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Effect of coal gangue-fly ash ceramic (CFC) media on municipal wastewater treatment in a pre-denitrification biological aerated filter

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ABSTRACT

Coal gangue-flyash ceramic (CFC) is a novel media, which is made up of flyash, coal gangue powder and some kinds of additive. In this study, CFC was used as filter medium for a pre-denitrification biological aerated filter (BAF) to treat municipal wastewater. The performances of the two pilot-scale pre-denitrification BAF systems were monitored for 3 months to compare the effect of CFC media with expanded clay media as BAF medium. In terms of started-up speed, the efficiency of the system with expanded clay media was slightly faster than that with CFC media. In terms of removing chemical oxygen demand (COD), ammonia (NH_4^+-N) and total nitrogen (TN), the efficiency of the system with CFC media almost could rival with expanded clay media. The average COD, NH_4^+-N and TN concentrations in the effluent were average 47.0 mg/L, 4.0 mg/L and 14.8 mg/L when HRT was 4 h, which were all up to the National Discharge Standard of Level 1-A (GB 18918-2002) in China. So it is feasible for CFC media to be applied as the media of BAF.

Keywords: Coal gangue-flyash ceramic; Pre-denitrification; Biological aerated filter; Municipal wastewater

1. Introduction

The biological aerated filter process is a biofilter technology for organic carbon removal and nitrification of primary and secondary wastewater [1,2]. It is a flexible process which provides a small footprint process option at various stages of wastewater treatment [3]. The most important advantage of this process is its compactness for construction, caused by the high volumetric removal rate and the simultaneous solid–liquid separation and biological reaction in the same reactor [4,5]. Stensel and Reiber found that the land required for a BAF system was approximately only one fifth of that needed for plastic medium trickling filters and one tenth of that needed for activated sludge plants [6]. In a recent development, BAF systems have been selected for many small or large towns for wastewater treatment or reuse purpose throughout the world [7].

Media selection is critical in the design and operation of BAF to achieve effluent quality requirements [8]. The media play a key role in maintaining a high amount of active biomass and a variety of microbial populations. The most frequently studied biofilm support media include clay-, schist- or plastic-based ones of various types, such as polyethylene, polystyrene, and polyester [9]. Superior substrate removal has been shown by BAF containing mineral media, such as expanded clay, compared to those using sand or plastic media with similar dimensions

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[10]. At present, commercial ceramic particles (CCP) as a kind of lightweight aggregate were applied to building materials and wastewater treatment as filter media. Generally, raw materials of CCP consist of clay mostly obtained from farmland, which may threaten sustainable development of agriculture in the long run. Thus, it is crucial to find appropriate materials to substitute for clay as much as possible [11]. Coal gangue mostly generated from coal exploit and coal fly ash mostly generated from coal combustion all cannot be made full use of due to its very large quantity. In addition, coal gangue and fly ash have similar mineral contents with clay [11]. So coal gangue and fly ash became a possible choice for the raw material of filter media.

In this research, a new filter material was developed by coal fly ash and coal gangue powder to produce coal gangue-fly ash ceramic (CFC) at high temperature (between 1100–1350°C) with a mass ratio of 9:1. The wastewater from a municipal wastewater treatment plant was fed to pre-denitrification biological aerated filters and the performance of biofilters with CFC media and expanded clay media was observed. For expanded clay is a common and superior filter media for BAF, and the aim of the study was to compare the efficiencies of these two media in removing organic pollutants, SS, ammonium nitrogen and TN simultaneously from raw wastewater.

2. Materials and methods

2.1. Pilot-scale system

Two parallel pilot-scale BAF systems were set up for this study, as shown in Fig. 1. The reactors were packed with CFC media and expanded clay media, respectively. The main part of the system was composed of two upflow biofilter columns connected in series. Each column was 1.5 m in height and 0.15 m in diameter, made of synthetic glass. The columns were packed with media of 1.0 m in height. To the first column functioning as denitrification, air was not provided, and, in contrast, to the second column functioning as nitration, air was provided to maintain the concentration of dissolved oxygen (DO) through diffusers located at the bottom of the column. The system was operated in cycles based on the direction of column 2 to column 1 (see Fig. 1). The recycle ratio was about 120%.

2.2. The media character

The CFC media were products made from waste materials — coal fly ash and coal gangue. Coal fly ash was generated in coal combustion and coal gangue was generated from coal exploit. In this test, coal fly ash was supplied by Donghua thermal power plant in Baotou city, China and coal gangue was supplied by Shiguai mine lot in Baotou city, too. During CFC production, the coal gangue was ground into powder at first. Then, the coal gangue powder and fly ash were mixed in a muller and transported into a rotational disk. Tap water was injected to make powdered materials become particles with similar diameter. Semi-manufactured CFC were diverted to the front of a rotary kiln to finish desiccation at the temperature of 100°C to 400°C for 3 h and fired with a high temperature of 1050°C. Finally, novel filter medium was obtained after cooling in a sinter machine gradually. Expanded clay media was purchased from a plant in Jiangxi, China. The characteristics of CFC and expanded clay are listed in Table 1.

2.3. The characteristics of municipal wastewater

The system was fed with municipal wastewater which after primary treatment in Dalian Malanhe Wastewater Treatment Plant (second stage), in China, and its characteristics are summarized in Table 2. All samples in

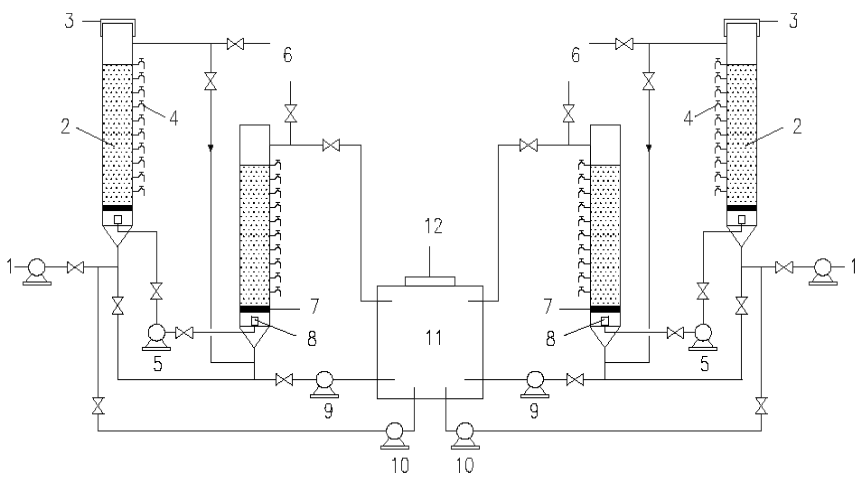


Fig. 1. Experimental facilities. 1. Influent, 2. Media, 3. Cover, 4. Water sample tap, 5. Air pump, 6. Backwashed wastewater, 7. Supporting layer, 8. Diffuser, 9. Backwash pump, 10. Reflux pump, 11. Water tank, 12. Effluent.

Table 1
Physical properties of the media

Medium	Parameter (mm)	Apparent density (g/cm^3)	Porosity (%)	Piled density (g/cm^3)	Specific surface area (cm^2/g)
CFC	4–6	1.6965	42.13	0.9817	1.6012×10^4
Expanded clay	4–6	1.4–1.6	>42	0.7–0.9	$>4\times10^4$

Table 2
Average influent characteristics

Parameter	Average value
Suspended solid (SS), mg/L	45–60
Chemical oxygen demand (COD), mg/L	160–200
Total nitrogen (TN), mg/L	30–40
NH_4^+-N, mg/L	25–35
Total phosphorus (TP), mg/L	2–3
pH	7.0–7.5

the experiments were measured according to Standard Methods [12].

3. Results and discussion

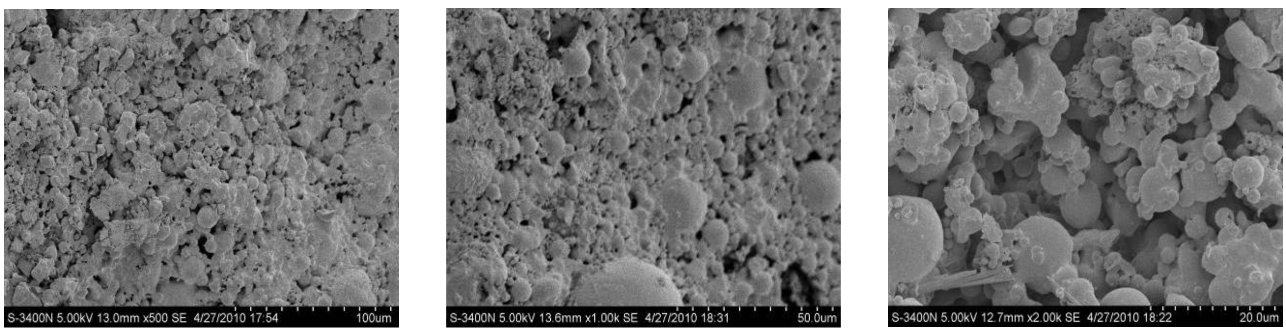
3.1. CFC media microstructure scanning electron microscopy (SEM) analysis

SEM images of CFC media are shown in Fig. 2. Fig. 2a is 500 time magnification SEM image, on which we can see many apertures and pores in the media. Most of the apertures and pores are in the middle scale (10–100 μm) and are randomly distributed. These pores were formed in firing process when much gas escaped and inflated without rules and organic in gangue burning loss. Fig. 2b is 1000 time magnification SEM image, on which we can see that part of pores were due to the release of internal gas when in the process that it overcame the surface tension of liquid substances. Fig. 2c is 2000 time magnification SEM image, and a fractal is presented on the media which was formed by the crystal material and non-crystal material in the gangue that made the media to have certain strength and hardness.

3.2. Reactor performance during start-up

The pre-denitrification biological aerated filter systems were inoculated with concentrated activated sludge in the A/O process from Dalian Fujiazhuang Wastewater Treatment Plant, China. The two systems were operated under the same conditions, and basic operation parameters on this period were as follows: HRT of 4 h, A/L of 4, and total flow rate of 3.75 L/h. During the phase of the beginning, the recirculation pump did not work, and the purpose was cultivating heterotrophic bacteria and nitrobacteria in column 2 on this period. A graph of COD and NH_4^+-N concentrations in the second column during this period for the two systems are presented in Fig 3.

As shown in Fig. 3a, the removal efficiency of COD was 43.3% and 46.4% respectively on the first day and did not change more in the next 1–2 days. It is because the primeval COD removal was due to physical retention of suspended particles by filtration through the medium bed. The grain sizes of the two kinds of media were the same, so the removal efficiency was approached too. For the medium with no biofilm the removal efficiency was very limited. From the 3rd to 8th day, the COD removal increased because of the biofilm growing. There was a little difference to the CFC media and expanded clay media: from the 6th day the expanded clay media column had



(a) (b) (c)

Fig. 2. CFC media SEM analysis.

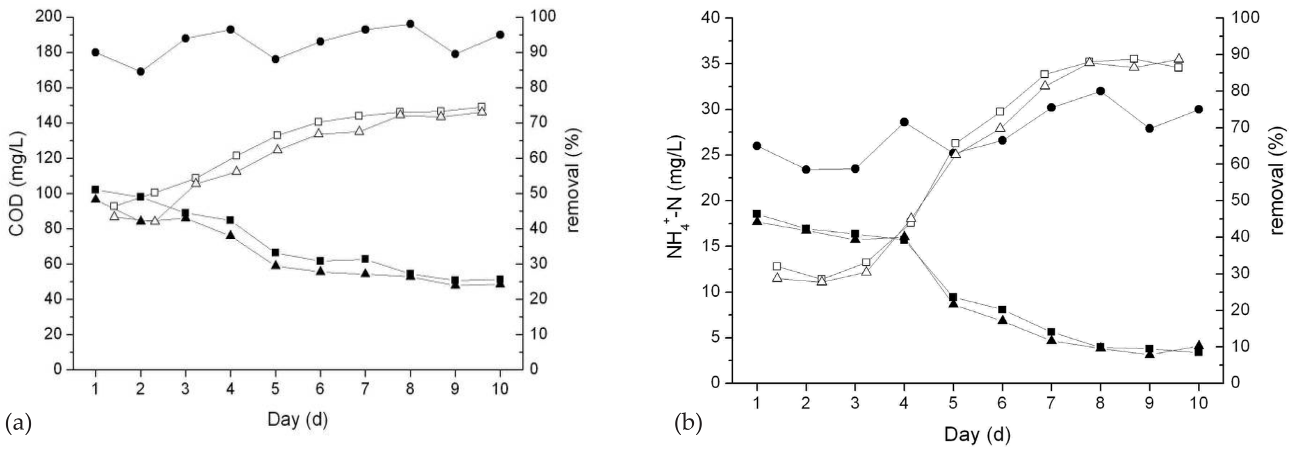


Fig. 3. COD concentrations and removals in influent and effluent during start-up EC expanded clay: -●- influent; -■-CFC effluent; -▲- EC effluent; -△- CFC removal; -□- EC removal.

no sharp changing trend for COD removal efficiency and for CFC media, it was from the 8th day. It maybe because the expanded clay media had a bigger specific surface area than CFC media, microorganisms could also attach to them quicker. On the 8th day, the removal efficiencies reached 72.2% and 73.1% respectively, which were lower than expected. It might be caused by the falling off of the biofilm from the medium which was not so steady in the beginning of the experiment.

As shown in Fig. 3b, the NH_4^+-N in the effluent ranged from 18.5 to 3.4 mg/L for CFC media column, and from 17.7 to 3.1 mg/L for expanded clay media column. NH_4^+-N removal efficiency of CFC media and expanded clay media systems varied from 27.7% to 30.4% and from 28.5% to 33.1%, respectively, from the 1st to 3rd day. From the 4th to 8th day, NH_4^+-N removal efficiency in the CFC media column came to a sharp rise as it did in the expanded clay media column from the 4th to 7th day, which rose from 45.1% to 87.7% for CFC media column, and from 44.2% to 88% for expanded clay media column, which represented that the microorganisms adapted to the environment in expanded clay media a little faster than that in CFC media. On the 10th day, backwashing operation was carried out for both column 1 and column 2 for the two BAF systems, and NH_4^+-N and COD removal efficiency in both the CFC column and expanded clay column were all returned to normal in about 5–6 h.

On the 11th day, the recirculation pump worked, recycle ratio was 120%. The purpose was cultivating denitrifying bacteria in column 1 on this period. The recycle water afforded nitrate and the air pump did not work to providing an anaerobic environment. Basic operation parameters in this period were as follows: HRT of 4 h, and recycle ratio of 120%. A graph of COD and TN concentrations in column 1 in this period for the two systems is presented in Fig. 4.

As shown in Fig. 4, during the period of cultivating denitrifying bacteria, effluent concentrations of COD and

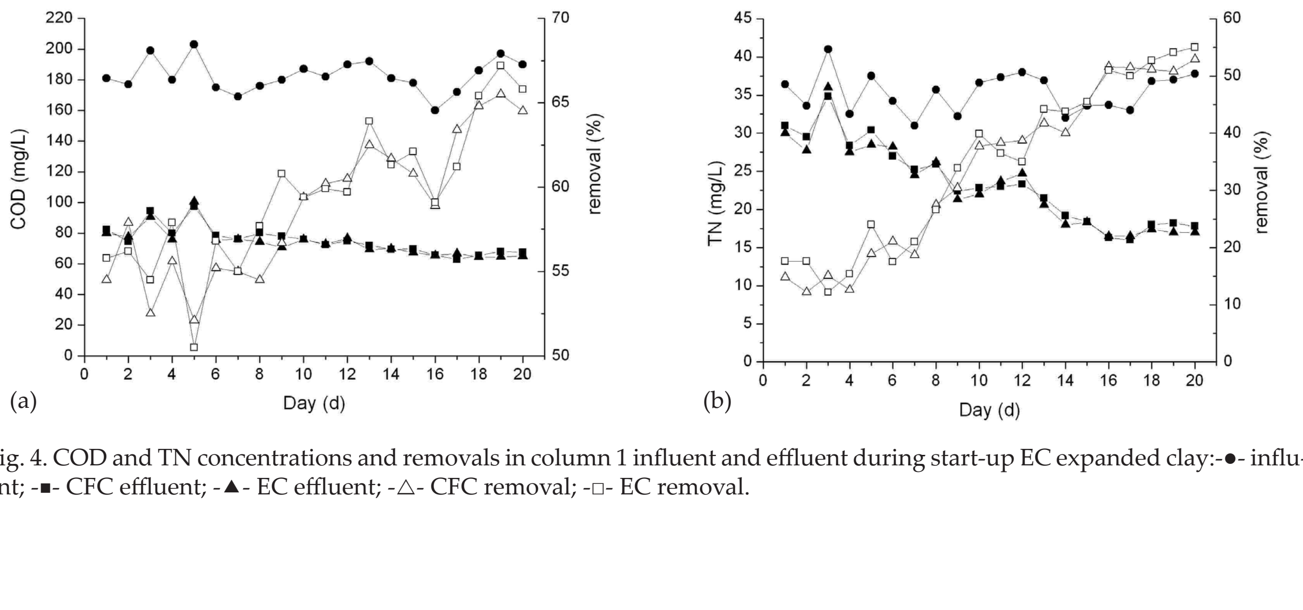


Fig. 4. COD and TN concentrations and removals in column 1 influent and effluent during start-up EC expanded clay:-●- influent; -■- CFC effluent; -▲- EC effluent; -△- CFC removal; -□- EC removal.

TN were the main references. It took about 20 days until the removal efficiencies of COD and TN reached about 67 mg/L 18 mg/L and 65 mg/L 17 mg/L, respectively for CFC BAF and expanded clay BAF. In the last several days, the removal efficiency tend to stable and expanded clay column had a little larger removal efficiencies than CFC column, so it was considered that the microorganisms adapted to the environment in expanded clay media better than CFC media, but the advantage was not big.

As shown in Fig. 4a, the removal efficiency of COD was high in the first 5 days, but compared with Fig. 4b which presents the TN removal efficiency in column 1 for the two systems we could find that the removal efficiency of TN was very limited in the same period. This shows that the COD was not mainly consumed during denitrification but in other pathways such as oxidation in the air and non-denitrify activities. And the COD removal efficiency fluctuated significantly, which might be caused by the falling off of biofilm from the medium, which was caused by the increased hydraulic load. The recycle water increased the hydraulic load and the 120% recirculation made the hydraulic load more than doubled. Impulsive force of water was increasing with the augment of hydraulic load. The enhanced impulsive force could force some biofilm to be out of BAFs, resulting in fluctuation of COD.

As time increased, the removal efficiency of TN began to increase. As shown in Fig. 4b, the TN in the effluent gradually decreased from the 6th, and kept this trend in the next 10 days. In the last few days the TN in the effluent ranged from 16.3 to 17.8 mg/L with an average of 17.2 mg/L for CFC media BAF, and from 16.5 to 17.4 mg/L with an average of 16.9 mg/L for expanded clay media BAF. The results indicated that the removal capacity of TN for the CFC media BAF was comparable to that of the expanded clay media BAF.

3.3. Effect of HRT on COD, NH_4^+-N and TN removals

HRT is a key operating parameter for BAF. According to the effective volume of the columns, three HRTs (6, 4 and 2 h) were selected and determined. During the whole experiments, A/L was kept at 4 and recycle ratio kept at 120%.

As shown in Fig. 5, the concentrations of COD in the effluent of CFC media and expanded clay media systems were in the ranges of 57.6–70.2 mg/L (on average 65.25 mg/L) and 59.1–72.0 mg/L (on average 63.7 mg/L), respectively, when the HRT was 2 h. When HRT was 4 h, the concentrations of COD in the effluent of CFC and expanded clay media systems were 40.2–53.2 mg/L (on average 47.0 mg/L) and 40.1–50.1 mg/L (on average 46.8 mg/L), respectively. And when HRT was 6 h, the concentrations of COD in the effluent of CFC and expanded clay media systems were 39.1–47.3 mg/L (on average 42.9 mg/L) and 33.8–47.8 mg/L (on average 42.5 mg/L), respectively. As

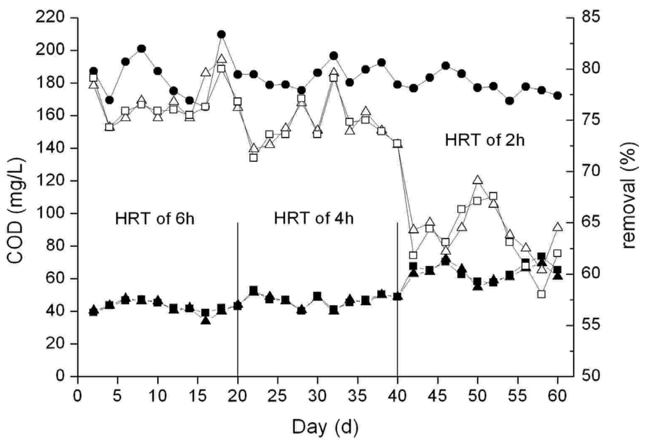


Fig. 5. COD concentrations and removals in influent and effluent in different HRT EC expanded clay: -●- influent; -■- CFC effluent; -▲- EC effluent; -△- CFC removal; -□- EC removal.

can be seen, CFC BAF had a slightly higher COD removal efficiency compared with expanded clay BAF at HRT shorter than 2 h and had a similar removal efficiency at HRT 4 h and 6 h. Because more surface area was supplied to microorganisms for contacting and digesting pollutants by expanded clay media than CFC media. But when the HRT was long enough, all the COD which could be degradation was removed, the biomass was not the limiting factor any more.

As depicted in Fig. 6, NH_4^+-N removal of both systems decreased remarkably when HRT was 2 h, and CFC media and expanded clay media systems had average NH_4^+-N removals of 75.9% and 76.8%, respectively. The concentrations of NH4+-N in the effluent of CFC media and

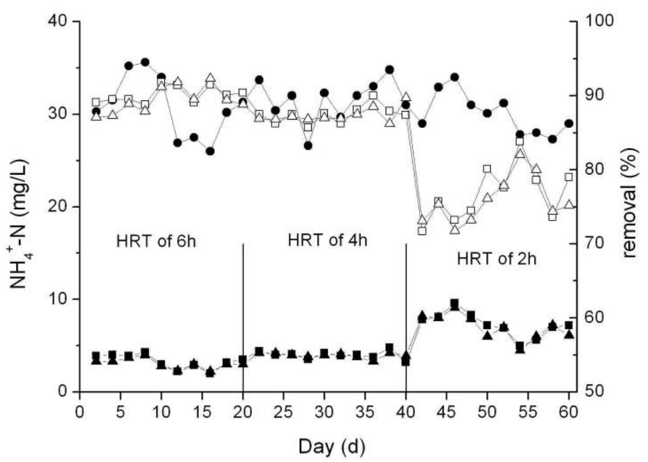


Fig. 6. NH4+-N concentrations and removals in influent and effluent in different HRT EC expanded clay: -●- influent; -■- CFC effluent; -▲- EC effluent; -△- CFC removal; -□- EC removal.

expanded clay systems were in the ranges of 9.6–5 mg/L (on average 7.3 mg/L) and 9.1–4.5 mg/L (on average 7.0 mg/L), respectively. When HRT was 4 h, the concentrations of NH_3-N in the effluent of CFC and expanded clay systems were 4.4–3.2 mg/L (on average 4.0 mg/L) and 4.2–3.3 mg/L (on average 4.0 mg/L), respectively. And when HRT was 6 h, the concentrations of NH_4^+-N in the effluent of CFC and expanded clay systems were 2.0–4.3 mg/L (on average 3.3 mg/L) and 2.2–3.7 mg/L (on average 3.1 mg/L), respectively. The data showed us that the removal rule was similar for COD and NH_4^+-N, but the short HRT (2 h) had greater influence on NH_4^+-N than COD removal. When HRT decreased from 6 to 4 h, nitrification was not affected obviously in both reactors. But the shorter HRT (2 h), corresponding to larger organic loads, resulted in a faster multiplication rate of heterotrophic bacteria, so autotrophies like nitrifying bacteria could not predominate in the competition of obtaining living space. As a result, nitrification was inhibited and NH_4^+-N removal decreased rapidly. It was also found that expanded clay media system had a slightly higher NH_4^+-N removal compared with CFC media system when HRT was 2 h, but removal effects were both very bad. On the other hand, the NH_4^+-N removal was similar when HRT was longer than 4 h. It was because HRT of 4 h was sufficiently long to allow biomass to degrade NH_4^+-N in the BAF for both kinds of media.

Fig. 7 shows the influence of HRT on TN removals. The concentrations of TN in the effluent of CFC and expanded clay media systems were in the ranges of 18.3–22.3 mg/L (on average 19.9 mg/L) and 18.0–22.5 mg/L (on average 19.5 mg/L), respectively, when the HRT was 2 h. When HRT was 4 h, the concentrations of TN in the effluent of CFC and expanded clay media systems were 13.0–16.6 mg/L (on average 14.8 mg/L) and 11.9–17.0 mg/L

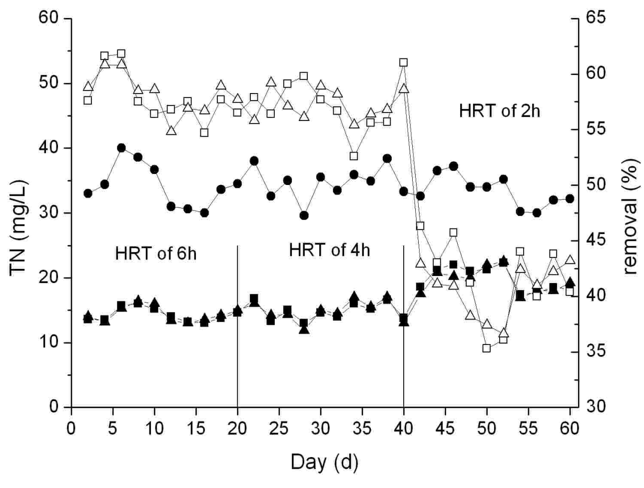


Fig. 7. TN concentrations and removals in influent and effluent in different HRT EC: expanded clay:-●- influent; -■- CFC effluent; -▲- EC effluent; -△- CFC removal; -□- EC removal.

(on average 14.8 mg/L), respectively. And when HRT was 6 h, the concentrations of TN in the effluent of CFC and expanded clay systems were 13.0–15.7 mg/L (on average 14.2 mg/L) and 13.0–16.0 mg/L (on average 14.4 mg/L), respectively. In terms of removing TN, expanded clay media did not show higher TN removal compared with CFC media system in any HRT obviously, as shown in Fig. 7. The main reason was the carbon source organic matter. Organic matter in raw water contained many difficult for degradation substances which had a long C-chain with thousands of glucose units and was not easy to be used by microorganisms. So, the concentration of organic matter was the main factor limiting denitrification even when the C/N ratio looked suffucient for denitrification. That is why there are many pre-denitrification processes need to add degradable external carbon sources such as carbinol.

Generally, with a HRT of 4 h, the concentrations of COD (on average 47.0 mg/L), NH_4^+-N (on average 4.0 mg/L) and TN (on average 14.8 mg/L) in the effluent from CFC media systems could meet the national discharge standard of level 1-A (GB 18918-2002) (State Environmental Protection Administration of China, 2002). Consequently, CFC media has a promising prospect utilized as BAF media in municipal wastewater treatment.

4. Conclusions

Novel filter media — coal gangue-fly ash ceramic (CFC) media was employed in a pre-denitrification BAF system. Expanded clay media and CFC media were used in parallel to treat municipal wastewater, and the results obtained were as follows:

1. The CFC media has good microstructure such as large numbers of apertures and pores; fractal structures and so on in SEM images.
2. In terms of started-up speed, the efficiency of the system with expanded clay media was slightly faster than that with CFC.
3. Both BAF systems had excellent COD, NH_4^+-N and TN removal efficiency when HRT was longer than 4h, and expanded clay media BAF had slightly higher removal efficiency than CFC media BAF.
4. CFC media BAF system has the COD, NH_4^+-N and TN removals in the range of 71.3–79.1%, 86.8–89.7%, 55.4–59.2% with a HRT of 4 h, and the effluent could meet the national discharge standard of level 1-A (GB 18918-2002) (State Environmental Protection Administration of China, 2002).

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