



The effect of zeolite addition on the treatment performance of sequencing batch reactor under low temperature

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ABSTRACT

In this study, two lab-scale sequencing batch reactors (SBRs) were used for the treatment of municipal wastewater at low temperature (15°C). These SBRs were a C-SBR (control SBR) and a Z-SBR (zeolite SBR). Both reactors were operated in similar conditions, except for addition of zeolite in the Z-SBR. The results showed that the average COD, TN, NH₄⁺-N and TP removal were 90%, 53%, 88% and 93% in Z-SBR compared with 90%, 35%, 75% and 93%. The results of COD removal showed that there was no significant difference between two reactors. Z-SBR had better removal capability of nitrogen than C-SBR. Z-SBR exhibited same TP removal with the C-SBR. A higher MLVSS concentration and lower SVI values were observed in Z-SBR compared to that of the C-SBR. The average MLVSS concentration for Z-SBR and C-SBR is 2900 mg l⁻¹ and 2120 mg l⁻¹, respectively. The SVI values were lower in Z-SBR (80-100 mL g⁻¹) than C-SBR (120-140 mL g⁻¹). The highest NH₄⁺-N removal efficiency was observed at pH value of 8.0. It was found that zeolite addition into SBR lessened the negative influences of low temperature and positively affected the performance and sludge settling capability. This work showed that the Z-SBR is an efficient modification of the activated sludge process for co-removal of organic matter and nitrogen at low temperature.

1. INTRODUCTION

The discharge of ammonium nitrogen into surface water causes the adverse environmental impacts, such as toxicity to aquatic organisms, depletion of dissolved oxygen and promotion of eutrophication [1]. Therefore, the removal of ammonium nitrogen from wastewater is extremely important. The physicochemical processes and biological nutrient removal have been used widely to remove ammonium nitrogen. Compared to the physicochemical methods, biological processes have been widely adopted in practice due to their more effective and relatively inexpensive [2].

Increasingly, the sequencing batch reactor has been demonstrated to be a viable alternative to continuous-flow activated sludge process for the biological treatment of both domestic and industrial wastewater [3]. The all major phases in SBR process occur in the same tank in sequential order namely, fill, react, settle, draw and idle [4]. The possibility to change the length of each phase individually provides considerable flexibility to the process [5].

Temperature is one of the most influential factors on the growth of nitrifying bacteria. It has been well accepted that a higher temperature enhances nitrification rate as bio-chemical driven bacterial processes accelerate as temperature increases [6]. Nitrifying bacteria are known to be very sensitive to low temperatures and nitrification can be strongly inhibited by low temperatures. Low temperatures are known to limit the activity of the microorganisms and very low temperatures can result in deactivation [7]. Many wastewater plants in Turkey are operated below around 20°C for most the year; therefore, effective methods should be developed to protect the nitrifying bacteria from low temperature.

Zeolites are crystalline hydrated aluminosilicates whose crystalline structure is formed by channels and cavities of strictly regular dimensions called micropores that can be found naturally and synthetically [8]. Natural zeolites exist abundantly, low cost and an additional benefit of using natural zeolites is their regenerative properties [9]. Zeolite is a well-known

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material for its ability to preferentially remove ammonium nitrogen from wastewater [10]. The addition of zeolite has been shown to effectively enhance nitrification rates in wastewater treatment systems [11-13]. Zeolite works as an ion exchanger material due to the ability to preferentially remove ammonium from wastewater [14]. However, it has not been found the reports on removing organic matter and ammonium nitrogen simultaneously from raw wastewater under the conditions of low temperature in a single reactor as sequencing batch reactor by using zeolite. The aim of study was to investigate the effect of zeolite powder addition on the performance of sequencing batch reactor in removing organic matter and ammonium nitrogen simultaneously under the conditions of low temperature.

2. MATERIALS AND METHODS

2.1. Reactor set-up and operation

Two similar-sized SBRs with working volume of 5 L were used in this study. These reactors were made of rigid plexiglas. The air was supplied by an air pump through a porous stone diffuser located at the bottom of each reactor. The complete cycle of the SBRs was 6 h, with four cycles performed per day. Each cycle consisted of five following phases: fill (15 min), aerobic phase (435 min) sludge settling (15 min) and effluent discharge (15 min). A certain amount of excess sludge was disposed at the end of the aerobic phase to maintain the SRT at approximately 20 days. The temperature of the mixed liquid was kept at 15 °C and the pH was maintained at around 7.5.

The natural zeolite was obtained from Bigadic (Turkey), then the zeolite was ground to powder form. Zeolite has a mean diameter of 0.1-0.2 mm. Batch zeolite powder addition was applied to compensate for the loss of zeolite powder at 1.0 g l⁻¹ through the cycle and the addition of zeolite powder into Z-SBR was conducted between fill and aeration phase of every cycle.

2.2. Seed sludge and wastewater

The both reactors were seeded with activated sludge collected from a local municipal wastewater treatment plant. The reactors were acclimatized for about 40 days prior monitoring. The wastewater was collected from outlet of grit tank of the same plant and its characteristics are summarized in Table 1.

Table 1. Characteristics of municipal wastewater

Parameter	Concentration
pH	7.52
COD, (mg l ⁻¹)	360
NH ₄ ⁺ -N, (mg l ⁻¹)	30
TN, (mg l ⁻¹)	48.6
TP, (mg l ⁻¹)	9
SS, (mg l ⁻¹)	120

2.3. Analytical Methods

The concentration of COD, TP and MLVSS were determined according to Standard Methods [15]. TN, NH₄⁺-N, nitrite and nitrate were measured by Standard Kit (Merck Specquorant). The water samples were measured in duplicate.

3. RESULTS AND DISCUSSION

3.1. Pollutant Removal Performance

As shown Figure 1, the average COD removal efficiency in the C-SBR and Z-SBR were similar, around 90%. The results indicated that addition of zeolite into the reactor did not enhance the efficiency of organic matter removal, because heterotrophic bacteria which responsible of degrading the carbonaceous components in the both reactors were enriched at low temperature.

The greatest differences in treatment's effectiveness were for total nitrogen and for ammonium nitrogen. TN and NH₄⁺-N removal efficiency for C-SBR are 35% and 75% respectively, while TN and NH₄⁺-N removal efficiency for Z-SBR are 53% and 88% respectively. The lower TN and NH₄⁺-N removal efficiency in C-SBR at the low temperature was probably due to several biomass washouts, not allowing a proper growth of nitrifying microorganisms as they have lower specific biomass growth rates. The addition of zeolite in Z-SBR was capable of enriching and retaining an active nitrifying biomass, that capable of promoting NH₄⁺-N removal to NO₃⁻-N at low temperature.

Both reactors exhibited similar TP removal performance (about 93%). It was concluded that low temperature in two reactors did not affect the removal efficiencies of TP.

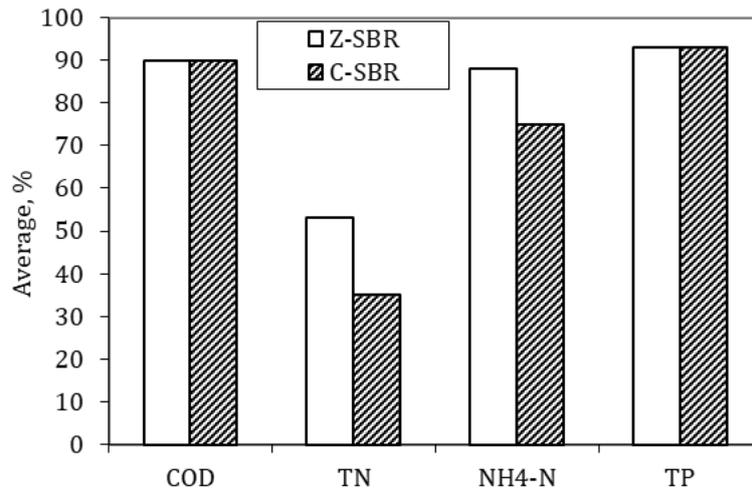


Fig. 1. Pollutant removal performance of C-SBR and Z-SBR.

3.2. Pollutant Removal Characteristics

The variation of COD removal with the function of the cycle period is depicted in Figure 2. The COD profiles for both SBRs have a general decreasing trend, however, it was observed for C-SBR, the COD decreased from 360 mg l⁻¹ to 40 mg l⁻¹ at a time period of 3.5 h, while it last 3h for Z-SBR. Due to the competitive advantage of heterotrophic microorganisms on ammonium oxidizing bacteria, COD removal was dominant reaction in the first three hours. After that, the COD concentration remained at a nearly constant level.

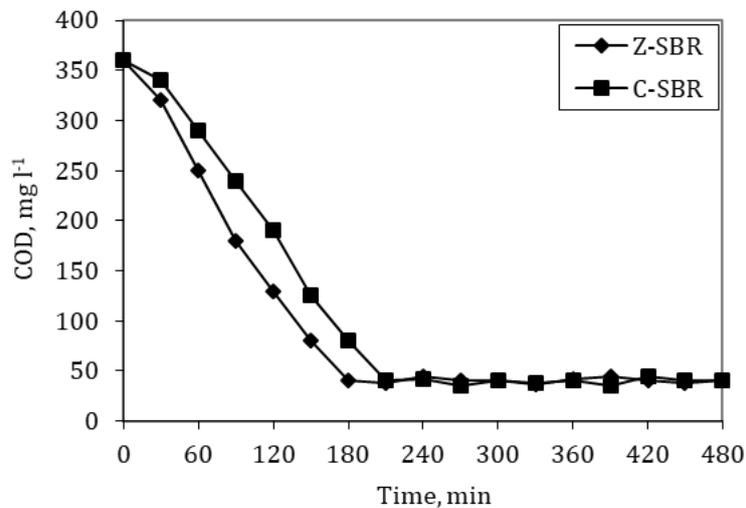


Fig. 2. Variation of COD profiles in C-SBR and Z-SBR.

It can be seen from Figure 3 that the NH₄⁺-N concentration remained unchanged at first 180 min and then decreased to 7.8 mg l⁻¹ at the next 150 min in C-SBR. For Z-SBR, NH₄⁺-N fell faster from 30 mg l⁻¹ to 22.8 mg l⁻¹ at the first 180 min, while the content of nitrite and nitrate was negligible over this period. Therefore, the reduction of NH₄⁺-N can be attributed to the adsorption and ion exchange of zeolite powder for NH₄⁺-N. During the period of minute 180-330, NH₄⁺-N decreased to 3.8 mg l⁻¹ in Z-SBR. These results indicated that the presence of zeolite materials in the reactor could improve the removal of ammonium at low temperature.

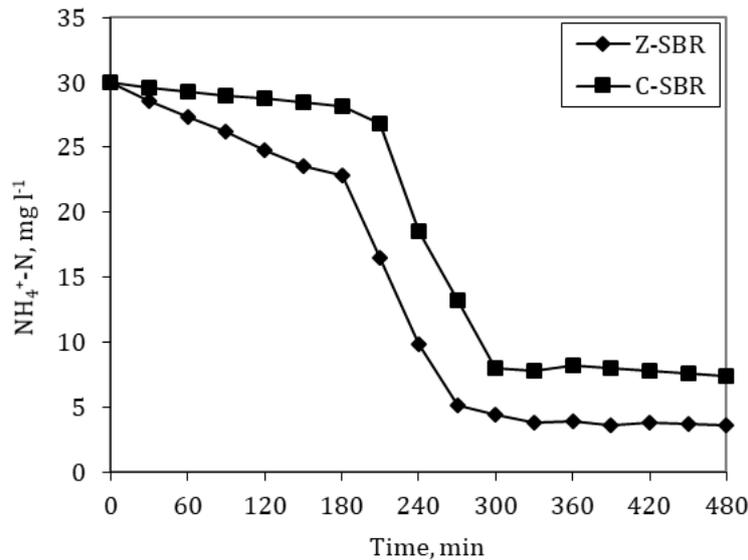


Fig. 3. Variation of $\text{NH}_4^+\text{-N}$ profiles in C-SBR and Z-SBR.

Figure 4 shows that the amount of NO_x (nitrite+nitrate) increased significantly after 240 min. For Z-SBR, the amount of NO_x from 1.8 mg l^{-1} to 10.5 mg l^{-1} in the 60 min and then kept almost stable, while for C-SBR, the amount of NO_x from 1.5 mg l^{-1} to 9.6 mg l^{-1} during 240-300 and then increased 19.8 mg l^{-1} in the next 180 min. Compared to the Z-SBR, the C-SBR has a higher concentration of NO_x left after 480 min. During the period of minute 240-300, the amount of $\text{NH}_4^+\text{-N}$ reduction (from 9.8 mg l^{-1} to 3.4 mg l^{-1}) in Z-SBR is lower than that (from 18.5 mg l^{-1} to 8 mg l^{-1}) in C-SBR, while the amount of NO_x increased in Z-SBR is more than that increased in C-SBR and this verified that nitrification rate is faster in the Z-SBR.

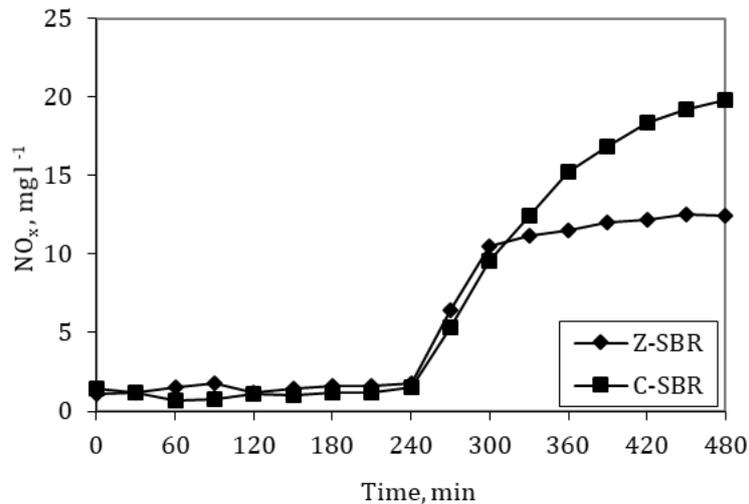


Fig. 4. Variation of NO_x profiles in C-SBR and Z-SBR.

It can be seen from Figure 5 that TN decreased from 48.6 mg l^{-1} to 31.6 mg l^{-1} in 480 min in C-SBR, while in Z-SBR TN decreased by 8.4 mg l^{-1} which is about equivalent to the amount of $\text{NH}_4^+\text{-N}$ reduction in the first 30 min and then TN was reduced to 19.8 mg l^{-1} at the aeration time point 270 min. During the period of 270-480 min, it was found that the TN rose to 23.2 mg l^{-1} with the extension of aeration and the amount of NO_x was detected to have a rise (from 6.4 mg l^{-1} to 12.4 mg l^{-1}). The $\text{NH}_4^+\text{-N}$ adsorbed by zeolite powder (about 7.2 mg l^{-1}) was nitrified by nitrobacteria. Compared to the C-SBR, there has a higher TN removal of 8.4 mg l^{-1} in Z-SBR which should be attributed to the enhanced simultaneous nitrification and denitrification (SND) took place in Z-SBR. The same effect of addition of zeolite was observed in submerged membrane bioreactor (SMBR) operating in continuous mode. It was found that a mean 25% higher total nitrogen (TN) removal took place in the test system compared to a control consisting of a SMBR without added zeolite [16].

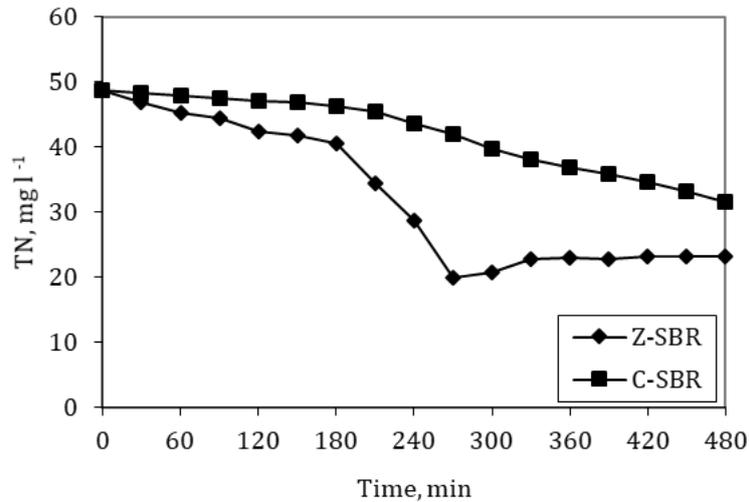


Fig. 5. Variation of TN profiles in C-SBR and Z-SBR.

The variation of TP concentration during a complete cycle is illustrated in Figure 6. In C-SBR and Z-SBR, TP concentration decreased to below 1 mg l⁻¹ at the time point 210 min. These results indicated that the low temperature did not have a detrimental effect on phosphorus removal.

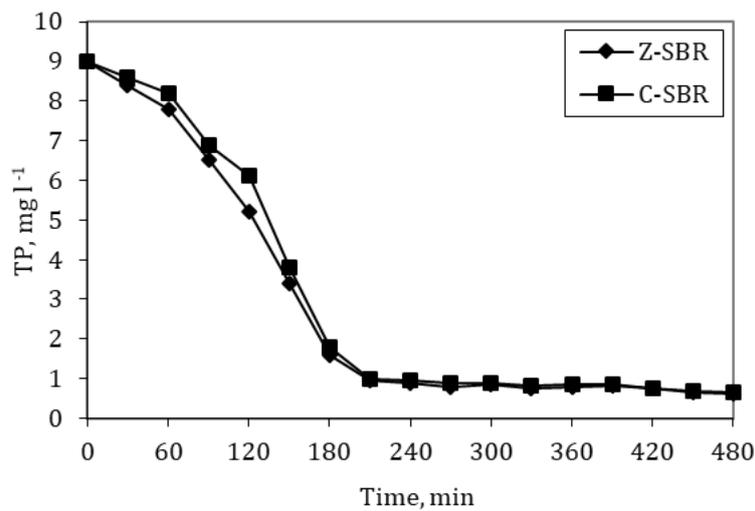


Fig. 6. Variation of TP profiles in C-SBR and Z-SBR

DO is an important parameter that significantly influences the organic and nitrogen removal processes in biological processes [17]. DO leaps could be directly related to COD and NH₄⁺-N concentrations, with the depletion of COD and NH₄⁺-N causing a sudden increase in the DO. With the extension of aeration time, DO rise continuously at one reaction cycle in these two reactors, as can be seen Figure 7. It was found that DO has a distinct leap at the time point of 190 min and then kept almost stable. In Z-SBR, another distinct DO leap was observed at time point 270 min while it took place at a late time point 330 min in C-SBR.

According to the experimental results illustrated in Figures 2-5, it was analyzed that time period 0-190 min was the stage of organics degradation. At this stage, supplied oxygen was slightly more than needed oxygen and DO in reactors rose slowly. The changes of DO in C-SBR and Z-SBR were similar during the organic degradation. After the biodegradable organics was degraded completely, DO leap happened and then reached a new balance at high level. At the following stage, supplied oxygen was consumed by nitrobacteria for nitrification. At time point minute 270, nitrification stage ended and a second DO leap took place, then DO reached now level 7.5-8.0 mg l⁻¹. In C-SBR, nitrification stage ended at time point minute 330 and DO jumped at around 7.0 mg l⁻¹. Therefore, combining the Z-SBR results shown in Figures 3-5, it could be seen that the addition of zeolite powder enhanced the nitrification ability from viewpoint of DO variation.

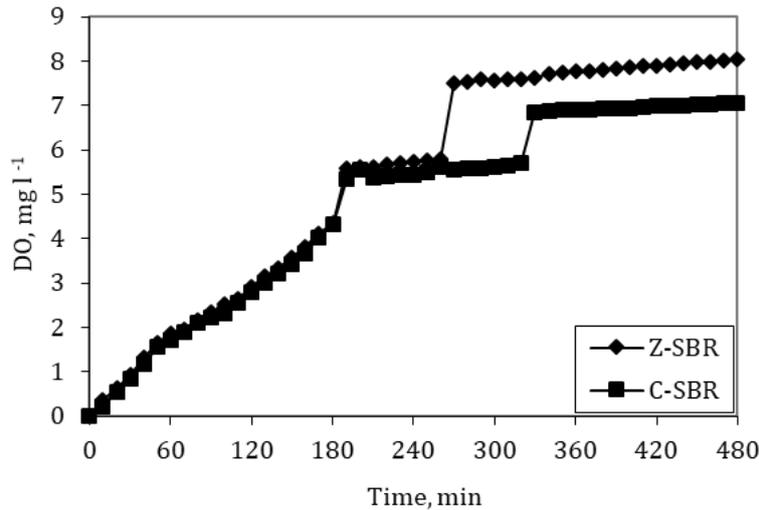


Fig. 7. Variation of DO profiles in C-SBR and Z-SBR.

3.3. Roles of Zeolite in the SBR

The ammonium is removed by zeolite through sorption and ion exchange. First, some portion of $\text{NH}_4^+\text{-N}$ in the influent is adsorbed onto the surface of zeolite. Then, zeolite concentrated with $\text{NH}_4^+\text{-N}$ and an aerated environment provides favorable conditions for autotrophic bacteria attachment. At the following stage, the adsorbed ammonium nitrogen was released into the liquid phase due to the chemical equilibrium and transformed to oxidized nitrogen by nitrifiers. In this stage, the zeolite was completely regenerated by nitrifiers. Therefore, zeolite can play an important role in ammonium removal as well as organic removal in the SBR.

3.4. Sludge Characteristics

Zeolite addition into reactor significantly increased the concentration of MLVSS. The average MLVSS concentration in Z-SBR was 2900 mg l^{-1} , although the C-SBR merely showed average biomass concentration of 2120 mg l^{-1} .

SVI is an important parameters affecting the performance of a wastewater treatment system. SVI was ranged from $120\text{-}140 \text{ mL g}^{-1}$ for C-SBR, while SVI was ranged from $80\text{-}100 \text{ mL g}^{-1}$ for Z-SBR. This shows that the addition of zeolite could have an apparent effect on the improvement of sludge compressibility and settleability.

3.5. pH

The average $\text{NH}_4^+\text{-N}$ removal efficiency in two reactors with different influent pH values were also investigated (Figure 8). The average $\text{NH}_4^+\text{-N}$ removal efficiency was improved with the increase of pH values (from 6.0 to 8.0). However, its removal efficiency was decreased when pH value was 9.0. Therefore, the optimal pH was 8.0 in two reactors. The activity of nitrifying microorganisms was restrained to some extent at pH value of 6 and 9, because they were sensitive to variety of pH. This was consistent with the results obtained by Guo et al. [18] that optimum $\text{NH}_4^+\text{-N}$ removal detected at pH value of 8.0.

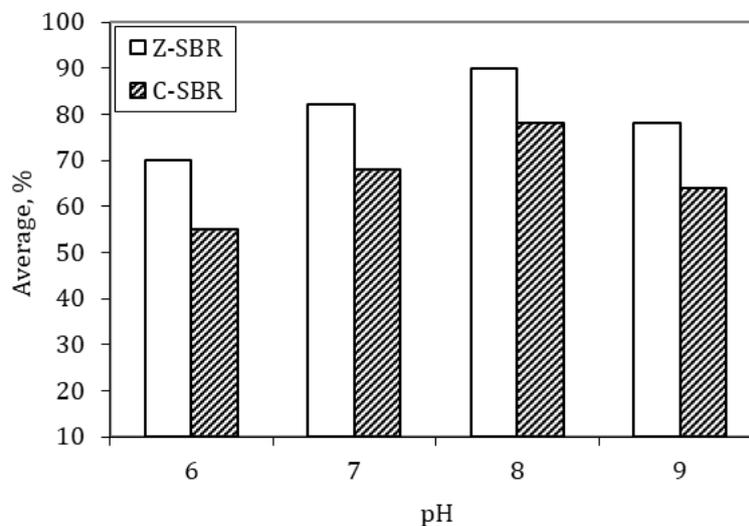


Fig. 8. Effect of influent pH values on $\text{NH}_4^+\text{-N}$ removal in C-SBR and Z-SBR.

4. CONCLUSIONS

Low temperature had a little effect on COD removal efficiencies. Both reactors could efficiently remove organic matter from wastewater. However, the nitrogen removal rate in Z-SBR was higher than C-SBR. Z-SBR represented the same phosphorus removal as the C-SBR. A high of MLVSS concentration was observed in Z-SBR compared to that in C-SBR. Z-SBR had lower SVI values than C-SBR. The best $\text{NH}_4^+\text{-N}$ removal performance of two reactors was obtained with pH values of 8. These results suggest that Z-SBR could be an alternative technology to treat municipal wastewater at low temperature.

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