg/L in the same hydraulic retention time (HRT) and sludge retention time (SRT) conditions as those of the CS process. The results of PCR-DGGE technology showed that the microbial diversity, uniformity and abundance of the ZCS process were all higher than that of the CS process. In addition, anoxic/oxic (A/O) process with the volumetric ratio of oxic tank to anoxic tank being 2:1 was preferred for the regeneration process. The pilot scale ZCS process with the capacity to treat up to 72 m^3/d of municipal wastewater was also monitored. The test results revealed that ammonium saturated zeolite could be biologically regenerated effectively and in time. The daily zeolite powder addition was limited to the amount that made up the loss due to the sludge excluding. Furthermore, the orthogonal experiments results showed that the most significant effects on nitrogen and ammonium removal were zeolite powder dose and external recycle ratio, respectively.

Keywords: ZCS process; Zeolite powder; Bio-regeneration; Nitrogen removal; Municipal wastewater

1. Introduction

The excessive accumulation of ammonium discharging into water can cause serious ecological problems such as: accelerated eutrophication of lakes and rivers, depletion of dissolved oxygen (DO), and toxicity of fish and other aquatic animals in water body [1]. The widely used methods for nitrogen removal are biological nitrification–denitrification, chemical treatment, ion exchange and air stripping [2]. Biological treatment technology, the classical, conventional and low-cost solution to these problems, can be easily inhibited by toxic shock, pH change, low dissolved oxygen and low temperature in winter [3]. An alternative to biological treatment is ion exchange with the advantages of high reaction rate, no sensitivity to fluctuation in ammonium influent concentration, good control of effluent quality, and little influence of low temperature in winter [4]; however, the cost of chemical regeneration remains high and desorption may occur at low ammonium loading rates [4–6].

More recently, a number of studies have been carried out for nitrogen removal by zeolite as ion exchange material combined with biological regeneration (bio-regeneration) process, which can overcome some drawbacks of ion exchange and biological treatment. It includes a dual mode process consisting of ion exchange and bio-regeneration mode in a single reactor using zeolite for ammonium removal, followed by bio-regeneration [7,8]. Several modified processes based on zeolite addition such as the novel O/A type process with natural zeolite circulation [9], the filtralite zeolite leca filter [10], and the modified zeolite sequencing batch reactor (zeo-SBR) [11] were also developed. These processes were used for the treatment

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* Corresponding author. Tel.: +86 21 65980400; fax: +86 21 65980400.
E-mail addresses: wuzhichao@mail.tongji.edu.cn (Z. Wu), anying_tongji@yahoo.com.cn (Y. An), zhiweiwang_tongji@yahoo.com.cn (Z. Wang), ketian831@163.com (S. Yang), chq496@163.com (H. Chen), zhouzhen.1981@yahoo.com.cn (Z. Zhou), mai_sh@smssc.com (S. Mai).

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of secondary and primary effluents, domestic wastewater, tannery wastewater, fertilizer industry-dinitro-toluene chemical wastewater, etc. Results showed that high efficiencies of ammonium and COD removal could be successfully achieved by those processes; however, the bacteria in some of the bio-regeneration modes only oxidized ammonium to nitrite, not to N_2 [4,7,8]. Although zeo-SBR has a special function of consistent ammonium exchange and bio-regeneration of zeolite-floc, and after 1.5d the total nitrogen removal efficiency reached 82% with water temperature maintained at 25 °C, 1.5d of HRT is too long and large treatment units are required for application. At the same time, the laboratory scale and the pilot studies were carried out by Tongji University for the feasibility of applying zeolite powder to enhance A/O biological nitrogen removal process. The operational data revealed an interesting phenomenon that the concentration of ammonium in effluent of the denitrification stage was lower than that of the nitrification phase, which likely meant that the removal of ammonium in anoxic tank was dominantly attributed to selective exchange of ammonium to the zeolite powder, while the oxic tank acting as the biological regeneration reactor.

Based on this idea, we developed a new process named zeolite enhanced contact–adsorption regeneration–stabilization process (ZCS), the schematic diagram of which was shown in Fig. 1. In the process, the high thickness of zeolite powder sludge utilizes its physical, chemical and biological synergistic function to adsorb pollutants (including suspended organic matter, soluble organism and ammonium) in the adsorption tank (T1). Then, the zeolite powder sludge with all these pollutants directly flows into the secondary clarifier (CL) for solid–liquid separation. After this, the concentrated zeolite powder sludge is pumped to the A/O process (T2 and T3) for bio-regeneration. At last, the renewed zeolite powder sludge comes out of the bio-regeneration phase under the hydraulic drive and returns to the adsorption tank for reuse. The cyclic process goes on. At the same time, the conventional biological adsorption is also maintained and can ensure a better effluent quality. Furthermore, the sludge settled character was significantly improved by powdered material addition [12], consequently achieving an extremely high concentration of the sludge in regeneration reactor and greatly shorten the HRT required due to the separation from the solution in advance.

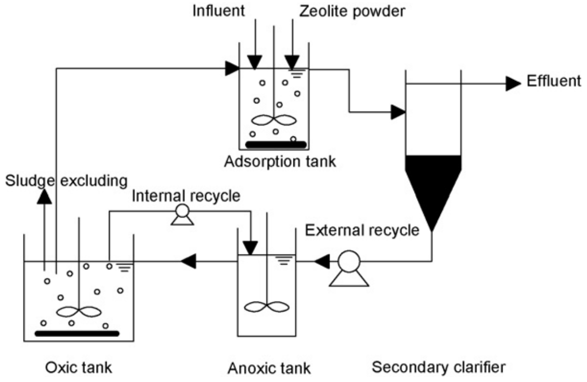

Fig. 1. The experimental setup.

This paper reports the application of the ZCS process for the municipal wastewater treatment. The feasibility and regeneration process optimization followed by a pilot scale experiment for performance evaluation were well studied. In addition, the orthogonal experiments results obtained from the laboratory scale ZCS process are also presented.

2. Materials and methods

2.1. Zeolite powder

Zeolite powder used in the experiments was provided by Jinyun Mining Co., Ltd. (Zhejiang Province, China), with characteristics as follows:

- Ion-exchange capacity: 5.3 meq/g
- Pore diameter: 3.5–4 Å
- Specific surface area: 230–320 m^2/g
- Solid density: 2.16 g/cm^3
- Si/Al ratio: 4.25–5.25
- Average particle size: 29.59 μm

The chemical composition of zeolite powder used in the study is the same as described by Wen et al. [13].

2.2. Batch experiments for the bio-regeneration mechanism of ammonium saturated zeolite powder

The main objective of this research was to identify the influence of real municipal wastewater with different conductivities upon the bio-regeneration efficiencies of ammonium saturated zeolite powder and to obtain experimental data to support the ion exchange mechanism postulated. At the same time, the capacity of nitrifying bacteria to this mechanism was also studied. The different conductivity solutions were prepared by diluting the secondary clarifier effluent of Shanghai Quyang Wastewater Treatment Plant (Quyang WWTP) with deionized water. The activated sludge was also taken from the secondary clarifier of Quyang WWTP.

Four groups of solutions were prepared for this experiment. For group A, 100 mL activated sludge, 1.25 g ammonium saturated zeolite powder and 250 mL deionized water were added into one 500 mL flask, and DO was kept at 2–3 mg/L; for group B, 100 mL activated sludge, 1.25 g ammonium saturated zeolite powder and 250 mL secondary clarifier effluent of Quyang WWTP were poured into one 500 mL flask with DO kept at 2–3 mg/L; for group C, 100 mL activated sludge, 1.25 g ammonium saturated zeolite powder and 250 mL secondary clarifier effluent of Quyang WWTP were added into one 500 mL flask with DO kept at 0.1–3 mg/L; and for group D, 1.25 g ammonium saturated zeolite powder and 250 mL secondary clarifier effluent of Quyang WWTP were added into one 500 mL flask. Samples were taken at certain intervals for 24 h and analyzed for the ammonium concentration.

Table 1
Factors and levels

No.	SRT (d)	Z_{T1} (g/L)	R	r	m	DO_{T1} (mg/L)	DO_{T3} (mg/L)
1	20	14.8	0.33	1	1	0.5	1
2	40	12.3	0.5	2	0.5	1	2
3	60	9.25	0	3	1	2	3

2.3. Continuous experiments of the ZCS process

Four sets of laboratory scale experiments were performed to verify the feasibility and for regeneration process optimization followed by a pilot scale experiment for performance evaluation. Numbers 1– 4 were all laboratory scale experiments with inflow of 6 L/h and the effective volume of adsorption tank of 3 L (with the apparent retention time of 0.5 h). Numbers 1–3 were the systems with zeolite powder addition, of which number 1 employed the single aeration tank as the regeneration reactor and numbers 2 and 3 both employed A/O process with the volumetric ratio of anoxic tank to oxic tank 1:2 and 2:1 individually. For A/O regeneration process, there were both internal recycles from oxic tank to anoxic tank to recircle the nitrate produced in the oxic tank back to the anoxic tank for denitrification. Number 4 was the reference system without zeolite addition with the same parameters as number 2. Number 5 was the pilot experiment with the inflow of 3 m^3/h, of which the volume of the adsorption tank, the anoxic tank and the oxic tank was 1.5 m^3, 2.5 m^3 and 5 m^3, respectively. Its parameters such as the volume of every tank were obtained from the former laboratory experiments. After this, in order to study the effects of different factors on long-term ammonium and nitrogen removal efficiencies of the ZCS process, the orthogonal experiments of three levels and seven factors were designed. The seven factors are SRT, zeolite powder concentration in the adsorption tank (Z_{T1}), external recycle ratio (R), internal recycle ratio (r), the mole ratio of additional carbon source (methanol) to nitrogen in oxic tank (m), DO in the adsorption tank and the oxic tank (DO_{T1} and DO_{T3}, respectively). The three levels of each factor are showed in Table 1. The arrangements of orthogonal experiments were listed in Table 2, which including eighteen sets of experiments. In the experiments, we took the effluent of aerated grit chamber and primary clarifier of Quyang WWTP as the influent. The typical wastewater quality is shown in Table 3.

In the laboratory scale experiments, peristaltic pumps were used to feed the reactor, recycle the sludge from the secondary clarifier to the regeneration tank and fulfill the internal recircle. Agitation facilities were set in all tanks to guarantee mass transferring requirements for reaction and suspension of the zeolite powder sludge. In the pilot scale experiment, agitators were also used in all tanks, microporosity aeration was used in the tanks needing aeration and the DO in oxic tanks was maintained at 2–3 mg/L. The SRT in each operation system was remained at 30d by excluding residual sludge from oxic tank of the bio-regeneration phase everyday. And the daily zeolite powder losses caused by sludge excluding were made up through fresh zeolite powder feeding everyday so that a steady concentration of zeolite powder in the reactor could be maintained. The organic proportion of the activated sludge was equivalent to f (f = MLVSS/MLSS = 0.83) with SRT of 30d under the same wastewater quality. In this process, the values of (MLSS × f − MLVSS)/f was used as the substitute of zeolite concentration.

2.4. Analytical methods

The concentrations of ammonium, nitrate, nitrogen, mixed liquid suspended solid (MLSS), and mixed liquid volatile suspended solid (MLVSS) in samples of the liquid were conducted in accordance with Standard Methods [14].

PCR-DGGE technology was adopted for comparison and analysis of population structure of sludge, respectively sampled from T1 of the CS process, T1, T2 and T3 of the ZCS process. The detailed experimental steps of DNA extraction, amplification and DGGE gel analysis were according to the methods described by Jiang et al. [15]. Shannon–Wiener Index was then used as an analysis method for microbial diversity of these samples. Formula of Shannon–Wiener Index can be expressed as Eq. (1).

$$H' = -\sum_{i=1}^{S} \frac{n_i}{N} \ln \frac{n_i}{N} \qquad (1)$$

where H' is Shannon Index; S is band number of each sample; n_i is individual number of species i; N is total individual number in a population. Here, individual number is expressed by peak area.

3. Results and discussion

3.1. Results of the bio-regeneration mechanism of ammonium saturated zeolite powder

The influences of real municipal wastewater with different conductivities upon the regeneration efficiencies of ammonium saturated zeolite powder were examined first. The results are illustrated in Fig. 2. As can be seen from the figure, the regeneration rate of ammonium saturated zeolite powder gets an increase with a rise in conductivity. Conductivity reflects the concentrations of "ion pump" in water, such as K^+, Na^+, Ca^{2+}, and Mg^{2+}. Higher conductivity means higher cation concentrations of the solution. The highest regeneration rate can reach 55% with conductivity in the range of 200–700 μs/cm. Excel Software was adopted to fit them and obtain linear equation of $y = 0.0372x + 30.358$ ($R^2 = 0.9093$).

Figs. 3 and 4 show the regeneration efficiencies of ammonium saturated zeolite powder and the nitrate concentration changes

Table 2
Orthogonal experiments of removal ammonium and nitrogen by ZCS process

No.	SRT	Z_{T1}	R	r	m	DO_{T1}	DO_{T3}	Nitrogen removal efficiency (%)	Ammonium removal efficiency (%)
1	1	1	1	1	1	1	1	67.39	78.65
2	1	2	2	2	2	2	2	64.08	83.05
3	1	3	3	3	3	3	3	58.38	87.16
4	2	1	1	2	2	3	3	60.07	84.86
5	2	2	2	3	3	1	1	66.01	79.73
6	2	3	3	1	1	2	2	61.29	87.09
7	3	1	2	1	3	2	3	67.15	88.77
8	3	2	3	2	1	3	1	64.06	88.46
9	3	3	1	3	2	1	2	60.75	77.07
10	1	1	3	3	2	2	1	64.91	91.62
11	1	2	1	1	3	3	2	66.45	79.68
12	1	3	2	2	1	1	3	60.77	80.63
13	2	1	2	3	1	3	2	65.80	89.72
14	2	2	3	1	2	1	3	64.08	88.6
15	2	3	1	2	3	1	1	62.44	78.33
16	3	1	3	2	3	1	2	64.03	89.70
17	3	2	1	3	1	2	3	63.94	82.22
18	3	3	2	1	2	3	1	58.10	82.60

	SRT	Z_{T1}	R	r	m	DO_{T1}	DO_{T3}
Nitrogen removal efficiency							
K_1	381.98	389.35	381.04	384.46	383.25	383.03	382.91
K_2	379.69	388.62	381.91	375.45	371.99	383.81	382.40
K_3	378.03	361.73	376.75	379.79	384.46	372.86	374.39
Rang	3.95	27.62	5.16	9.01	12.47	10.95	8.52
Ammonium removal efficiency							
K_1	500.79	523.32	480.81	505.39	506.77	494.38	499.39
K_2	508.33	501.74	504.5	505.03	507.80	511.08	506.31
K_3	508.82	492.88	532.63	507.52	503.37	512.48	512.24
Rang	8.03	30.44	51.82	2.49	4.43	18.10	12.85

Note: Rang = K_{max}; K_{min}; K: sum of each level; removal efficiencies are average values.

in solutions of group A–D, respectively. There were no significant changes of zeolite powder regeneration efficiency and nitrate concentration, which were stable at the level of 10% and 9.5 mg/L with deionized water as mother liquor; however, they could respectively be enhanced to 94% and 31 mg/L in the secondary clarifier effluent as mother liquor with DO of 2–3 mg/L after 16 h. This results clearly indicate that the regeneration rate is limited by the cation in the circumstance, which is a competitive sorbent to NH_4^+ and can replace it from zeolite powder. Without adding sludge, the solution of group D reached the equilibrium between NH_4^+ from ammonium saturated zeolite and cation from the secondary clarifier effluent after a short time. And the ammonium saturated zeolite was partial regenerated with regeneration efficiency reaching 42%. Furthermore, the regeneration efficiency of ammonium saturated zeolite at the anoxic condition of group C was approximately equal to that of group D. After 4 h, oxygen restoration began in the group C and nitrification microbe began to effect, which increased the regeneration efficiency of ammonium saturated zeolite and nitrate concentration. And they were leveled off at 75% after ceasing oxygen restoration at 17 h.

Combined with the results mentioned above, it can be inferred that bio-regeneration of zeolite powder is not the nitrification effects on ammonium due to nitrifying bacteria entering into

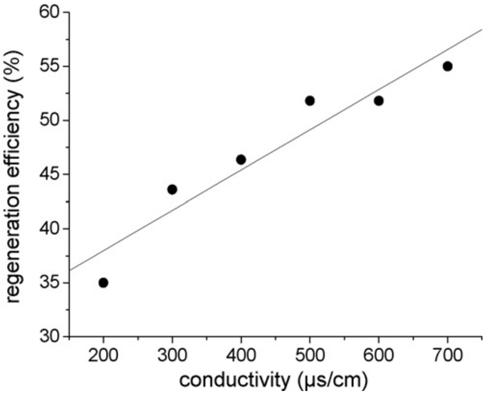

Fig. 2. Relationship between conductivity and regeneration efficiency of zeolite powder.

Table 3
Characteristics of raw wastewater to the laboratory scale and the pilot experiments

Item	Effluent of aerated grit chamber	Effluent of primary clarifier
COD (mg/L)	266.0–695.9	70.0–361.0
NH_4^+–N (mg/L)	24.7–50.5	21.7–40.8
NO_3^-–N (mg/L)	0.10–2.98	0.13–2.92

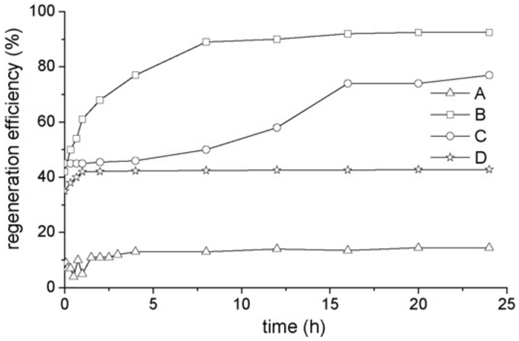

Fig. 3. Time variation curve of zeolite powder regeneration efficiency under different conditions. A, B and C were the systems with activated sludge addition, of which A, B kept DO at 2–3 mg/L and C kept DO at 0.1–3 mg/L. Without aeration and activated sludge addition, D used secondary clarifier effluent as mother liquor, which was the same as B, C and different from A that using deionized water as mother liquor.

the internal space of zeolite, but a series of equilibrium processes: firstly, ion exchange equilibrium is reached between cation and NH_4^+ from ammonium saturated zeolite, achieving partial regeneration of ammonium saturated zeolite (Eq. (2)); then NH_4^+ concentration is decreased by nitrification effects of microbe (Eq. (3)), accelerating the equilibrium in the second reaction to move to the right side; a new equilibrium process will be built as the NH_4^+ desorbing from zeolite powder drops to negligible values. It also can be assumed that the main mechanism of ammonium removal by zeolite powder is ion exchange not adsorption.

$$Z-NH_4+(K^+, Na^+, Ca^{2+}, Mg^{2+}) \leftrightarrow (K^+, Na^+, Ca^{2+}, Mg^{2+}) + NH_4^+ \quad (2)$$

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (3)$$

3.2. The optimization of the regeneration process

The feasibility of the ZCS process was verified through laboratory scale experiments in Quyang WWTP for one year. The results are shown in Table 4.

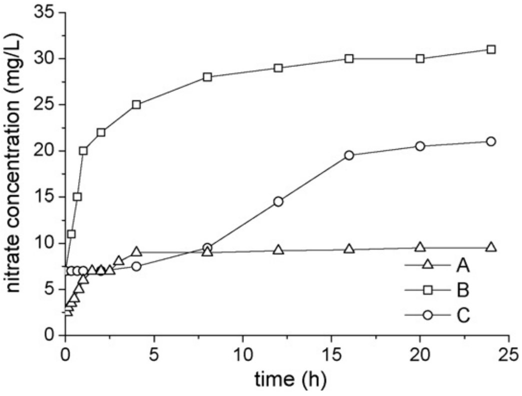

Fig. 4. Time variation curve of nitrate in mixture liquor under different conditions. A, B and C were the systems with activated sludge addition, of which A, B kept DO at 2–3 mg/L and C kept DO at 0.1–3 mg/L. B and C used secondary clarifier effluent as mother liquor while A used deionized water as mother liquor.

Table 4
Parameters and results of the laboratory scale experiments

Item	1	2	3	4
Zeolite concentration in regeneration tank (g/L)	9.82	9.64	10.26	0
VSS in regeneration tank (g/L)	7.26	7.21	7.52	4.41
Zeolite concentration in the adsorption tank (g/L)	3.01	3.31	3.42	0
VSS in the adsorption tank (g/L)	2.42	2.40	2.51	2.14
Ammonium effluent concentration (mg/L)	17.7	12.5	16.4	21.2

All values in the table were the monthly average ones measured after stable operation.

The excellent regeneration process must be carefully picked to ensure the ammonium saturated zeolite powder sufficiently renewed. The results of run 1–3 indicate that the regeneration effect of A/O process is significantly superior to that of single aeration tank process for that A/O process has strong ability to intensify nitrification [16]. But the nitrate produced during the nitrification needs effective denitrification in order to meet the total nitrogen (TN) target in the effluent. Moreover the volumetric ratio of anoxic tank to oxic tank should be properly determined. Taking run 3 as an example, the HRT of oxic tank is too short to regenerate the ammonium saturated zeolite powder sufficiently. When the volumetric ratio of oxic tank to anoxic tank is 2:1, the effluent water quality is relatively better. Consequently, A/O process with the volumetric ratio of oxic tank to anoxic tank being 2:1 was preferred for the regeneration process.

Lab-scale ZCS process and CS process were started simultaneously with SRT controlled at 30d. Compared with CS process, the ammonium removal efficiency is from 35.37 to 61.89%, which indicated that ammonium removal efficiency of the ZCS process was significantly higher than that of the CS process under the same influent ammonia nitrogen concentration. Furthermore, sludge bulking occurred during CS process operation within 1 month, and deteriorated settling performance and denitrification due to high concentration of nitrate in secondary clarifier induced vast efflux of sludge and then compelled the process to stop operation.

3.3. Comparison analysis of microbial diversity in ZCS process

Fig. 5 shows the DGGE fingerprints of sludge from adsorption tank of CS, and three different tanks of the ZCS process. Bands 1 and 2 marked in fingerprints of samples from three different tanks of the ZCS process did not exist in sludge of traditional adsorption tank, demonstrating that there were some significant differences in microbial population structure between ZCS process and CS process. DGGE fingerprints were then analyzed by Smart Viewer gel imaging system, and Shannon Indexes for the four samples are calculated and shown in Fig. 6. Shannon Indexes of three tanks of the ZCS process are respectively, 2.68, 2.49 and 2.51, which are all higher than that of the CS process, demonstrating that microbial species are more diversified than traditional CS process. It is probably owing to

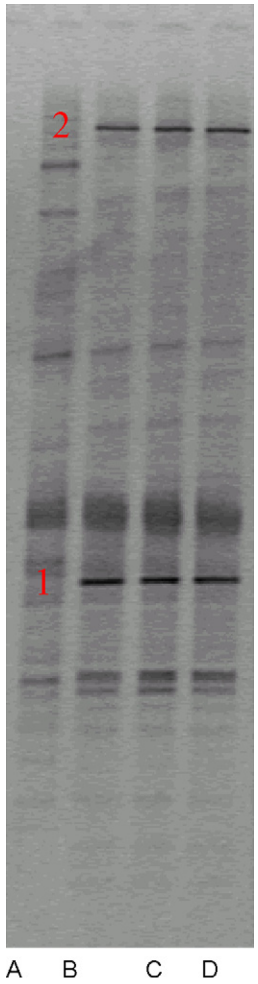

Fig. 5. DGGE fingerprint of sludge from CS process and ZCS process. (A) Sludge from adsorption tank of CS process. (B–D) Sludge from adsorption, oxic and anoxic tank of ZCS process.

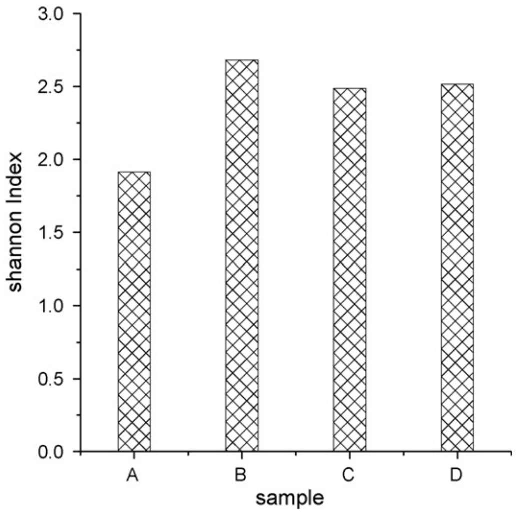

Fig. 6. Shannon Indexes of different samples. (A) Sludge from adsorption tank of CS process. (B–D) Sludge from adsorption, oxic and anoxic tank of ZCS Process.

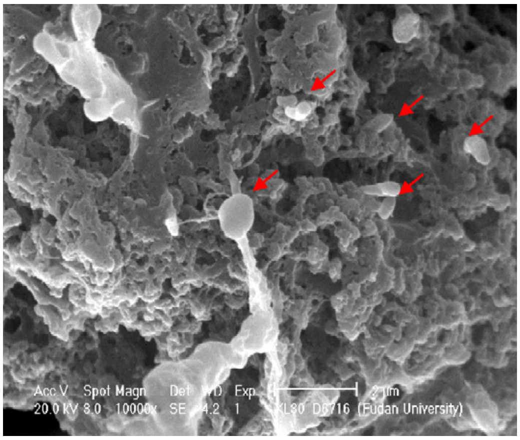

Fig. 7. Surface of zeolite powder after biofilm formation (10,000×).

attached interface that can be provided for microbe growth, which makes zeolite powder sludge have both advantages of suspended activated sludge process and biofilm process.

Fig. 7 shows the electron microscope (10,000×) scanning results of zeolite powder particle surface in maturated zeolite sludge. The positions pointed by arrowheads with the similar brightness are bacilliform and elliptoid microbe, demonstrating that the addition of zeolite powder is favorable for attached growth of microbe. Combined with conclusions of PCR-DGGE, it could be concluded that the addition of zeolite powder will enhance microbial diversity, uniformity and abundance of the system.

3.4. Results of the pilot scale experiment

Based on the parameters attained from the laboratory scale experiments, the pilot experiment was engaged to make a perfect practical application. Table 5 shows the operation parameters. The daily sludge yield of steps 1, 2 and 3 were respectively 2.358 kgVSS/d, 1.874 kgVSS/d and 1.724 kgVSS/d, which had a tendency of decreasing with the increase of zeolite addition. The SV_{30} (settled volume in 30 min) of the sludge in the adsorption tank remained at 15% all the year round, while SV_5 (settled volume in 5 min) remained at 30%. The two parameters together indicated that the sedimentation performance and sludge concentrate performance were both perfect [17]. Taking step 2 as an example, SVI (settled volume index) was 46.2 mL/g SS (13.7 mL/gVSS), which ensured the continuous and stable performance of the system.

Fig. 8 shows the results of ammonium removal with different influent resources. As to step 1, when the ammonium–zeolite loading in the adsorption tank was maintained at around 8 mgNH_4^+–N/g zeolite, the corresponding effluent ammonium concentration was approximately 10.7 mg/L (the average removal efficiency was 65.8%). When the zeolite powder concentration increased (step 2), the ammonium–zeolite loading in the adsorption tank was then decreased to 5 mgNH_4^+/g zeolite. And the ammonium removal capability of the system was significantly improved with the average effluent ammonium concentration being approximately 6.83 mg/L (the average removal efficiency was 78.0% with the maximum 91.5%). Moreover,

Table 5
Experimental conditions of pilot scale experiments

Item Influent resource	Step1 Effluent of aerated grit chamber	Step2 Effluent of aerated grit chamber	Step3 Effluent of primary clarifier
COD sludge loading rate (kg COD/VSS/d)	0.4938	0.6214	0.2306
COD volume loading rate (kg COD/m^3/d)	3.882	3.882	1.326
HRT (h)	3	3	3
MLVSS (g/L)			
T1	3.270	3.250	2.720
T2	8.720	7.040	6.320
T3	8.810	6.750	6.370
Zeolite concentrations (g/L)			
T1	4.750	7.670	10.100
T2	13.70	18.01	22.76
T3	13.40	18.67	22.11
Ammonium–zeolite loading in the adsorption tank (mgNH$_4$$^+$–N/g zeolite)	8	5	3
Daily addition dosage of the zeolite powder (kg/d)	3.61	5.00	6.09
External recycle ratio	0.55	0.75	0.75

its capability to resist shock loading was also significantly improved. When taking the primary clarifier outlet as influent, the ammonium removal efficiency decreased though the ammonium–zeolite loading in the adsorption tank was reduced to 3 mgNH$_4$$^+$–N/g zeolite. The average effluent ammonium concentration was approximately 11.6 mg/L (the average removal efficiency was 63.2%). Furthermore, the capability of the system to resist shock loading was also deteriorated. And pH in oxic tank decreased to about 5.7 during this period. This phenomenon could be due to the organism recirculated to the anoxic tank was too little to accelerate denitrification with the decreasing of the influent COD loading rate. As a result, there was not sufficient alkalinity in the subsequent oxic tank to accelerate nitrification, and the nitrification efficiency decreased indirectly. Hence, the zeolite powder could not be renewed sufficiently and timely, and the ammonium removal efficiency of the system was subsequently deteriorated.

From the above results, it can be seen that the zeolite powder addition can obviously intensify the system's ability to ammonium deprivation. Furthermore, the ammonium removal capability increased with the dosage of the zeolite powder added. According to the report in the anaerobic/anoxic/oxic process by Baeza et al. [16], the maximal nitrification rate was 50 g NH$_4$$^+$–N/kg VSS/d. However, in our studies, it was around 340 g NH$_4$$^+$–N/kg VSS/d calculated by their methods. If the adsorption of ammonium to zeolite were not taken into account, the result was inconceivable. It indicated that zeolite powder has played a key role in the ammonium removal in the ZCS process. The daily addition dosage of the zeolite powder can be calculated as

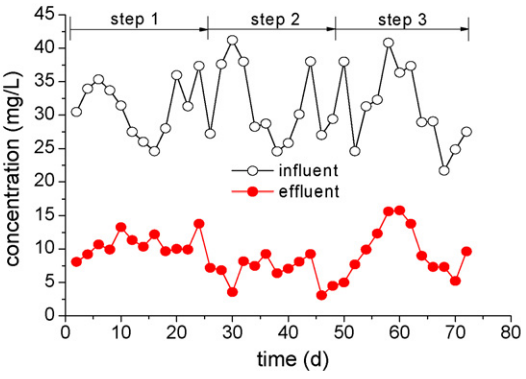

Fig. 8. The ammonium removal effect of pilot experiment.

$$\Delta C = \frac{C_{T1}V_{T1} + C_{T2}V_{T2} + C_{T2}V_{T2}}{\theta} \tag{4}$$

where ΔC is the daily addition dose of the zeolite powder (kg/d); C_{T1}, C_{T2}, C_{T3} are the zeolite powder dose of the T1, T2, T3, g/L; V_{T1}, V_{T2}, V_{T3} are the volume of the T1, T2, T3, m^3 and θ is the SRT, 30d.

Taking step 2 as the an example, $\Delta C = 5$ kg/d. Based on our former experiments, in municipal wastewater the Langmuir model provided a close fit for the ammonium ion exchange equilibrium with the zeolite powder used at the normal temperature. The Langmuir equation can be expressed as follows:

$$q = \frac{0.12c}{1 + 0.12c} \tag{5}$$

where q is the amount of ammonium adsorbed per unit weight of zeolite powder, mg/g; c is the equilibrium ammonium concentration in solution, mg/L. According to Eq. (5), the theoretical maximal amount of ammonium adsorbed per unit weight of zeolite powder was only 10 mg/g, therefore the additional zeolite powder could only remove 50 gNH$_4$$^+$–N/d theoretically. While the average daily ammonium removal during the pilot experiments was 2.25 kg NH$_4$$^+$–N/d, far more than the above value. All this proved that the ammonium saturated zeolite powder was well regenerated in this process.

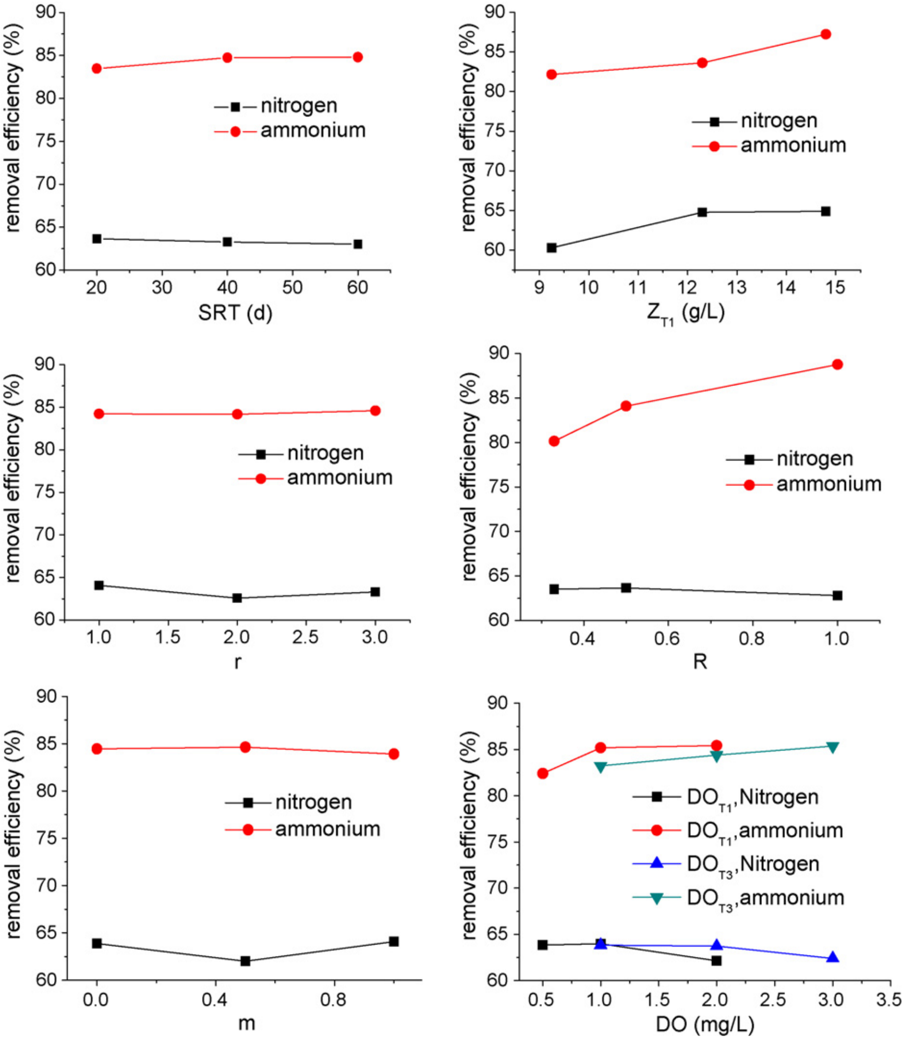

Fig. 9. Effects of different factors on the ammonium and nitrogen removal efficiencies.

3.5. Results of orthogonal experiments

The last eight rows of Table 2 show the results of different factors affecting on the ammonium and nitrogen removal efficiencies by ZCS process. The most significant effects among the seven factors on nitrogen removal were found to be zeolite powder concentration, followed by m, DO_{T1}, r, DO_{T3}, R and SRT; While the seven factors influencing ammonium removal efficiency were in a descending order as follows: R, zeolite powder concentration, DO_{T1}, DO_{T3}, SRT, m and r.

Fig. 9 shows the effects of different factors on the ammonium and nitrogen removal efficiencies by ZCS process. The change of SRT does not show significant effects on the ammonium and nitrogen removal efficiencies, so SRT of 40d was recommended for the process. The zeolite powder concentration in the adsorption tank is the most key factor affecting nitrogen removal efficiency and inferior to external recycle ratio to influence ammonium removal efficiency. The ammonium and nitrogen removal efficiencies increased with the zeolite powder concentration in the adsorption tank added, it means that the optimal zeolite concentration of the system could be adjusted according to the water quality requirement of the effluent. The nitrogen removal efficiency kept almost unchanged with external recycle ratio in the range of 0.33–1, but the ammonium removal efficiency directly increased to 88.8% when external recycle ratio is 1. A further increase of the recycle ratio may also improve ammonium removal efficiency but will increase the energy cost of the process. On the contrary, Change in ammonium removal efficiency was negligible with increase in internal recycle ratio from 1 to 3. And the results obtained indicate that by using a recycle ratio of 1, good denitrification could be obtained. Generally, the carbon source is very important to anoxic phase, but it is beneficial for nitrogen removal when m is respectively, equal to 0 and 1. Further studies should be needed for this phenomenon. Taking economic factor and treatment effect into account, the process can still perform well without additional carbon source. The ammonium and nitrogen removal efficiencies all increased with the DO in the adsorption tank varying from 0.5 to 1 mg/L; however, the ammonium removal efficiency decreased and nitrogen removal efficiency increased slowly from 1 mg/L. The ammonium removal efficiency increased with the increase of DO of oxic tank from 1 to 3 mg/L, while the trend is contrary to

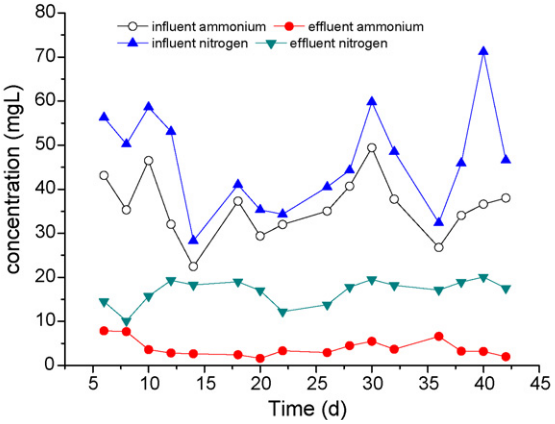

Fig. 10. Operation results under the optimal conditions.

that of the nitrogen removal efficiency which decreased quickly after 2 mg/L, below which the nitrogen removal efficiency slight decreased.

From the study mentioned above, the optimum ammonium and nitrogen removal efficiencies of the ZCS process conditions were determined, which were: SRT of 40d, zeolite powder concentration in the adsorption tank of 14.8 g/L, *R* of 1, *r* of 1, *m* of 0, DO_{T1} of 1 mg/L and DO_{T3} of 2 mg/L. Fig. 10 shows the operation results of the ZCS process under the optimal conditions. From Fig. 10, it can be seen that the concentrations of ammonium and TN in effluent could meet grade B of the first level ($COD < 60$ mg/L, $NH_4^+ < 8$ mg/L, $TN < 20$ mg/L) in “Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant of China (GB18918-2002)”.

4. Conclusions

ZCS process is a novel nitrogen removal process developed by utilizing preferential ion exchange of zeolite to ammonium, which was used to treat municipal wastewater, and long-term experiments results obtained are as follows:

(1) The effluent ammonium concentration of the ZCS process was around 6.83 mg/L, indicating that ammonium removal efficiency was enhanced over 27% when the influent ammonium concentration varying from 24.7 to 50.5 mg/L in the same HRT and SRT conditions as those of the CS process. And the pilot scale operation results indicated that zeolite powder played a key role in the ammonium removal in the ZCS process and the ammonium saturated zeolite powder was well regenerated in the A/O process.

(2) Combined with Shannon Index, results of PCR-DGGE technique showed that microbial diversity, uniformity and abundance of the ZCS process were all higher than that of the CS process. Attached growth microbe observed by electron microscope scanning demonstrated that ZCS process incorporated advantages of suspended activated sludge process and biofilm process, and then enhanced systematic resistance to shocking load and removal efficiency of pollutants.

(3) The orthogonal experiments of three levels and seven factors indicated that the optimum ammonium and nitrogen removal efficiencies of the ZCS process conditions are: SRT of 40d, zeolite powder concentration in the adsorption tank of 14.8 g/L, *R* of 1, *r* of 1, *m* of 0, DO_{T1} of 1 mg/L and DO_{T3} of 2 mg/L. Under the optimal conditions, the concentrations of ammonium and TN in effluent could meet grade B of the first level in “Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant of China (GB18918-2002)”.

(4) The hydraulic retention time of the ZCS process is only 3 h, so the occupied area of the wastewater treatment plant could be significantly reduced with this new process relieving the contradiction between the stringent standards and the limited urban land in China. Moreover, it provides a completely new technology for the upgrading of the existing plant.

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