



Domestic wastewater treatment using biological aerated filtration system with modified zeolite as biofilm support

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ABSTRACT

Modified zeolite and natural clinoptilolite were applied to treat domestic wastewater in two two-stage up-flow biological aerated filters (BAF) to compare their abilities to act as biofilm supports. The results showed that the two-stage BAF with modified zeolite brought a relative superiority to natural clinoptilolite two-stage BAF in terms of chemical oxygen demand and ammonia nitrogen removal under the conditions of temperature 20–26°C and dissolved oxygen above 4.00 mg l⁻¹. In addition, the detection of the amount of heterobacteria and nitrobacteria of two two-stage BAFs also showed that modified zeolite medium was more suitable to the attached growth of nitrobacteria, which is helpful to the improvement of nitrification performance in two-stage BAF with modified zeolite.

Keywords: Modified zeolite; Biological aerated filter; Start-up; Ammonia nitrogen; COD_{Cr}

1. Introduction

Biological aerated filters (BAFs) are fixed film reactors that use media with a high specific surface area and high porosity for secondary and tertiary treatment of wastewater [1]. They can combine biochemical oxygen demand, solids and ammonia nitrogen (NH₃-N) removal in a single unit [2]. In a single unit, nitrification is highly influenced by competition between heterotrophic and autotrophic microorganisms. Nitrifying organisms are adversely easily impacted by high organic loads [3–5]. Media selection is critical in the design and operation of BAF to achieve effluent quality requirements. As BAF

technology is applied to wastewater treatment, the selection of granular media plays an important role in maintaining a high amount of active biomass and a variety of microbe populations. The most frequently studied BAF support media include clay-, schist- or plastic-based ones of various types, such as phosphorylethanolamine, polyethylene and polystyrene [6–9].

Zeolites are a natural mineral, which can be described chemically as aluminum silicates. They are used for different applications as, for example, ion exchange, molecular sieves and air-drying [10–12]. Natural zeolite has an adsorption capacity for organic substances and is also capable of cation exchange for example NH₄⁺ [13]. In terms of removing organic matter and total kjeldahl nitrogen, the performance of

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the BAF with natural zeolite was superior to that with sand. Ion-exchange capacity of natural zeolite with NH_4^+ leads to higher nitrogen removal [14,15].

In this study, a new zeolite filter material was developed and used as biofilm support of a two-stage BAF. These particles were used as biofilm supports in two-stage BAF, and their effectiveness in domestic wastewater treatment was compared with natural clinoptilolite. The main objective of the experiments was to study the start-up process (the process of biofilm forming on the surface of the filter media in two-stage BAF is called the start-up processes) and performance of the two-stage BAF system using modified zeolite as biofilm support.

2. Materials and methods

2.1. Modified zeolite characterization

The natural clinoptilolite (light greyish white) was collected at Weifang, Shandong, PR China. The chemical composition of the mineral is shown in Table 1. Under investigation, we choose the optimal condition to synthesize the modified zeolite. 7.5 g of the natural clinoptilolite was placed in a Ni crucible and fused with 9 g of NaOH powder at 550°C for 2 h. The melt was ground, and 75 ml of water was added so as to prepare the NaOH solution of 3 mol l⁻¹. The mixture was homogenized, transferred into a Teflon-lined stainless-steel autoclave and heated at 100°C for 8 h. The products were filtrated and stirred with 50 ml 1 mol l⁻¹ NaCl. In order to remove the alkali absorbed by the zeolite, 1 mol l⁻¹ HCl was dropped into the mixture until the pH got to 6. The products were filtrated and dried.

2.2. Reactor description

A scheme of the BAF pilot-plant system is shown in Fig. 1. Two columns that enable carbon oxidation (C column) in BAF A and ammonia oxidation (N column) in BAF B, respectively, comprised the

pilot-plant system. The two units, operated in series, were 2.30 m in height and 0.15 m in diameter. The columns contained a modified zeolite media approximately 3.00–5.00 mm in diameter with an average specific surface area of 36.17 m²g⁻¹. The A and B column contained 1.50 m of media and 0.20 m of supporting layer, respectively. There were water inlets at the bottom and outlets at the top of A and B. A and B used a prominent metering pump to supply wastewater. The physicochemical characteristics of particles are shown in Tables 1 and 2. Air was provided to the columns through diffusers in a distribution manifold located at the floor of the column. There were all two two-stage BAFs, of which one was run as control reactor packed with natural clinoptilolite and the other with modified zeolite as test reactor.

As shown in Table 2, modified zeolites were superior to natural zeolite in many ways, including higher total porosity, larger total surface area and lower bulk and apparent density. According to the investigation of Kentet al. [1], these characteristics were essential for filter materials suitable for use as BAF media. Overall, it is feasible to introduce modified zeolite into wastewater treatment by BAFs.

The biofilter was periodically backwashed in order to remove the accumulated suspended solids (SS) and the excess biomass produced. Each column was backwashed in a co-current manner at regular intervals (24 h for the A column, 48 h for the B column). The backwash sequence included air scour, followed by air scour and water backwash, at finally water scour. The backwash air application rate was 4.0 l min⁻¹.

2.3. Wastewater characteristics

Throughout all the experimentation period, the wastewater used for the laboratory experiment was obtained from University of Jinan in Shandong province, China. The BAF was fed with domestic wastewater with an $\text{NH}_3\text{-N}$ loading ranging between 44.51 and 55.24 mg l⁻¹ and organic carbon concentration ranging between 362.00 and 554.00 mg l⁻¹. The characteristics of domestic wastewater are summarized in Table 3.

2.4. Analytical methods

During operation, influent and effluent samples were taken regularly from May 2006 to November 2006, and the concentrations of COD_{Cr} and $\text{NH}_3\text{-N}$ were analysed according to standard methods (State Environmental Protection Administration of China, 2002) [16]. Additionally, turbidity and colour of the

Table 1
The comparison on component between natural zeolite and modified zeolite

Filter material (%)	Natural clinoptilolite	Modified zeolite
SiO ₂	67.29	71.25
CaO	1.86	4.21
MgO	3.40	1.84
Fe ₂ O ₃	3.84	2.68
Al ₂ O ₃	12.13	14.42
Loss	10.00	3.20

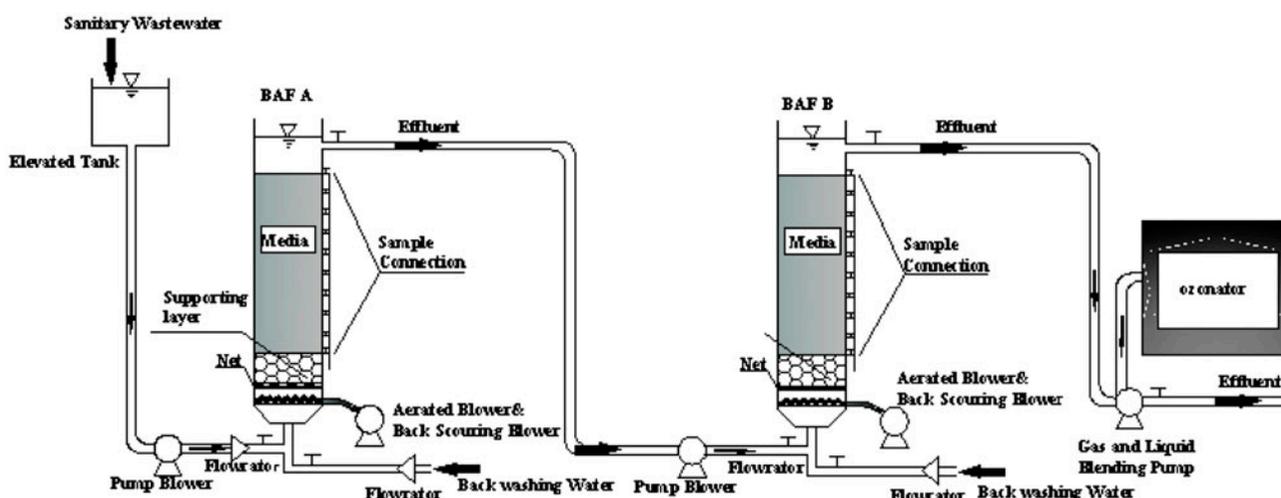


Fig. 1. Experimental scheme of laboratory-scale two-stage modified BAF system.

Table 2

The comparison on elemental property between natural zeolite and modified zeolite

Filter material	Natural clinoptilolite	Modified zeolite
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	13.79	36.17
Particle diameter (mm)	3–5	3–5
Density (kg m^{-3})	2,293.60	2,349.60
Biomass of biofilm (g g^{-1})	0.052	0.068

Table 3

Characteristics of domestic wastewater fed to a two-stage BAF system

Parameter	Range
CODcr (mg/l)	362.00–554.00
$\text{NH}_3\text{-N}$ (mg/l)	44.51–55.24
Temperature ($^\circ\text{C}$)	20–26
pH	7.4–7.8
Turbidity (NTU)	50.24–65.93
Colour (CPU)	550–770

influent and effluent were determined using the HI-93727 colour instrument. The temperature, dissolved oxygen (DO) and pH were routinely monitored during the experimental period. Probes were used to measure the temperature, pH and dissolved concentrations during the experimental period. Ports, at intervals of 0.15 m from the base of the columns, allowed samples to be drawn at specific intervals so that substrate removal profiles could be examined.

Generally, samples were drawn at the end of the filter run, but occasionally samples were also taken immediately after backwashing to examine the recovery of effluent quality.

2.5. Batch $\text{NH}_3\text{-N}$ sorption experiments

To investigate the relationship between $\text{NH}_3\text{-N}$ removals varied with sorption time on modified zeolite, the batch $\text{NH}_3\text{-N}$ sorption experiments were detected. In a series of 250-mL Erlenmeyer flasks, 100 mL of $\text{NH}_3\text{-N}$ concentration (100 mg l^{-1}) and 10.00 g modified zeolite material (heated at 100°C for 2 h) were added. The flasks were capped and placed on an orbital shaker at 300 rpm and room temperature ($19\text{--}21^\circ\text{C}$). At the end of the adsorption process, the suspension in each flask was filtered through a $0.45\text{-}\mu\text{m}$ membrane filter and the filtrate was analysed for $\text{NH}_3\text{-N}$. The quantity of $\text{NH}_3\text{-N}$ uptake by modified zeolite was calculated from the decrease in its concentration in solution. The same experiments were done on natural clinoptilolite as contrast test. The duplicate experiments demonstrated the high repeatability of this batch procedure, and the experimental error for most cases could be controlled within 5%.

2.6. Counting of heterotrophic and nitrifying bacteria bacterial population

Samples of media covered with biomass were collected at the middle section of the biofilters. A membrane filter method was used to count viable heterotrophic and nitrifying bacteria. To count heterotrophic bacteria, albumin agar medium was

used. Counts of cultivable heterotrophic free living and attached bacteria were performed by the spread plate method on albumin agar medium sterilized by autoclaving (121°C, 1 atm for 20 min). Dilutions were performed in 34 g l⁻¹ sterile sodium chloride solution. Plates were set-up in duplicate for each dilution. Only plates having between 20 and 200 colonies were considered. Incubation time was 10 days at 25°C. Bacterial concentrations were expressed as CFU per ml for free living bacteria and as CFU per gram of wet packing for attached ones. Because the surface area of the packing material was not well defined, all data are expressed as mean. For nitrifying bacteria, nitrobacteria, a medium containing the nitrite ion was used. The same experiment steps were done on nitrifying bacteria. These media and details of viable cell counting are described in literature [17].

3. Results and discussion

3.1. Influence on adsorption time of NH₃-N removal

To investigate the relationship between sorption time and NH₃-N removal rate of the two kinds of filter material (modified zeolite and natural clinoptilolite), eight solutions with the same initial NH₃-N concentration ($C_0 = 100 \text{ mg l}^{-1}$) were detected at different time intervals (5, 10, 20, 30, 40, 60, 90, 120 min separately) for modified zeolite and natural clinoptilolite, respectively. The results are shown in Fig. 2. The NH₃-N treated by modified zeolite shows greater absorption in comparison with natural clinoptilolite. It is conditioned by increase in adsorption capacity due to the growth of the pore volume. With the adsorption time increasing, the NH₃-N removal rate on modified zeolite material was enhancing obviously in the first 40 min and reached 58.5% at 40 min, then the removal rate was enhancing very slowly with time increasing after 40 min.

3.2. Start-up process of two-stage modified zeolite BAFs

In order to investigate the modified zeolite ion-exchange properties, the start-up process adopts natural biofilm manner, avoiding the use of activated sludge biofilm effect for ion exchange.

Domestic wastewater was passed up flow through the reactors at 4.00 l min⁻¹ and the air at 12.00 l min⁻¹. During the start-up period, the effluent DO concentration remained above 4.00 mg l⁻¹, pH ranged from 7.52 to 7.76. Influent COD_{Cr} concentrations ranged from 386.00 to 432.00 mg l⁻¹, and ammonium nitrogen concentrations ranged from 44.93 to 52.63 mg l⁻¹.

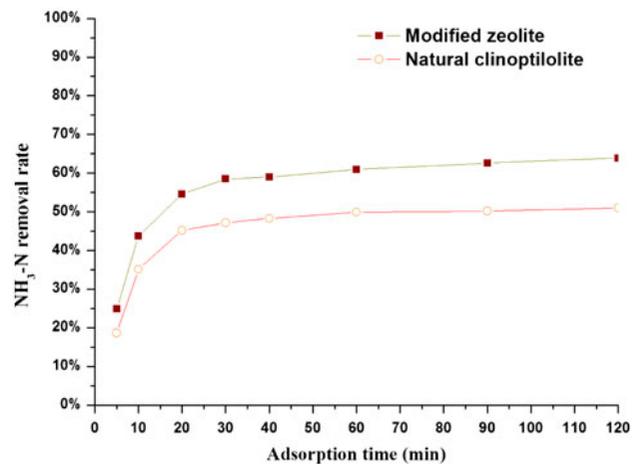


Fig. 2. The relationship between adsorption time and NH₃-N removal rate.

The COD_{Cr} and NH₃-N removal rates in two-stage modified zeolite BAFs at the start-up process are presented in Fig. 3. In the COD_{Cr} and NH₃-N removal efficiencies in modified zeolite two-stage BAFs during the first 5 days, the average removal rates of COD_{Cr} and NH₃-N in modified zeolite BAF A were 40.37 and 89.62%, respectively, while those in modified zeolite two-stage BAFs B were 52.99 and 98.88%, respectively. It demonstrated that the ion exchange and adsorption of modified zeolite played an important role at the start-up first period. In two-stage modified zeolite BAF A, the COD_{Cr} removal rates significantly increased from 5 to 15 days, while NH₃-N removal rates obviously descended. After 15 days of operation, BAF A had stable pollutants removal efficiency. The average removal rates of COD_{Cr} and NH₃-N were 87.55 and 34.17%, respectively. In two-stage modified

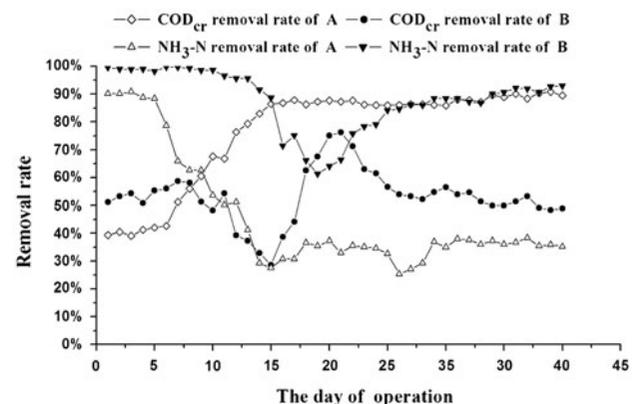


Fig. 3. COD_{Cr} and NH₃-N of removal rates in two-stage modified zeolite BAFs at the start-up process.

zeolite BAF B, from 5 to 25 days, COD_{Cr} removal efficiencies firstly decreased, then increased, then decreased, while NH₃-N removal rate decreased first and then gradually increased. After 25 days of operation, two-stage modified zeolite BAF B also reached stable pollutants removal efficiency. The average removal rates of COD_{Cr} and NH₃-N were 52.37 and 88.80%, respectively. Some authors report that organic matter is mainly consumed in the first aerobic stage, which apparently allows lower competition between nitrifiers and heterotrophs in the next aerobic stage [18]. So, we can speculate that heterotrophic bacteria, which would reduce COD_{Cr} and convert organic nitrogen to ammonium nitrogen and nitrifying bacteria, contested living space in modified zeolite BAF B.

Overall, the two-stage modified zeolite BAF A whose function is removing organic contamination starts up quicker than the two-stage modified zeolite BAF B whose function is removing ammonium nitrogen. Moreover, the start-up process of two-stage modified zeolite BAF A takes 15 days, and the start-up process of two-stage modified zeolite BAF B needs 25 days.

3.3. Overall reductions in two-stage modified zeolite BAFs

The two two-stage BAFs were monitored for 4 months after the start-up of the biofilters. Throughout the experiment, DO was maintained above 4 mg l⁻¹ and water temperature was kept between 20 and 26 °C. The effluent pH decreased slightly when compared with that of the influent, the average being 7.52 (7.4–7.8). Three the flows, 4.0, 5.0, and 6.0 l min⁻¹ were adopted, coincided with stage one, stage two and stage three, respectively. The COD, NH₃-N, turbidity and colour of influent and effluent in two two-stage BAFs during stage one to three are presented in Figs. 4–7 and Tables 4–7.

The COD_{Cr} concentrations in and out of two-stage modified zeolite BAF and removal rate at different flow rates are shown in Fig. 4. Most of the COD_{Cr} was removed in modified zeolite BAF A. In order to avoid the influence to nitrification in modified zeolite BAF B by carbonaceous material, so we expected that heterotrophic bacteria should reduce most of COD_{Cr} in the two-stage modified zeolite BAF A. However, having a second biofilter did result in further reduction. The results for the COD_{Cr} removal agree very well with the one of Westerman [19] who showed that most of the COD_{Cr} occurred in the first biofilter in the up-flow BAFs for the treatment of flushed swine manure. The COD_{Cr} percentage reduction was lower at higher inlet flow rate. When the flow rate was changed from 4.0 to 6.0 l min⁻¹, the average COD_{Cr} removal rate decreased

from 89.07 to 81.43%. This was just expected because heterotrophic bacteria should reduce most of the oxygen demand from carbonaceous material in modified zeolite BAF A. Modified zeolite BAF B did

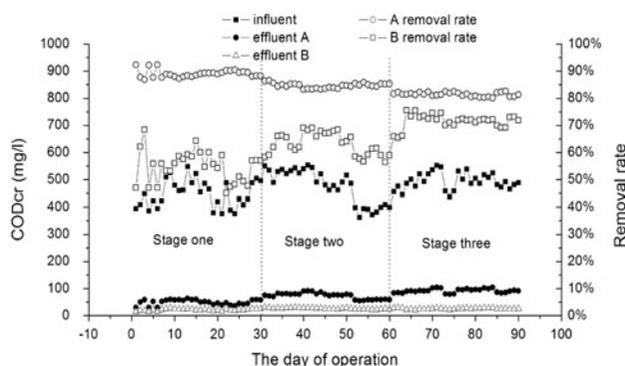


Fig. 4. Influent and effluent COD_{Cr} at different flow rates in two-stage modified zeolite BAFs.

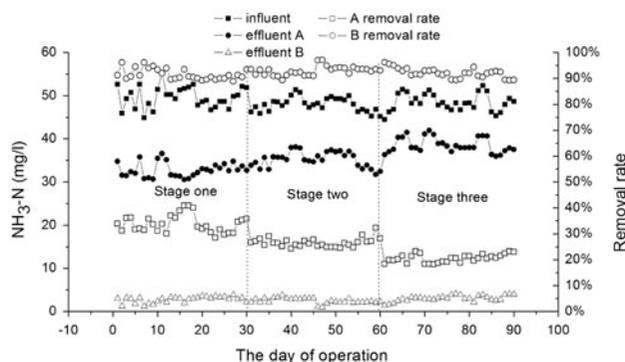


Fig. 5. Influent and effluent NH₃-N at different flow rates in two-stage modified zeolite BAFs.

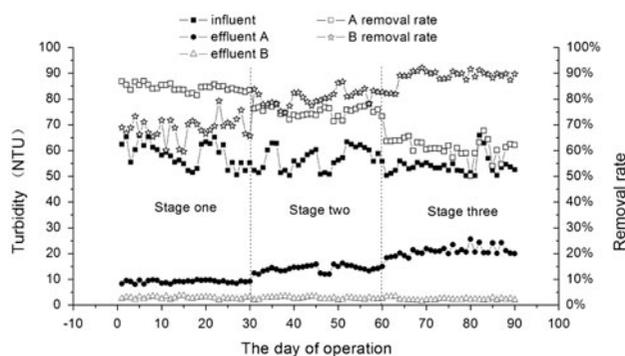


Fig. 6. Influent and effluent turbidity at different flow rates in two-stage modified zeolite BAFs.

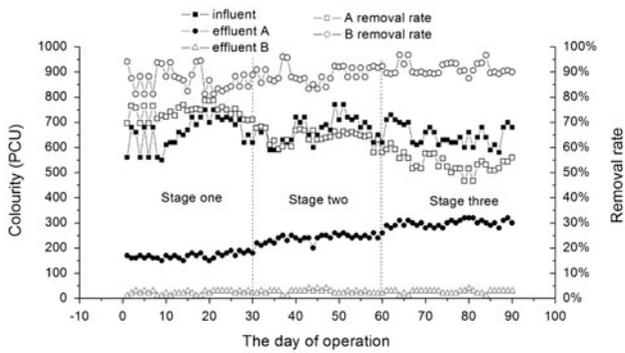


Fig. 7. Influent and effluent colour at different flow rates in two-stage modified zeolite BAFs.

remove COD_{Cr} in further, but removal rate was lower than the modified zeolite BAF A, ranged from 45.00 to 75.58%. The removal rate had a tendency of increasing gradually with the increase in the flow rates. However, the COD_{Cr} concentrations of the effluent in the two-stage modified zeolite BAFs were all lower than 32.00 mg l⁻¹. With the increase in the flow rates, the COD_{Cr} concentrations of the effluent in modified zeolite BAF A had a tendency of increasing but by the retreatment of modified zeolite BAF B the COD_{Cr} concentrations of the effluent can maintain a lower level.

The COD_{Cr} of influent and effluent in two two-stage BAFs is presented in Table 4. From Table 4, it was found that two two-stage BAFs both processed excellent removals towards COD_{Cr}. Modified zeolite two-stage BAF had a slightly higher COD_{Cr} removal efficiency compared with natural zeolite two-stage BAF. Modified zeolite and natural zeolite two-stage BAFs had average COD_{Cr} removals of 94.75 and 89.38%, respectively. The concentrations of COD_{Cr} in the effluent of modified zeolite and natural zeolite two-stage BAFs were in the ranges of 16.00–31.30 mg l⁻¹ (on average, 24.85 mg l⁻¹) and 49.56–60.18 mg l⁻¹ (on average, 54.85 mg l⁻¹), respectively.

The NH₃-N concentrations in and out of two-stage modified zeolite BAF and removal rate at different flow rates are shown in Fig. 5. As can be seen from Fig. 5, the NH₃-N removal rate in two-stage modified zeolite BAF was lower, ranging between 18.20 and 40.86%, and with the increase in the flow rates the NH₃-N removal rate had a tendency of decreasing. When flow rates increased from 4.0 to 6.0 l·min⁻¹, the high organic loads which also increased made the NH₃-N removed rate decrease in two-stage modified zeolite BAF A. Most of NH₃-N reduction occurred in two-stage modified zeolite BAF B which had a high NH₃-N removal rate averaged 92.18%. Throughout the experiment, the NH₃-N concentrations of effluent in

Table 4
The comparison on COD_{Cr} removal rate between natural zeolite and modified zeolite

Filter material	A			B			Total Removal rate/ %
	Influent COD _{Cr} /mg l ⁻¹	Effluent COD _{Cr} /mg l ⁻¹	Removal rate/%	Influent COD _{Cr} /mg l ⁻¹	Effluent COD _{Cr} /mg l ⁻¹	Removal rate/%	
Natural clinoptilolite	473.44 (362.00–554)	110.26 (84.82–135.67)	76.96 (74.15–79.77)	110.26 (84.82–135.67)	54.85 (49.56–60.18)	50.25 (41.48–58.92)	89.38 (87.55–90.05)
Modified zeolite	473.44 (362.00–554)	71.51 (30.28–104.07)	85.05 (80.19–92.36)	71.51 (30.28–104.07)	24.85 (16.00–31.30)	63.21 (45.00–75.58)	94.75 (93.57–95.94)

the two-stage modified zeolite BAFs were all lower than 4.06 mg l^{-1} . Our observations are consistent with those obtained by Gilmore et al. [20] who stated that the second stage of a pilot-scale, two-stage (carbon oxidation stage one, ammonia oxidation stage two) fixed film BAF system was able to effectively oxidize ammonia at ammonia-N loadings up to $0.6 \text{ kg m}^{-3} \text{ d}^{-1}$ [20]. Gilmore et al. [20] also proved that the second stage of a two-stage BAF was dominated by nitrifying bacteria (*Nitrosomonas* and *Nitrobacter*). According to the operation result shown in Figs. 4 and 5, it has lower organic loads in two-stage modified zeolite BAF B, which will do well to the nitrifying bacteria growth and reproduction, so more $\text{NH}_3\text{-N}$ can be removed. Similar results were obtained by Carrera et al. [21] who noted an exponential decrease in nitrification rate which was observed when the influent COD increased.

The $\text{NH}_3\text{-N}$ of influent and effluent in two two-stage BAFs is presented in Table 5. As shown in Table 5, the average residual $\text{NH}_3\text{-N}$ concentration in the effluent from the two-stage BAF with modified zeolite was 2.78 mg l^{-1} while the residual from the other was 7.66 mg l^{-1} . The $\text{NH}_3\text{-N}$ removal efficiency of the two-stage BAFs with modified zeolite and natural zeolite averaged about 94.31 and 84.28%, respectively.

The turbidity in the influent and effluent from two-stage modified zeolite BAF was also plotted against the day of operation (Fig. 6). The relative reductions between SS and CODcr are similar. Most of the turbidity was also removed in two-stage modified zeolite BAF A, and with the increase in the inlet flow rates, the turbidity removal rate also decreased a little. In the two-stage modified zeolite BAF A, turbidity removal was depending on hydraulic load. When flow rates increased from 4.0 to $6.0 \text{ l}\cdot\text{min}^{-1}$, the residual turbidity concentration in the effluent also increased from 9.07 to 20.78 NTU . Some of the turbidity may be filtered by the media in two-stage modified zeolite BAF A, but it is also being utilized by the bacteria attached in the media and converted to microbial biomass. However, the two-stage modified zeolite BAF B did result in further reduction in the turbidity. The turbidity of the effluent in two-stage BAF can maintain a lower level ranging from 1.09 to 3.65 NTU .

The turbidity value of influent and effluent in two two-stage BAFs is presented in Table 6, but show no significant difference. The influent turbidity value varied from 50.24 to 85.93 NTU . The effluent turbidity value out of two-stage BAFs supported by modified zeolite and natural zeolite averaged 2.63 and 2.06 NTU , respectively.

Table 5
The comparison on $\text{NH}_3\text{-N}$ removal rate between natural zeolite and modified zeolite

Filter material	A			B			Total Removal rate/%
	Influent $\text{NH}_3\text{-N}$ / mg l^{-1}	Effluent $\text{NH}_3\text{-N}$ / mg l^{-1}	Removal rate/%	Influent $\text{NH}_3\text{-N}$ / mg l^{-1}	Effluent $\text{NH}_3\text{-N}$ / mg l^{-1}	Removal rate/%	
Natural clinoptilolite	48.72 (44.51–55.24)	39.01 (34.45–43.57)	19.95 (10.57–29.30)	39.01 (34.45–43.57)	7.66 (6.38–8.94)	80.36 (77.08–83.64)	84.28 (81.65–86.90)
Modified zeolite	48.72 (44.51–55.24)	35.54 (30.57–41.49)	26.95 (18.20–40.86)	35.54 (30.57–41.49)	2.78 (1.02–4.06)	92.18 (88.90–97.10)	94.31 (91.60–97.84)

Table 6
The comparison of turbidity removal rates between natural zeolite and modified zeolite

Filter material	A				B				Total Removal rate/%
	Influent turbidity/NTU	Effluent turbidity/NTU	Removal rate/%	Influent turbidity/NTU	Effluent turbidity/NTU	Removal rate/%	Influent turbidity/NTU	Removal rate/%	
Natural clinoptilolite	56.40 (50.24–85.93)	13.98 (9.33–18.63)	75.21 (66.97–83.46)	13.98 (9.33–18.63)	2.06 (1.45–2.67)	85.26 (80.90–89.63)	13.98 (9.33–18.63)	79.40 (59.58–92.10)	96.35 (95.26–97.43)
Modified zeolite	56.40 (50.24–85.93)	14.73 (8.03–25.62)	73.49 (50.12–86.92)	14.73 (8.03–25.62)	2.63 (1.59–3.65)	79.40 (59.58–92.10)	14.73 (8.03–25.62)	79.40 (59.58–92.10)	95.32 (93.35–97.08)

Table 7
The comparison on colour removal rate between natural zeolite and modified zeolite

Filter material	A				B				Total Removal rate/%
	Influent colour/PCU	Effluent colour/PCU	Removal rate/%	Influent colour/PCU	Effluent colour/PCU	Removal rate/%	Influent colour/PCU	Removal rate/%	
Natural clinoptilolite	660 (550–770)	242 (180–330)	63.33 (50.00–72.73)	242 (180–330)	30.15 (20–50)	87.54 (79.33–91.73)	242 (180–330)	89.13 (81.25–96.77)	95.43 (92.42–95.97)
Modified zeolite	660 (550–770)	236 (150–320)	64.03 (46.67–78.67)	236 (150–320)	24.67 (10–40)	89.13 (81.25–96.77)	236 (150–320)	89.13 (81.25–96.77)	96.27 (93.87–98.61)

Table 8
The amount of heterobacteria and nitrobacteria in two two-stage BAFs

Filter material	A		B	
	Heterobacteria (CFU/ml)	Nitrobacteria (CFU/ml)	Heterobacteria (CFU/ml)	Nitrobacteria (CFU/ml)
Natural clinoptilolite	3.2×10^9	4.1×10^5	1.2×10^6	2.1×10^9
Modified zeolite	4.3×10^9	6.2×10^5	1.9×10^6	4.6×10^9

The colour in and out of two-stage modified zeolite BAF and removal rate are plotted against the day of operation in Fig. 7. As can be seen from Fig. 7, the colour of effluent was all below 40 PCU in two-stage modified zeolite BAFs. With the increase in the flow rate, the colour of the effluent in two-stage modified zeolite BAF A increased gradually. When the flow rate ranged from 4.00 to 6.00 l min⁻¹, the averaged colour removal rates decreased from 74.21 to 53.82% in two-stage modified zeolite BAF A. However, the two-stage modified zeolite BAF B still kept on a higher colour removal rate.

The colour value of influent and effluent in two two-stage BAFs is presented in Table 7. Colour value varied from 550 to 770 PCU. The colour removal effluent of each two-stage BAFs supported by modified zeolite and natural zeolite averaged 96.27 and 95.97%, respectively.

Overall, in terms of removing NH₃-N and COD_{Cr}, the performance of the two-stage BAF with modified zeolite was superior to that with natural zeolite. In terms of removing turbidity and colour, the two two-stage BAFs with modified zeolite and natural zeolite both processed excellent removals towards turbidity and colour. The results indicate that it is feasible for modified zeolite to be applied as the media of two-stage BAF.

In the two-stage BAF with modified zeolite, the removal of COD_{Cr}, turbidity and colour mainly happened in the two-stage BAF A, and more NH₃-N was removed in two-stage BAF B. The COD_{Cr} and NH₃-N removal of the two-stage modified zeolite BAF happened in different reactors, which will improve nitrification and ion-exchange capacity of the modified zeolite in two-stage BAF B and be more effective on removing NH₃-N.

3.4. Counting of heterotrophic and nitrifying bacteria bacterial population

Samples for viable cell counting of heterotrophic and nitrifying bacteria were taken at the same positions of the biofilter (1.2 m distance from the bottom). The results of cell counting are shown in Table 8. It was found that two two-stage BAFs A are

dominant heterotrophic bacteria, and two two-stage BAFs B by autotrophic bacteria based. It was also found that there was no significant difference of heterotrophic bacteria amount in these two two-stage BAFs A. The CFU count of heterotrophs was 3.2×10^9 and 4.3×10^9 CFU mL⁻¹ in biofilm grown on two two-stage BAFs A with natural clinoptilolite and modified zeolite, respectively. On the other hand, a more distinct difference of nitrobacteria amount was observed in these two two-stage BAFs B. The numbers of nitrifiers were greater on modified zeolite two-stage BAFs B than natural clinoptilolite. In the biofilm grown on modified zeolite two-stage BAFs B, the CFU count of heterotrophic bacteria and nitrobacteria was 1.9×10^6 and 4.6×10^9 , respectively, while those on natural clinoptilolite two-stage BAFs B were 1.2×10^6 and 2.1×10^9 CFU mL⁻¹, respectively. It concludes that a more favourable environment for the growth of nitrobacteria would be provided in the two-stage BAF B supported by modified zeolite. The result was in line with the former research report [17,22,23].

4. Conclusions

Based on the results obtained, the following conclusions can be drawn:

- (1) The ion exchange and adsorption of modified zeolite played an importance role at the start-up first period. The BAF A starts quicker than the BAF B.
- (2) In order to ascertain the application of modified zeolite, modified zeolite and natural clinoptilolite were applied as the media of two-stage BAF to treat domestic wastewater in two laboratory-scale up-flow two-stage BAFs. The results showed that the two-stage BAF with modified zeolite brought a relative superiority to natural clinoptilolite two-stage BAF in terms of chemical oxygen demand (COD_{Cr}) and NH₃-N removal under the conditions of temperature 20–26°C and DO above 4.00 mg l⁻¹. The effluent COD_{Cr}, NH₃-N, turbidity and colour of the

two-stage modified zeolite BAF were 16.00–31.30 mg l⁻¹, 1.02–4.06 mg l⁻¹, 1.59–3.65 NTU and 10–40 PCU, respectively.

- (3) The detection of the amount of heterobacteria and nitrobacteria of two two-stage BAFs indicated that a more favourable environment for nitrifying bacteria was provided in two-stage BAF with modified zeolite.

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