A novel anoxic–aerobic biofilter process using new composite packing material for the treatment of rural domestic wastewater
L. T. Pan and Y. Han

ABSTRACT
A pilot scale experiment was conducted to evaluate the characteristics of contaminants removal in a continuously two-stage biological process composed of an anoxic biofilter (AF) and an biological aerated filter (BAF). This novel process was developed by introducing new composite packing material (MZF) into bioreactors to treat rural domestic wastewater. A comparative study conducted by the same process with ceramsite as packing material under the same conditions showed that a MZF system with a Fe proportion in the packing material performed better in chemical oxygen demand (COD) removal (average 91.5%), ammonia (NH4+-N) removal (average 98.3%), total nitrogen (TN) removal (average 64.8%) and total phosphorus (TP) removal (average 90%). After treatment of the MZF system, the concentrations of COD, NH4+-N, TN and TP in effluent were 20.3 mg/L, 0.5 mg/L, 11.5 mg/L and 0.3 mg/L, respectively. The simultaneously high efficiencies of nitrification, denitrification and phosphorus removal were achieved by the coupling effects of biological and chemical processes in the MZF system. The results of this study showed that the application of MZF might be a favorable choice as packing material in biofilters for treatment of rural domestic wastewater.

Key words | biofilter, decentralized treatment, nitrogen removal, packing material, phosphorus removal, rural domestic wastewater

INTRODUCTION
With the development of the rural economy and society and the improvement of the living standards of people in the rural areas of China, there has been a significant growth in rural domestic sewage emission. The lack of proper sewage collection and treatment facilities (Li & Yu 2008) has resulted in water pollution and the threat to the safety and hygiene of drinking water in rural areas (Babatunde et al. 2008). The confluence of rainwater and wastewater in the process of sewage collection along with the economic restriction, technology limitations and poor management make it hard to apply centralized municipal wastewater treatment models to the decentralized domestic sewage in rural areas. Thus, it is urgent to find solutions that not only consider actual conditions but also satisfy environmental standards for effluent.

According to the existing wastewater treatment processes (Liang et al. 2011; Wu et al. 2011; Ye et al. 2012; Li et al. 2015) and integrated treatment equipment (Jia et al. 2011; Yang et al. 2011; Wang et al. 2011) which have been developed so far, it is still hard to dispose of rural domestic sewage to reach standards due to difficulty in the removal of total nitrogen (TN) and phosphorus. So, the key to tackling the problem of pollution brought by rural domestic sewage lies in the high removal rate of nitrogen and phosphorus. Biological filters filled with packing material are favorable for the attached growth of microorganisms. Compared with the prior technologies, this process has the advantages of less occupied area, convenient control system, high contaminant removal and low maintenance costs. And study on the new material exploitation and application which can be introduced into the biological filter process to deal with low strength domestic sewage has been a hot topic in the environment protection field (Xiong et al. 2003; Tong et al. 2009; Feng et al. 2014).

In this paper, two pilot scale anoxic–aerobic biofilter processes filled with new composite packing material...
(MZF) and normal ceramsite, respectively, were operated for rural domestic sewage treatment under the same conditions for around 2 months, and attention was mainly focused on the performance and mechanism of nitrogen and phosphorus in the process using MZF.

MATERIALS AND METHODS

The treatment process and operating procedure

The experimental system is shown in Figure 1. In this study, a bench scale system consisted of an anoxic biofilter (AF) and a biological aerated filter (BAF). Both the anoxic and the subsequent aerobic biofilter were made of plexiglass and had a working volume of 0.4 L (ø30 × 1,000 mm). The effluent of anoxic biofilter was fed into the aerobic biofilter. Both of the reactors were filled with a new type of composite packing material (MZF), which contained Fe and carbon as the main ingredients and were developed by Tongji University. Before MZF material was put into use, it was first soaked in a diluted (5%) hydrochloride acid solution for 1 h, and finally cleaned by deionized water.

In this study, a comparative experiment was conducted in an identical two-stage process using ceramsite as its packing material.

The bottom of the aerobic biofilter reactor was equipped with micro aeration devices, and the value of dissolved oxygen (DO) was kept above 4 mg/L. The hydraulic retention time (HRT) for both the reactors were adjusted to 3 h, with 100% ratio of nitrification liquid reflux. Both systems were operated under the same experimental conditions.

Analytical methods

The total experiment duration was 60 days and the start-up phase was studied in our preview study (Pan et al. 2015). A while after the start-up phase, the performance in both systems gradually stabilized. Thereafter, the experiments were conducted and the data were recorded after a period of time. In this study, the stable running phase was continuously run for over 30 days. The samples were collected from the influent and effluent of the apparatus every day to ensure the stability and performance of both systems, while results of every fifth day of last 30 days were shown and discussed.

All samples were stored at 4 °C and analyzed within 24 h. According to standard methods (Environmental Protection Agency (EPA) of China, 1989), chemical oxygen demand (COD)_cr, TN and total phosphorus (TP) concentrations of the samples were determined using the potassium dichromate method, the potassium persulfate oxidation-ultraviolet spectrophotometric method, the molybdenum-antimony spectrophotometric method, respectively. NO_3-N and NO_2-N concentration were measured by the ultraviolet spectrophotometry. NH_4-N was measured by Nessler’s reagent colorimetric method according to Chinese national standard methods (EPA of China, 2002). The pH value was determined using a pH meter (Model 252, Thermo Orion). The DO value was monitored using a DO meter (Model 842, ORION). The concentration of Fe in water was detected by inductive coupled plasma emission spectrometer (ICP). The elements in biofilm were determined by X-ray fluorescence spectrometry.

All measurements were replicated three times and were presented as mean values. If the standard errors (SE) were greater than 0.01, the test was repeated to control for errors.

Characteristics of raw wastewater

The raw wastewater used in this study was from domestic sewage in a rural area (Chongming County, Shanghai, China). The parameters of the wastewater sample are shown in Table 1. There existed little fluctuation in the inflow quality and the average concentration of each parameter during the 60-day operation period are present.

After the treatment, the effluent of the wastewater should achieve the Chinese National Pollutant Discharge Standard of Municipal Wastewater Treatment Plant (GB18918-2002) A standard: COD ≤ 50 mg/L, TN ≤ 15 mg/L, NH_4-N ≤ 5 mg/L, TP ≤ 0.5 mg /L and pH 6–9.
RESULTS AND DISCUSSION

Comparison of COD removal

COD removal efficiency was measured during the 30-day stable running phase, which is shown in Figure 2.

The results indicated that both systems achieved excellent COD removal of over 85%, with the average concentrations of COD in effluent steadily reduced to 20.3 mg/L and 35 mg/L in the MZF and ceramsite system, respectively. MZF system had a slightly higher COD removal rate as compared to ceramsite system (reaching up to 91% COD removal on average).

Considering the effect of internal recycle, the performances of the AF and BAF in both systems were studied. The results showed that the COD removal efficiencies of AF and BAF in the MZF system were 73% and 41.2%, respectively, and the removal efficiencies in the ceramsite system were 58% and 37%, respectively. The results demonstrated that the removal of COD mainly occurred in the anoxic stage in both systems. This was partially due to the occurrence of the denitrification function, in which the organic matters would be consumed in anoxic conditions. Gas chromatograph-mass spectrometer (GC-MS) analysis (not shown) indicated that after being treated by the anoxic stage, the organic mass in the effluent of both AFs increased, the number of organic compounds detected in the MZF AF was two times that in the ceramsite AF, indicating that MZF material which contained Fe might provide more Fe source for the synthesis enzymes and thus enhanced microbial activity, removing macromolecular organic matter and persistent organic compounds more efficiently. Iron corrosion could take place on the surface of MZF material. Therefore, contaminant adsorption on to corrosion products and contaminant co-precipitation with corrosion products inevitably occurred.

Comparison of nitrogen removal

As the dominant inorganic nitrogen compound, the variation of NH$_4^+$-N was studied. TN as another control index was also measured in this experiment.

As is shown in Figure 3, the average NH$_4^+$-N in MZF system effluent was about 0.5 mg/L with the average NH$_4^+$-N removal rate of 98.3%, while it was about 1.5 mg/L in the effluent of the ceramsite system with the NH$_4^+$-N removal rate of 95%.

In the ceramsite system, because of the effect of the internal recycle of the final effluent (100%), the actual NH$_4^+$-N concentration in the influent was around half that of raw wastewater. In ceramsite AF, the concentration of NH$_4^+$-N is a little bit higher than in the influent because

### Table 1: Characteristics of the raw wastewater

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Range</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>unitless</td>
<td>6.1–8.6</td>
<td>7.3</td>
</tr>
<tr>
<td>SS</td>
<td>mg/L</td>
<td>33–40</td>
<td>36</td>
</tr>
<tr>
<td>BOD$_5$</td>
<td>mg/L</td>
<td>172.2–254</td>
<td>210.2</td>
</tr>
<tr>
<td>COD$_{cr}$</td>
<td>mg/L</td>
<td>246.3–356.5</td>
<td>301</td>
</tr>
<tr>
<td>NH$_4^+$-N</td>
<td>mg/L</td>
<td>17–35.2</td>
<td>23.5</td>
</tr>
<tr>
<td>NO$_3^-$-N</td>
<td>mg/L</td>
<td>0.12–0.3</td>
<td>0.22</td>
</tr>
<tr>
<td>NO$_2^-$-N</td>
<td>mg/L</td>
<td>0.02–0.1</td>
<td>0.06</td>
</tr>
<tr>
<td>TN</td>
<td>mg/L</td>
<td>32.3–43.5</td>
<td>36.1</td>
</tr>
<tr>
<td>TP</td>
<td>mg/L</td>
<td>3.1–8</td>
<td>5.5</td>
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Figure 2 | COD profile in MZF and ceramsite system.

Figure 3 | NH$_4^+$-N profile in MZF and ceramsite system.
the organic N like proteins decomposed under anoxic conditions. So, the aerobic stage played a dominant role in the removal of NH$_4^+$-N with the removal efficiency of about 92% in the ceramsite system. In the MZF system, the average concentration of NH$_4^+$-N in AF was 2.5 mg/L with the average removal efficiency of 83.2%, while it was about 0.5 mg/L in the effluent of BAF with the removal efficiency of 80%.

Obviously, in this study, performance of the MZF and ceramsite system had a huge difference in terms of the NH$_4^+$-N removal in anoxic stage. Normally, anoxic biological process did little contribution to the NH$_4^+$-N removal as the performance in ceramsite AF. Therefore, partial nitrification (PN) or anaerobic ammonium oxidation phenomena might occur in MZF AF. In addition, the high removal of NH$_4^+$-N in MZF AF may be due to the fact that the new composite packing material MZF had the adsorption to NH$_4^+$-N. The coupling interaction might occur between the packing material and microorganism which could strengthen the removal of NH$_4^+$-N in the system.

As shown in Figure 4, the MZF system also performed better on TN removal than the ceramsite system. The average concentration of TN in the final effluent of the MZF and the ceramsite systems were 11.5 mg/L and 17.2 mg/L, respectively. So, it is obvious to see that the difficulty in the treatment of TN makes it hard for wastewater to be discharged up to the standard by the traditional biological anoxic and aerobic filter process. The average TN removal by ceramsite system was only 43%, while the MZF system had a better removal rate of 64%, with 21% TN removal enhancement obtained by the MZF system compared to the ceramsite system. The removal efficiency of TN by AF and BAF were also investigated. It was found that the removal efficiencies of TN by AF and BAF were 18.2% and 14.3% in the ceramsite system, respectively, while 38.5% and 15.3%, respectively, in the MZF system.

Conventionally, TN removal takes place under anoxic conditions, so it is interesting that in both systems around 15% of TN removal occurred in BAFs. This could be due to two aspects: the simultaneous nitrification and denitrification (Vijayalayan et al. 2014) and bacterial assimilation which is responsible for 25–30% of the nitrogen loss in biological treatment processes.

The removal efficiencies of NH$_4^+$-N and TN and removal route of NH$_4^+$-N in the two systems seemed to be quite different according the above descriptions. Therefore, the forms of nitrogen in different stages were studied. Figure 5 gives the experiment results of the contents of different forms of nitrogen in both systems.

It is found that the DO was around 0.1 to 0.3 mg/L in MZF AF, and a good ammonia conversion was obtained with a high concentration of nitrite in the effluent of the reactor. As is shown in Figure 5, a stable nitrite accumulation in the MZF AF effluent was obtained during 30 days’ operation, while in ceramsite AF, the form of nitrogen was mainly NH$_4^+$-N with a little amount of nitrate along with the reflux liquid. Generally, the key to removing nitrogen is
the denitrifying bacteria’s capability of the reduction of NO₃-N in the anoxic stage. Compared with nitrate, denitrifiers favor nitrite because the reduction of nitrite to nitrogen needs fewer electrons than the reduction of nitrate. As a result, MZF AF performed better in the TN removal than ceramsite AF.

From Figure 5, the difference in the form of nitrogen confirms that the removal route of nitrogen in the MZF system was quite different from normal biological nitrogen removal processes. In addition, the observation of the stable accumulation of nitrate and relatively high removal efficiency of TN in MZF AF indicated that the combination of partial nitrification (PN) and anaerobic ammonium oxidation (Anammox) might occur in the MZF AF according to the following reactions.

PN:

\[
2\text{NH}_4^+ + 3\text{O}_2 \rightarrow 2\text{NO}_2^- + 4\text{H}^+ + 2\text{H}_2\text{O} \quad (1)
\]

Anammox:

\[
\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \quad (2)
\]

Anammox bacteria have a highly unusual physiology, in that they live by consuming ammonia in the absence of oxygen. In MZF AF, there remained a little DO in the surface of the biofilm where the nitrifiers oxidized ammonia to nitrite, consumed oxygen, and so created a relatively anerobic condition the needs of Anammox process.

Also, the oxygen absorption type of iron corrosion might occur because of the characteristics of MZF packing material which contains Fe. The corrosion with oxygen absorption could form an absolute anaerobic microenvironment for the growth of Anammox bacteria on the biofilm, enhancing the TN removal.

Notably, a higher pH value was observed in the MZF AF than in the influent, which could be due to the pH alteration by corrosion of iron:

\[
\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Fe}^{2+} + 2\text{OH}^- \quad (3)
\]

The slight changes in the microenvironment pH around the cells could lead to variations in the activity and stability of enzymes and proteins. Thus, in such system, conditions might prevail in which both nitrifiers and anaerobic ammonia oxidizing bacteria co-exist. Meanwhile, the cathodic hydrogen produced by the above reaction (Equation (5)) could be used as an electron donor by autotrophic denitrifiers and proceeded by the following reaction to enhance the removal of TN:

\[
2\text{NO}_3^- + 5\text{H}_2 \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 2\text{OH}^- \quad (4)
\]

\[
2\text{NO}_2^- + 3\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} + 2\text{OH}^- \quad (5)
\]

The fact that (i) DO remained around 0.15–0.3 mg/L in the effluent of MZF AF, (ii) the NH₄⁻-N removal rate was stably high in MZF AF, and (iii) nitrite formation was stable over a long period of time led to the conclusion that it was not affected by microbial adaptations but associated with intrinsic characteristics of the Fe-assisted microbial growth system in MZF system. And MZF AF system could achieve the simultaneous removal of NH₄⁻-N and TN in one space.

Comparison of TP removal

Comparison of the performances between the MZF and ceramsite system in TP removal showed that MZF as packing material had more remarkable effect on phosphorus removal (from Figure 6). After the treatments of the MZF system and the ceramsite system, the concentrations of TP in the final effluent was steadily reduced to about 0.3 mg/L and 1.8 mg/L, respectively, with TP removal rates of 90% and 52%. Generally, the biological filter process had little effect on the removal of phosphorus because the alteration of anaerobic and aerobic did not exist in either anoxic biofilter nor aerobic biofilter, theoretically. However, the results of this experiment showed that both systems could contribute to the TP removal. Due to the nitrification liquid reflux, there existed an incomplete anaerobic condition in the anoxic stage, forming an environment in which an anoxic conditions and an anaerobic condition occurred alternately and providing denitrifying phosphate accumulating bacteria with the living surroundings, thereby making it possible for the phosphorus uptake in the anoxic stage. Also, a small amount of TP could be removed by the assimilation of microbes.

In the MZF system, the effluent TP was kept lower than 0.55 mg/L and 0.37 mg/L, with consistent average removal rates of 72.6% and 33.3% in the AF and BAF, respectively. In the ceramsite system, the TP removal rates were 25.7% and 13.1% in AF and BAF, respectively. It can be inferred that the enhancement of MZF material in the systems was the major reason for TP removal rather than the microorganisms. MZF contains the element of Fe, so the phenomenon could be attributed to the chemical precipitation between...
PO₄³⁻ and Fe²⁺ ions, which was formed mainly by anaerobic corrosion. The precipitate would either be adsorbed or intercepted into the biofilm. Moreover, phenomena such as ion exchange, complexation and accumulation would also help remove phosphorus (Pons et al. 2004).

It is interesting that TP removal mainly occurred in the MZF AF. Usually, the pH value would be decreased in the anaerobic environment because of the production of organic acid during the organic matter decomposition. So, in the MZF, acidizing reactions under anaerobic or anoxic conditions would do more to contribute to the synergistic effect of biochemistry on the removal of phosphorus than the aerobic condition. Therefore, in the MZF system, TP removal efficiency in AF was 39% higher than in BAF.

<table>
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<th>Analysis of element migration in effluent</th>
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<tr>
<td>Element</td>
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<tr>
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</tr>
<tr>
<td>Fe</td>
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The migration feature of the typical elements in the effluents and detached biofilm were studied, respectively. The result of Fe migration in effluent is shown in Table 2.

From Table 2, the raw wastewater had the highest concentration of Fe compared with the effluent whether from the MZF system or the ceramsite system. In both systems, the concentration of Fe was reduced to a different degree in each stage of the process. So, it could be inferred that Fe must be transferred to solid matters in the form of organic and inorganic substances. In addition, due to the high surface reactivity and large surface areas, microbes on the biofilm also played some role in the adsorption or enrichment of free Fe. It was known that the precipitation of Fe²⁺ and Fe³⁺ in form of FePO₄ along with Fe(OH)₂, Fe(OH)₃ can be very rapid, thus Fe²⁺ or Fe³⁺ from the corrosion of Fe would be hard to accumulate in the aquatic phase. No significant difference in the effluent of either system demonstrated that the new composite packing material MZF had its special role in the interface of packing material and biofilm.

X-ray fluorescence spectrometry was applied to investigate the detached biofilm from both systems. The results are displayed in Table 3.

Only influent contained the phosphorus element, so phosphorus was regarded as the characteristic element to illustrate whether the biofilm adsorbed phosphorus. From Table 3, in the MZF system, the content of phosphorus in anoxic biofilm was 3.42% and 3.82% in aerobic biofilm, while the content of Fe reached as high as 38.5% and 31.3% in AF and BAF, respectively. The result indicated that because of the flocculation precipitation of iron hydroxides and FePO₄, the biofilm began to absorb the precipitates, thus enhancing the TP removal. The elements of Fe and phosphorus detected in the biofilm detached from the ceramsite system were primarily from the raw wastewater,

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<th>Analysis of element migration in detached biofilm</th>
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<tr>
<td>Element (%)</td>
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<tr>
<td>AF BAF</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>P</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>Ca</td>
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<tr>
<td>Al</td>
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<tr>
<td>Si</td>
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**Figure 7** | Diagrammatic mechanism of the contaminants removal in MZF AF.
and both of the elements showed relatively high content due to the function of bio-adsorption of microbes. The ceramisite material had a relatively high content of Al and Si, which existed mainly in the form of Al₂(SiO₃)₃ without any effect of coagulation and sedimentation treatment on the removal of phosphorus (Chen et al. 2010). In general, the results validated the previous view that the high removal rate of phosphorus was due to the adsorption and precipitation of hydroxides and FePO₄.

**Schematic pollutant removal mechanisms**

It is remarkable that MZF AF had simultaneous high removal of nitrogen and phosphorus. According to the results and discussion above, the supposed removal mechanism of nitrogen and phosphorus might be described as in Figure 7.

**CONCLUSIONS**

A comparison experiment was conducted between the anoxic–aerobic biofilter process using new composite packing material (MZF) and normal ceramisite packing material, respectively, for the treatment of rural domestic sewage. The results showed that the MZF system had a better performance, and 6.6% of COD, 5.2% of NH₄⁺-N, 21.5% of TN and 40% of TP removal enhancements were achieved by the MZF system compared with the ceramisite system.

According to the forms of nitrogen presented in MZF AF, the observation of the stable accumulation of nitrite and simultaneous high removal of NH₄⁺-N and TN indicated the occurrence of PN and Anammox and the TN enhancement by Fe corrosion-assisted effect in the reactor. The removal of TP in the MZF system was mainly achieved due to the chemical precipitation induced by the microenvironment, meaning that MZF had its special role in the interface of packing material and biofilm.

**REFERENCES**


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