Simultaneous Removal of TOC Compounds and NO_3^- in a Combined System of Chemical and Biological Processes for the Treatment of Wastewater from Rubber Thread Manufacturing

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Abstract

The inhibitory effects of 2-mercaptobenzothiazole (MBT), sulfur, stearic acid and Zn^{2+} contained in rubber thread wastewater on aceticlastic methanogens or nitrifying bacteria were investigated. It was found that Zn^{2+} inhibited strongly the activity of aceticlastic methanogens. After the pH of rubber thread wastewater was adjusted to 5, Zn^{2+} was removed to less than 5 mg l^{-1} by coagulation with addition of Na_2S . After removal of Zn^{2+} in rubber thread wastewater, the TOC compounds and NH_4^+ were efficiently treated in anaerobic treatment followed by biological nitrification with recirculation. In this process, the TOC compounds and NO_3^- were simultaneously removed in the UAFP reactor. However, the TOC removal efficiency in the UAFP reactor decreased from 90% to 80% at the same TOC loading rate by recirculating the effluent from the nitrification reactor. Methane gas evolution rate also decreased proportionate to the decrease in the TOC removal efficiency. In addition, energy production of $19.5 \text{ kcal (l of rubber thread wastewater)}^{-1}$ would be expected in the simultaneous treatment process.

Key words : rubber thread wastewater, Zn^{2+} removal, simultaneous removal, upflow anaerobic filter process (UAFP), denitrification, biological nitrification

INTRODUCTION

The rubber industry is traditionally one of the largest industries in Malaysia. The rubber product manufacturing sub-sector, particularly relating to latex products, has been expanding rapidly in recent years in response to increasing demand in the world market. The wastewaters generated from the manufacture of latex products, such as rubber thread, rubber gloves, condoms and so on, are highly polluting due to the use of

some hazardous chemicals in the processes. In the case of rubber thread, the raw wastewater contains not only acetic acid, stearic acid, 2-mercaptobenzothiazole (MBT) and sulfur, but also high concentration of Zn^{2+} . It is normally treated by chemical coagulation followed by biological treatment using anaerobic and then aerobic ponds. In the coagulation process, lime is added to remove Zn^{2+} in the pH range of 8 to 9. Large quantities of sludge are generated from this process amounting to $1 \text{ m}^3 \text{ (m}^3 \text{ wastewater)}^{-1}$.

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This sludge is categorized as a scheduled waste under the environmental regulations and is allowed to be disposed in approved facilities only. [Note: A scheduled waste is one which falls within the categories of waste listed in the First Schedule of the Environmental Quality (Scheduled Wastes) Regulations 1989, commonly referred to as a hazardous waste]. Instead of this process, chemical coagulation with addition of Na_2S followed by anaerobic treatment has been developed in order to reduce the amount of Zn-laden sludge and surplus biological sludge. As a result, the amounts of coagulated sludge and surplus sludge were reduced to 1/2 and 1/3 respectively. Moreover, the treatment time was also reduced to 1/3 compared to the conventional process¹⁾.

However, NH_4^+ was not treated biologically at that time. The concentration of NH_4^+ in the rubber thread wastewater ranges from 100 to 200 mg l^{-1} . No study on the simultaneous removal of TOC and NO_3^- in methane fermentation has so far been reported, probably because of the negative effect of the redox potential against methanogens.

In this study, simultaneous removal of TOC compounds and NO_3^- in the anaerobic treatment followed by nitrification treatment with recirculation was carried out, using the rubber thread wastewater after being removed of Zn^{2+} by coagulation with $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. Since the raw wastewater contains not only acetic acid and NH_4^+ , but also stearic acid, MBT, sulfur and Zn^{2+} as described above, the impact of these compounds on methanogens and nitrifying bacteria was first investigated and subsequently simultaneous removal of TOC compounds and NO_3^- in the anaerobic treatment was studied.

MATERIALS AND METHODS

Wastewater Synthetic wastewater A containing (in g l^{-1}): glucose, 35; corn steep liquor, 35; KH_2PO_4 , 2; $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$, 5; Na_2CO_3 , 3; and $\text{FeCl}_3 \cdot \text{H}_2\text{O}$, 1 was used for the acclimation of mesophilic anaerobic sludge. Synthetic wastewater B containing (in g l^{-1}): $(\text{NH}_4)_2\text{SO}_4$, 1.415; K_2HPO_4 , 0.236; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.048; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 1.89×10^{-3} ; FeCl_2 .

$4\text{H}_2\text{O}$, 0.04×10^{-3} (pH 7.4; NH_4^+ 362.5 mg l^{-1}) was used for acclimation of nitrifying bacteria. Wastewater collected from a rubber thread factory in Malaysia was used throughout the continuous treatment study. In this study, the wastewater was collected from Heveafil instead of Rubberflex used in the previous study¹⁾. Both wastewater contained only acetic acid as volatile fatty acids.

Mesophilic anaerobic sludge and activated sludge A mesophilic anaerobic digestion sludge (hereinafter called mesophilic sludge) and an activated sludge were provided by Hokubu Sewage Works (Kumamoto, Japan). The mesophilic sludge was acclimated with synthetic wastewater A by a draw-and-fill method in the laboratory²⁾. The nitrifying bacteria were acclimated with synthetic wastewater B. In contrast, the activated sludge was acclimated directly by feeding the anaerobically treated wastewater into the activated sludge tank.

Inhibition test against methanogens 0.2 ml of CH_3COONa solution (292.85 mg l^{-1}) was added into each vial with a stirring bar to give the final concentration of 70 mM, and each solution of stearic acid, MBT, sulfur or Zn^{2+} was added to give the appropriate concentration. These vials were sealed with a rubber stopper and an aluminum cap, and then a needle was penetrated into the rubber stopper to allow N_2 to be purged through for 1 min to create the anaerobic condition. After that, the vials were immersed in a waterbath for 1 h to stabilize under agitation at 100 rpm. 10 ml aliquots of acetoclastic methanogens culture broth acclimated in a continuous stirred tank reactor (CSTR), which was made of pyrex glass, were transferred to each vial and the vials were connected to volumetric pipettes using vinyl tubes. After 1 h, the gas evolution rate was measured at 0.5 h intervals manually³⁾.

Inhibition test against nitrifying bacteria

276 ml aliquots of nitrifying bacteria culture broth acclimated in a CSTR, which was made of acrylic resin, was transferred to a 500-ml conical flask and 12 ml of each of $(\text{NH}_4)_2\text{SO}_4$ solution (9.16 g l^{-1}) and NaHCO_3 solution (23.1 g l^{-1}) were then added to give the final NH_4^+ concentration of 100 mg l^{-1} . The

solution was divided into 4 portions and transferred to 300 ml conical flasks, and stearic acid or MBT solution was added to give the appropriate concentrations. While each conical flask was cultured in a shake-bath at 30 °C, NH_4^+ was measured at an appropriate interval.

Coagulation The effect of pH on the removal efficiency of Zn^{2+} was studied using a jar tester carried out in the same manner as described in the previous paper¹¹. With respect to the amount of Na_2S , a series of 400-ml samples of the rubber thread wastewater adjusted at pH 5 were prepared in 500-ml beakers and Na_2S was added to achieve the molar ratio of $\text{Na}_2\text{S} : \text{Zn}^{2+}$ to range from 1 to 1.5. Coagulation test was carried out in the same manner.

Anaerobic treatment Figure 1 shows a schematic diagram of the single-phase anaerobic treatment using upflow anaerobic filter (UAF) reactor with a working volume of 0.78 l, which was used in the previous study¹¹.

An aliquot of 800 ml of the acclimated mesophilic sludge (VSS, 5,110 mg l^{-1}) was introduced into the reactor. The liquid in the reactor was then circulated overnight at 37 °C by pump P-2. During acclimation, 10 fold-diluted synthetic wastewater A was fed into the reactor at a TOC volumetric loading rate of 1-4 g $\text{l}^{-1}\text{d}^{-1}$, increasing stepwise. After acclimation was completed, as indicated by the TOC removal efficiency of around 90%, the treatment study was started by feeding the pre-treated rubber thread wastewater

with added Ni^{2+} and Co^{2+} using peristaltic pump P-1. The final concentration of Ni^{2+} and Co^{2+} was 250 and 100 mg l^{-1} respectively. The pre-treated wastewater which was removed of Zn^{2+} was prepared according to the findings of the coagulation tests.

Nitrification treatment Figure 2 shows a schematic diagram of biological nitrification process using submerged filter reactor made of acrylic resin, which had a total volume of 2.5 l with a fixed-bed volume of 1.6 l. Commercial hair-curlers (20 mm in diameter) were cut into half and were packed in the fixed-bed as the support medium. The temperature was controlled at 30 °C via a bimetal sensor and the pH was maintained at 7-8 by feeding a 5% NaHCO_3 solution automatically, using a pH controller (HB-96K2, Denki Kagaku Keiki Co. Ltd., Japan). Aeration was supplied from one side of the reactor through a ball filter using a blower, ensuring that the reactor content was well mixed. 2 l aliquots of activated sludge were added into the reactor and aerated for one day. Synthetic wastewater B was then fed at a flow rate of 500 ml d^{-1} using peristaltic pump P-1 and the acclimation of this reactor was carried out for about three weeks at a $\text{NH}_4^+\text{-N}$ loading rate of 0.2 mg $\text{l}^{-1}\text{d}^{-1}$. After acclimation was completed, with the concentration of $\text{NH}_4^+\text{-N}$ being less than 10 mg l^{-1} , the treatment study was started by feeding the anaerobically treated rubber thread wastewater instead.

Fig. 1 Schematic diagram of an anaerobic treatment system using an Upflow Anaerobic Filter Process (UAF) reactor

Fig. 2 Schematic diagram of biological nitrification system using a submerged filter reactor

Simultaneous removal of TOC compounds and NO_3^-

The UAFP reactor, activated sludge tank and nitrification reactor were connected in series. The effluent from the nitrification reactor was recirculated into the bottom of the UAFP reactor with a recirculation ratio of 2. The activated sludge tank installed between the UAFP and the nitrification reactors was the same as that used in the previous study¹⁾. The aeration vessel, made of acrylic resin, had a partition wall that separated the settling zone of 0.7 l from the aeration zone with a working volume of 2 l. The temperature was controlled at 30 °C via a bimetal sensor. Aeration was introduced through a ball filter. An aliquot of 2.7 l of activated sludge (MLSS, 1,140 mg l⁻¹) was introduced into the reactor, and the anaerobically treated rubber wastewater was fed into the reactor.

Analytical methods All parameters, except SS, MLSS, VSS and BOD₅, were analyzed for supernatants obtained after centrifugation at 8,000 x g for 10 minutes. SS, MLSS, VSS and BOD₅ were analyzed by Standard methods⁴⁾. Soluble TOC was analyzed with a TOC autoanalyzer (TOC-500, Shimadzu, Kyoto)⁴⁾. Acetic acid was analyzed by a post-label method using a HPLC as described in the previous paper¹⁾. The methane content of the biogas was measured with a TCD (thermal conductivity detector) gas chromatography (KOR-2G, GL Science Co., Tokyo) on a packed column (Porapak Q, GL Science Co., Tokyo). MBT was analyzed whereby the absorbance was measured at 225 nm (870-W detector, Japan Spectroscopic Co. Ltd., Tokyo) after being separated from the wastewater by HPLC (880-PU, 860-CO, Japan Spectroscopic Co. Ltd.) on a L-column ODS (15 cm x 4.6 mm diameter) in an oven kept at 35 °C. Solvent for the mobile phase was prepared of 20 mM phosphate buffer (pH 7.4) and acetonitrile solution, and each solution was then fed at a rate of 0.8 ml min⁻¹ and 0.2 ml min⁻¹ respectively. NH_4^+ was measured by using HACH reagents (HACH Co. World Headquarters, USA). A sample solution containing $\text{NH}_4^+\text{-N}$ (0-2.5 mg l⁻¹) was prepared and 3 drops of mineral stabilizer, 3 drops of PVA solution and 1 ml of Nessler solution were then added into the

sample solution. Absorbance was measured at 425 nm using DR/2000 spectrometer. The cations and anions were analyzed by using an ion chromatograph (High-pressure Chromatography Module CRB; DIONEX Corp., California, USA with a Conductivity-Detector-3 (CDM-3)) which employed an Anion Self-Regenerating Suppressor ASEA-I 4 mm (P/N 043190) after separation on columns designed for the cation and anion analysis (for cations, IonPac CG12 (P/N 44002) and IonPac CS12 4mm (P/N 44001); for anions, IonPac AG12A 4mm (P/N 46035) and IonPac AS12A 4mm (P/N46034); DIONEX Corp., Ca, USA). The determination of heavy metal ions was performed on an atomic absorption spectrophotometer (AA 640-13S, Shimadzu). Protein analysis was carried out by the Lowry-Folin method⁵⁾ in which the measurement was presented with the Folin phenol reagent after alkaline copper treatment and the color was measured with a UV-VIS spectrometer (160A, Shimadzu). Total sulfur was measured by using an Elemental Analyser (Antek-7000), which was carried out at 1100 °C.

RESULTS AND DISCUSSION

Composition of rubber thread wastewater

The composition of rubber thread wastewater collected from Heveafil was as follows (mg l⁻¹): TOC, 4018; IC, 0; Acetic acid, 7,100; SS, 31; Protein, 230, MBT, 73.5; Stearic acid, 56.9; NH_4^+ , 177; Zn^{2+} , 206; NO_3^- , 4.7; PO_4^{3-} , 1.4; SO_4^{2-} , 23.2; T-S, 18.5. Compared to the composition of rubber thread wastewater used in the previous research¹⁾, TOC concentration was slightly higher, but NH_4^+ and Zn^{2+} were almost the same. T-S, MBT and stearic acid were measured in this experiment. It has been reported that Zn^{2+} inhibited strongly the growth of microorganism^{6, 7)}, especially methanogens, and Ni^{2+} and Co^{2+} accelerated the methanogenic reaction^{3, 8-13)}. Zn^{2+} in the wastewater was removed by coagulation mentioned below to mitigate the inhibition, and subsequently Ni^{2+} and Co^{2+} were added to achieve the concentration of 0.4 and 0.12 mg (l of pre-treated wastewater)⁻¹ respectively to accelerate the methane fermentation rate.

Inhibition of acetoclastic methanogens or nitrifying bacteria by MBT, sulfur, stearic acid and Zn^{2+}

Figure 3 shows the relative gas production rate of acetoclastic methanogens with addition of MBT, stearic acid, sulfur or Zn^{2+} . MBT at concentrations of 0-100 mg l^{-1} did not inhibit the activity of methanogens. Stearic acid at a concentration of 100 mg l^{-1} inhibited slightly the activity. Sulfur at a concentration of 100 mg l^{-1} decreased the activity of methanogens to 60%. In contrast, the activity of methanogens decreased sharply with an increase of Zn^{2+} added and it was found that Zn^{2+} even at a low concentration of 10 mg l^{-1} inhibited strongly as shown in Fig. 3.

The activity of nitrifying bacteria was not inhibited by MBT or stearic acid at the concentration range of 0-100 mg l^{-1} (data not shown.).

Removal of Zn^{2+} by coagulation with Na_2S

As apparent from the above inhibition tests, Zn^{2+} concentration has to be decreased to less than 10 mg l^{-1} . The coagulation of Zn^{2+} with Na_2S is generally represented by the following chemical equation¹⁾.

As apparent from this equation, a problematic situation would arise due to the evolution of H_2S in the coagulation process. To alleviate this problem, Na_2S was added to the rubber thread wastewater in a molar ratio of 1 : 1 to the concentration of Zn^{2+} . Zn^{2+} was removed almost completely even at pH 5 and the concentration was reduced to around 20 mg l^{-1} as almost the same as in the previous study¹⁾ and very little H_2S was evolved because of the high solubility of H_2S being 2,500 mg l^{-1} at 40 °C¹⁴⁾. However, the remaining concentration of Zn^{2+} of about 20 mg l^{-1} would still inhibit the activity of acetoclastic methanogens. The amount of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ added to the rubber thread wastewater had to be studied. As shown in Fig. 4, Zn^{2+} concentration in the rubber thread wastewater, adjusted to pH 5, decreased with an increase of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. Zn^{2+} concentration decreased to around 5 mg l^{-1} when $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was added to become

Fig. 3 Effects of MBT, stearic acid, sulfur and Zn^{2+} on the activity of acetoclastic methanogens

Fig. 4 Effect of the amount of Na_2S added on the removal of Zn^{2+} in the rubber thread wastewater adjusted pH 5

the molar ratio of 1.2. The amount of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ added was determined to be 1.2 as the molar ratio to depress the evolution of H_2S . Under these conditions, the concentrations of Zn^{2+} , MBT, T-S and stearic acid decreased to 4.8, 65.2, 10.9 and 47.9 mg l^{-1} respectively. It was found that these concentrations did not inhibit the activity of aceticlastic methanogens, judging from Fig. 3.

Anaerobic treatment of pre-treated wastewater After acclimation with ten-fold diluted synthetic wastewater A, rubber thread wastewater, with Zn^{2+} removed by coagulation at pH 5, was fed from the bottom of the UAFP reactor. Figure 5 shows the variation of effluent quality and gas production over the study period. Although TOC loading rate was increased from 2 $\text{g l}^{-1} \text{d}^{-1}$ to 4 $\text{g l}^{-1} \text{d}^{-1}$ rapidly, the effluent quality (TOC and VFA) did not deteriorate and TOC removal efficiency was kept at about 90% during the study period. The gas production rate was 3470 $\text{ml l}^{-1} \text{d}^{-1}$ at a TOC loading rate of 4 $\text{g l}^{-1} \text{d}^{-1}$ and the methane content was 85% on the average. On the basis of these results, the gas yield was 964 $\text{ml (g TOC consumed)}^{-1}$, corresponding to about 52% of the theoretical value (1870 $\text{ml (g TOC consumed)}^{-1}$). However, the methane yield was 820 $\text{ml methane (g TOC consumed)}^{-1}$, corresponding to about 88% of theoretical value if the methane content was 50% of the evolved biogas. Accordingly, the low gas yield seemed to be due to the high dissolution of CO_2 from the evolved gas into the effluent. In contrast, when the TOC loading rate was

Fig. 5 Effluent quality, TOC removal efficiency, and gas evolution rate during anaerobic treatment by the UAFP of the wastewater after coagulation with Na_2S at pH 5

increased to 3 and 4 $\text{g l}^{-1} \text{d}^{-1}$ in the previous work¹⁾, the effluent quality deteriorated. However, improvement was observed within a week. The slight difference seemed to be due to the low concentration of Zn^{2+} remaining in the rubber thread wastewater after coagulation in this work. The methane content varied from 80 to 85% (data not shown), which was almost the same as in the present work.

MBT and stearic acid were completely decomposed and the concentration of T-S also decreased to 2.5 mg l^{-1} during the anaerobic treatment. As a result, TOC concentration decreased to 180 mg l^{-1} from 4,000 mg l^{-1} . However, NH_4^+ increased from 177 to about 210 mg l^{-1} probably due to hydrolysis of protein during the anaerobic treatment.

Biological nitrification of effluent from the UAFP reactor The anaerobically treated effluent was collected and stocked in a refrigerator. After acclimation with the synthetic wastewater B, the effluent treated anaerobically was fed from the top of the nitrification reactor. Figure 6 shows the variation of effluent quality over the study period. An operational error occurred on the 34th day and the pH in the reactor increased to more than 8. As a result, NH_4^+ removal efficiency decreased sharply. In order to restore the situation, synthetic wastewater B was fed into the reactor instead on the 37th day. NH_4^+ removal efficiency increased sharply and reached about 100%. Then, the

Fig. 6 Effluent quality and NH_4^+ removal efficiency during biological nitrification treatment of synthetic wastewater B and anaerobically treated wastewater. (I, synthetic wastewater B was fed; II, anaerobically treated wastewater was fed instead of synthetic wastewater B)

anaerobically treated effluent was fed again. NH_4^+ removal efficiency decreased slightly, but was restored to more than 95%. The concentration of NH_4^+ remaining in the effluent was only 10 mg l^{-1} and the concentration of NO_3^- increased to about 690 mg l^{-1} , while NO_2^- was not detected in the effluent. It was found that remaining NH_4^+ in the anaerobically treated effluent was oxidized to NO_3^- in the nitrification reactor without any difficulty.

Simultaneous removal of TOC compounds and NO_3^- in the UAFP reactor As mentioned above, the nitrification worked well. The UAFP reactor, the activated sludge tank and the nitrification reactor were then connected in series as described in materials and methods. The effluent from the nitrification reactor was recirculated into the UAFP reactor with a recirculation ratio of 2.

Figure 7 shows the variation of TOC, NH_4^+ and NO_3^- in the effluents from the UAFP reactor, the activated sludge tank and the nitrification reactor over the simultaneous treatment study period. After three days of recirculation of the effluent from the nitrification reactor to the UAFP reactor, the concentration of NO_3^- in the UAFP reactor was still maintained at about 120 mg l^{-1} . However, the NO_3^- concentration had decreased sharply. It was found that the simultaneous removal of TOC compounds

Fig. 7 Effluent quality from the UAFP, the activated sludge tank and the nitrification reactor during anaerobic treatment, aerobic treatment followed by nitrification treatment with recirculation. (symbols: ○, effluent quality from the UAFP; □, effluent quality from the activated sludge tank; △, effluent quality from the nitrification reactor)

and NO_3^- worked well and biogas was also evolved in the methane fermentation. When the TOC loading rate was increased to $8 \text{ g l}^{-1} \text{ d}^{-1}$ in the UAFP reactor, the concentrations of TOC and NH_4^+ increased slightly and the concentration of NO_3^- decreased slightly in the nitrification reactor. When the TOC loading rate was further increased to 10 g l^{-1}

d^{-1} , NH_4^+ increased sharply and NO_3^- decreased as shown in Fig. 7. It was found that a NH_4^+ loading rate of $0.3 \text{ g l}^{-1}\text{d}^{-1}$ in the fixed-bed of the nitrification reactor was overloading. If a nitrification reactor with a larger fixed-bed zone in this treatment test was used, the quality of effluent from the nitrification reactor would be better. Using the steady-state data at each loading rate in the UAFP reactor, the activated sludge tank and the nitrification reactor, TOC concentration, TOC removal efficiency, gas evolution rate, and NH_4^+ removal efficiency were depicted in Fig. 8. Although the TOC removal efficiency decreased slightly from 80 to 72% with an increase in TOC loading rate, the gas evolution rate increased linearly in the anaerobic treatment. The closed circle symbol at a TOC loading rate of $4 \text{ g l}^{-1}\text{d}^{-1}$ was the gas evolution rate as shown in Fig. 5. The gas evolution rate decreased from $3,470 \text{ ml l}^{-1}\text{d}^{-1}$ (methane content 85%) to $2,600 \text{ ml l}^{-1}\text{d}^{-1}$ (methane content 90%) by recirculation of the effluent from the nitrification reactor to the UAFP reactor. From calculation of the experimental data as described below, the decreased amount of methane evolution rate was $610 \text{ ml l}^{-1}\text{d}^{-1}$.

$$3,470 \times 0.85 - 2,600 \times 0.9 = 610 (\text{ml l}^{-1}\text{d}^{-1})$$

In order to clarify the cause of decrease, the decreased amounts of methane evolution rate by the decrease of the TOC removal efficiency and the denitrification in the UAFP reactor were calculated as below:

From the decrease of TOC removal efficiency from 90% to 80% in the UAFP reactor by recirculation of the effluent from the nitrification reactor, the decreased amount was $374 \text{ ml methane l}^{-1}\text{d}^{-1}$.

$$4 \text{ g l}^{-1}\text{d}^{-1} \times (0.9 - 0.8) \times 1,870 \text{ ml g}^{-1} \text{ TOC} \\ \times 0.5 = 374 \text{ ml methane l}^{-1}\text{d}^{-1}$$

where, $1,870 \text{ ml}$ is the theoretical gas evolution per gram TOC consumed¹⁵⁾; 0.5 is methane content in biogas from acetic acid.

When acetic acid is used as an electron donor, the denitrification reaction occurs as follows¹⁶⁾:

Fig. 8 Effect of loading rate on treatment efficiency during anaerobic treatment, aerobic treatment followed by nitrification treatment with recirculation of the pretreated wastewater removed of Zn^{2+} by coagulation.

NH_4^+ -N loading rate:

○ = {(feeding rate in the nitrification reactor) × (NH_4^+ -N inlet concentration in the nitrification reactor)} / the volume of the fixed bed zone of the nitrification reactor

● = {(feeding rate in the activated sludge tank) × (NH_4^+ -N inlet concentration in the activated sludge tank)} / the total volume of the aeration zone of the activated sludge tank and the fixed bed zone of the nitrification reactor

Assuming that 1 M NH_4^+ was oxidized to 1 M NO_3^- , 11.7 mM NO_3^- was formed from NH_4^+ of 210 mg l^{-1} . When 11.7 mM NO_3^- was denitrified, 7.3 mM CH_3COOH was consumed. As 1 mol methane and 1 mol CO_2 are evolved from 1 mol CH_3COOH by methane fermentation, the amount of 7.3 mmol methane gas decreased. Accordingly, the decreased amount of methane evolution rate is 168 ml $\text{l}^{-1}\text{d}^{-1}$ at a TOC loading rate of 4 g $\text{l}^{-1}\text{d}^{-1}$.

$$(7.3 \text{ mmol l}^{-1} \times 22.4 \text{ ml mol}^{-1} \times 0.8 \text{ l d}^{-1}) / 0.78 \text{ l} = 168 \text{ ml methane l}^{-1}\text{d}^{-1}$$

The simultaneous removal of TOC compounds and NO_3^- caused the decrease of methane evolution rate (610 ml $\text{l}^{-1}\text{d}^{-1}$). As apparent from the above calculations, more than 60% was due to the decrease of TOC removal efficiency (374 ml methane $\text{l}^{-1}\text{d}^{-1}$) and about 30% was due to the decrease amount of acetic acid consumed by denitrification (168 ml $\text{l}^{-1}\text{d}^{-1}$). It was found that the TOC compounds and NO_3^- could be simultaneously removed in methane fermentation (UAFP reactor), but methane fermentation was inhibited slightly by NO_3^- and dissolved oxygen.

As described above, the gas evolution rate decreased by the simultaneous removal of TOC compounds and NO_3^- in the UAFP reactor. However, energy of 19.5 kcal was produced from one liter of the rubber thread wastewater, as calculated from low calorific value of methane (8.57 kcal l^{-1} methane).

TOC loading rate in the activated sludge tank also increased proportional to an increase in the TOC loading rate in the UAFP reactor. As a result, TOC removal efficiency also decreased slightly from 85 to 70%, but TOC concentration in the effluent was still less than 80 mg l^{-1} at a TOC loading rate of 2 g $\text{l}^{-1}\text{d}^{-1}$ as shown in Fig.8.

In contrast, the NH_4^+ removal efficiency was kept at around 90% at a $\text{NH}_4^+\text{-N}$ loading rate of over 0.05-0.12 g $\text{l}^{-1}\text{d}^{-1}$, which was defined as the value of (feeding rate in the activated sludge tank) $\times$ (inlet $\text{NH}_4^+\text{-N}$

concentration in the activated sludge tank) / (total volume of the aeration zone of the activated sludge tank and the fixed-bed zone of the nitrification reactor). However, the removal efficiency decreased sharply from over 90% to 61% when increasing the TOC loading rate in the UAFP reactor to 10 g $\text{l}^{-1}\text{d}^{-1}$, which was equivalent to $\text{NH}_4^+\text{-N}$ loading rate of 0.3 g $\text{l}^{-1}\text{d}^{-1}$ in the fixed-bed zone of the nitrification reactor.

As described above, the anaerobic treatment worked well at a TOC loading rate of 10 g $\text{l}^{-1}\text{d}^{-1}$, but nitrification did not work well because of overloading. The experimental conditions and the quality of effluent were shown in Table 1 at a TOC loading rate of 8 g $\text{l}^{-1}\text{d}^{-1}$ in the anaerobic treatment. Though the TOC removal efficiency in the anaerobic treatment was 80%, it increased to 90% in the anaerobic treatment followed by biological treatment process, which was the same as that in the anaerobic treatment without recirculation at a TOC loading rate of 4 g $\text{l}^{-1}\text{d}^{-1}$ as shown in Fig. 5. The TOC compounds and NH_4^+ still remained in the effluent from nitrification. Under this condition, the effluent BOD was found to be less than 20 mg l^{-1} . In order to improve the quality, a nitrification reactor with a slightly larger fixed-bed zone should be used. As apparent from Fig. 6 and Table 1, the remaining NO_3^- should be easily removed in another denitrification reactor using methanol as an electron donor.

In conclusion, it was found that Zn^{2+} inhibited strongly the activity of aceticlastic methanogens. Zn^{2+} was removed to less than 5 mg l^{-1} by coagulation with addition of Na_2S . After removal of Zn^{2+} in rubber thread wastewater, the TOC compounds and NH_4^+ were efficiently treated in anaerobic treatment followed by biological treatment with recirculation. In this process, the TOC compounds and NO_3^- were simultaneously removed in the UAFP reactor. However, the methane gas evolution rate decreased slightly by the denitrification and the decrease of TOC removal efficiency in the anaerobic treatment. In addition, the production of energy of 19.5 kcal (l of rubber thread wastewater) $^{-1}$ would be expected in the simultaneous treatment process.

Table 1 Effluent quality during simultaneous removal process (anaerobic treatment, aerobic treatment followed by nitrification treatment with recirculation) of TOC compounds and NH_4^+ of rubber thread wastewater at a TOC loading rate of $8 \text{ g l}^{-1} \text{ d}^{-1}$ in the UAFP reactor

Treatment conditions					
Feeding rate (l d^{-1})	1.6	4.8	4.8	4.8	
Reactor volume (l)		0.78	0.8(aeration zone)	1.6(fixed-bed zone)	
Loading rate	—	$8.1 \text{ g-TOC l}^{-1} \text{ d}^{-1}$	$2.1 \text{ g-TOC l}^{-1} \text{ d}^{-1}$	$0.15 \text{ g-N l}^{-1} \text{ d}^{-1}$	
HRT (hrs)	—	3.9	4.0	8.0	
pH (—)	5.0	—	8.0	7.6~8.2	
Temperature ($^{\circ}\text{C}$)	—	37	30	30	
Quality (mg l^{-1})					
TOC	4,018	3,904	1,321*	343	76
IC	0	0	43*	446	400
NH_4^+	177	177	64*	76	63
NO_3^-	4.71	—	—	11	60
Acetic acid	7,100	7,050	—	548	—

* , calculated value

—, not measured

Loading rate ($\text{g l}^{-1} \text{ d}^{-1}$) = $\frac{\text{feeding rate } (4.8 \text{ l d}^{-1}) \times \text{inlet concentration of TOC or } \text{NH}_4^+ \text{ in each reactor}}{\text{each reactor volume}}$

HRT (hrs) = $\frac{\text{feeding rate } (4.8 \text{ l d}^{-1})}{\text{each reactor volume}}$

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