Pergamon

Wat. Sci. Tech. Vol. 35, No. 8, pp. 161–168, 1997.

Printed in Great Britain.
0273–1223/97 $17·00 + 0·00

PII: S0273-1223(97)00163-7

SIMULTANEOUS COD REMOVAL AND DENITRIFICATION OF WASTEWATER BY BIO-ELECTRO REACTORS

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ABSTRACT

Application of a bio-electro reactor process for the treatment of wastewater containing nitrate and internal source of hydrogen donor as organic matter was experimentally investigated. The bio-electro reactor consisted of immobilized denitrifying bacteria electrode as cathode and carbon electrode as anode. Hydrogen gas was produced on the cathode surface by the electrolysis of water when electric current was applied, and immediately utilized to reduce biologically nitrate to nitrogen gas by the cathodic immobilized denitrifying bacteria. Consumption characteristics of organic matter and utilization of hydrogen gas derived from the electrolysis of water for denitrification was studied by batch experiments. Continuous treatment experiments using a synthetic wastewater containing nitrate and organic matter were carried out to investigate the denitrification and organic matter removal performances. Denitrification occurred with simultaneous utilization of organic matter existed as internal source of hydrogen donor in the wastewater and hydrogen gas by electrolysis of water. Hydrogen gas was utilized efficiently for denitrification even if excess amount of organic hydrogen donor existed in wastewater. In this bio-electro reactor system, it was confirmed that COD as well as nitrate was removed simultaneously by applied electric current in continuous experiment, though further investigation are necessary to analyze the COD removal by applied electric current in detail.

KEYWORDS

Bio-electro reactor; Biofilm; COD removal; Denitrification; Electric current, Electrolysis; Electron donor; Hydrogen gas; Nitrate.

INTRODUCTION

It is very important to remove nutrients sufficiently from wastewater as well as organic matter. Nitrogenous compounds is one of the principal nutrients of concern in treated wastewater effluents. Discharges containing nitrogenous compounds such as nitrate and ammonium accelerate the eutrophication of lakes and reservoirs, and stimulate the growth of algae and aquatic plants in shallow stream. Moreover, the significant concentration in treated wastewater effluent may have other adverse effects presenting a public health hazard and affecting the suitability of wastewater for reuse.

Biological denitrification of wastewater processes often have some advantages as cost, nitrogen removal efficiency, process stability and control, comparing with other chemical and physical processes. Many biological denitrification processes have been developed for treatment of different kinds of wastewater (Tchobanoglous and Burton, 1991). In biological denitrification treatment processes, nitrate is reduced to nitrogen gas by utilizing hydrogen donor. The hydrogen donor requirements can be provided to the treatment system by internal sources such as organic matter containing in the wastewater and cell material, or by an external source such as methanol and ethanol. The nitrate removal process by the addition of organic matter

as external source of hydrogen donor has high denitrification rate. However, the residual organic matter in the treated wastewater must be removed by post-treatment because of the excessive addition. The biological nitrate removal supported by the organic matter as volatile fatty acid containing in wastewater can eliminate the necessity to add some organic hydrogen source, but have relatively lower denitrification rate; however, addition of external source of organic matter such as methanol is sometimes indispensable when the concentration of organic matter is too low to denitrify efficiently. Utilization of hydrogen gas as electron donor may be an alternative for biological denitrification without remaining of the organic matter added as external hydrogen source to wastewater, though poor solubility of hydrogen gas in water cause low efficiency in the utilization of provided hydrogen gas and nitrite accumulation due to incomplete denitrification (Kurt *et al.*, 1987). So, it is necessary to develop an efficient supplying method of hydrogen gas to the treatment reactor.

In our previous study (Sakakibara *et al.*, 1993, 1994), a novel denitrification method of nitrate-pollute water was investigated using a bio-electro reactor system. The bio-electro reactor consisted of immobilized denitrifying bacteria electrode as cathode and carbon electrode as anode. Hydrogen gas was produced on the cathode surface by the electrolysis of water when the electric current was applied, and immediately utilized to reduce biologically nitrate to nitrogen gas by the cathodic immobilized denitrifying bacteria. This bio-electro reaction system has the ability to generate hydrogen gas efficiently and utilize the hydrogen gas to the denitrification. Denitrification can be carried out and controlled by applying low electric current and voltage which are needed to occur the electrolysis of water.

In this study, application of a bio-electro reaction process for the treatment of wastewater containing nitrate and internal source of organic hydrogen donor at various concentrations was experimentally investigated. Consumption characteristics of organic matter and utilization of hydrogen gas derived from the electrolysis of water for denitrification was studied by batch experiments. Continuous treatment experiments using synthetic wastewater containing nitrate and organic matter were carried out to investigate the denitrification and organic matter removal performances of the bio-electro reactor.

EXPERIMENTAL

Batch experiment

Schematic diagram of the bio-electro reactor used for the batch experiment is shown in Fig.1(a). The reactor consisted of immobilized denitrifying bacteria on carbon electrode as cathode and carbon electrode as anode. The liquid volume in the reactor was about 7.9 L and the total apparent surface area of cathodes was about 1270 cm^2. The reactor was immersed in water bath to maintain a constant temperature of 38°C.

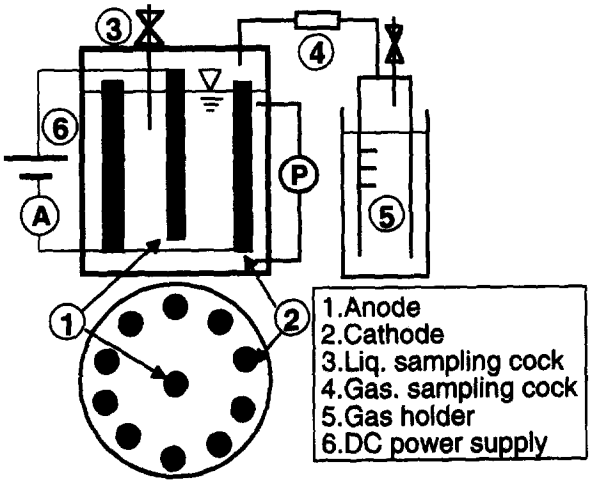

Fig. 1(a) Schematic diagram of bio-electro reactor for batch experiment

The immobilized denitrifying bacteria electrode was prepared through the following procedure; a mixed culture slurry of denitrifying bacteria obtained from actual denitrification facilities of exudate of sanitary landfill was inoculated into the reactor and periodically aqueous solution of nitrate, acetate, n-butyrate and other trace nutrients was added in order to adhere the bacteria on the electrode surface for about two months. After the slurry was discharged completely from the reactor, the adhered denitrifying bacteria on electrodes were acclimatized with periodical addition of aqueous solution of nitrate and other trace inorganic nutrients, and electric current of 100 mA was also applied continuously for two months.

Acetate was used as the supplementary organic matter to the reactor because frequently is an intermediate product of complex organic matter fermentation in anaerobic systems. The experimental conditions for the batch operation are shown in Table 1. C/N ratio shown in Table 1 expressed the relation of concentration between total carbon in acetate and total nitrogen in nitrate of the inlet to the system.

Table 1 Batch experimental conditions

run No.	initial nitrate conc.[mg-N/L]	initial C/N ratio[-]	current [mA]	temp. [°C]
B-1	34.7	0	100	38
B-2	29.2	0.7	100	38
B-3	36.7	1.0	100	38
B-4	35.4	1.5	100	38
B-5	37.4	4.5	100	38
B-6	37.6	4.7	0	38

Nitrogen and hydrogen gases were determined by TCD gas chromatography with activated carbon column. Nitrate and nitrite ions were measured by liquid chromatography. Acetate and other volatile fatty acids were measured by FID gas chromatography. The oxidation-reduction potential(ORP) was measured by Ag/AgCl/sat. KCl electrodes.

Continuous experiment

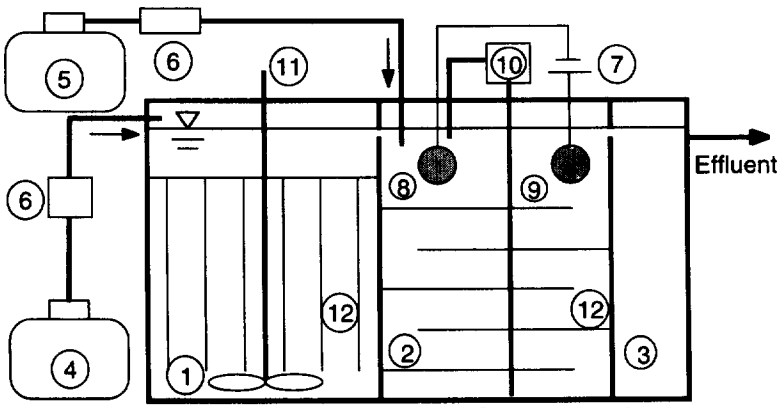

Fig. 1(b) Schematic diagram of experimental apparatus for continuous operation using prepared synthetic wastewater

Schematic diagram of the experimental apparatus for continuous operation is shown in Fig. 1(b). The reactor consisted of anaerobic reactor of about 58 L (Reactor-I), denitrification reactor of about 30 L (Reactor-II) and settling tank of 13 L. To adhere the anaerobic bacteria, the anaerobic reactor was equipped with supporting media made by non-weaved synthetic fiber sheet. The denitrification reactor was equipped with plastic plate covered by non-weaved synthetic fiber sheet as supporting media of denitrifying bacteria. Two 16 mm diameter and 350 mm long carbon rod electrodes were set on the denitrification reactor; the electrode with immobilized denitrifying bacteria on the surface was used as cathode and the other one was used as anode. Prior to the experimental run, the anaerobic reactor was inoculated with anaerobic digestion sludge obtained from municipal wastewater treatment facility and aqueous solution of milk was fed into the reactor to attach the anaerobic bacteria on the supporting media and to cultivate the bacteria for three months. The denitrification reactor was inoculated with mixed culture denitrifying bacteria and a solution of nitrate and milk was fed to the reactor to immobilize denitrifying bacteria on carbon electrode used as cathode and on the supporting media for three months. After the immobilization and cultivation of microorganism, each reactor was washed out and continuous experiments were carried out under different conditions; COD concentration from 50 to 500 mg/l, nitrate concentration of about 40 mg/l, hydraulic retention time(HRT) from 6 to 22 h and applied electric current from 0 to 40 mA. The temperature maintained at 36 °C by water bath. Solution of milk used as prepared synthetic wastewater containing organic matter was fed into the anaerobic reactor and was overflowed into the denitrification reactor. Nitrate was fed to the denitrification reactor directly. COD and nitrate concentrations of both effluent and influent of each reactor were measured.

RESULTS AND DISCUSSION

Nitrate removal characteristics of bio-electro reactor

Fig. 2 shows the time course of nitrate removal under the condition of applied electric current and no addition of acetate (Run B-1). ORP and pH in the reactor are also shown. Nitrate concentration was decreasing linearly with the elapse of time. Hydrogen gas produced by the electrolysis of water and nitrite were not detected when nitrate was remained in the reactor. This result indicates that biological denitrification in the biofilm of denitrifying bacteria occurred and was supported efficiently by the hydrogen gas produced by electrolysis of water.

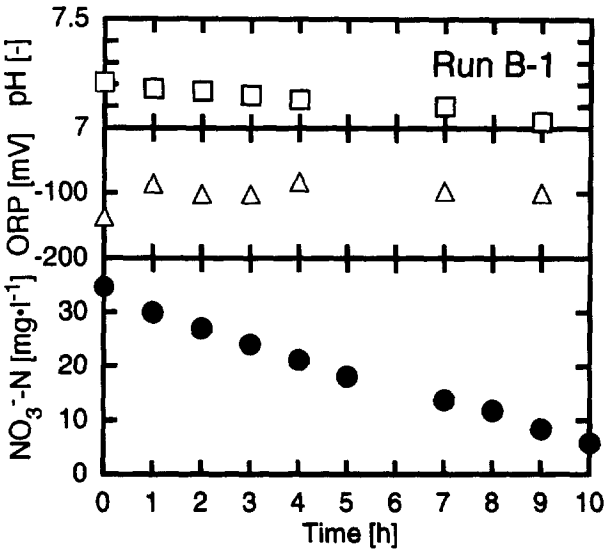

Fig. 2 NO_3^--N concentration, ORP and pH values at Run B-1 (C/N=0, 100 mA of applied electric current)

Hydrogen gas is produced by the electrolysis of water on the cathode as eq. (1) when electric current is applied.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1)$$

Nitrate diffuses from the bulk solution into the cathodic biofilm and is biologically reduced to nitrogen gas by the hydrogen produced by electrolysis of water in the biofilm as eq. (2).

$$2NO_3^- + 5H_2 \rightarrow N_2 + 4H_2O + 2OH^- \quad (2)$$

Assuming that current efficiency for hydrogen production is 100% and that the hydrogen produced by electrolysis of water was utilized stoichiometrically for the denitrification reaction as eq. (2); the theoretical nitrate reduction rate to nitrogen gas under the condition of 100 mA of electric current was 1.3 mg-N/L/h approximately. The observed experimental result of the denitrification rate was higher than the theoretical value. This result suggests that endogenous denitrification may occur as well as denitrification supported by hydrogen used as electron donor. The pH was maintained around neutral value and ORP showed anoxic condition during reaction period. The author (Kinoshita 1988) referred to the fact that CO_2 formation occurs instead of oxygen gas formation by electrolysis of water when carbon electrode is used as anode. In the case of oxygen formation occurs efficiently on anodic electrode by the electrolysis of water, the ORP value may show the oxic condition. The obtained experimental results were confirmed that in this system other electrochemical oxidation occurs on anode instead of O_2 formation. So, a favorable condition for denitrifying bacteria was seemed to formed since CO_2 produced instead of O_2 acted as buffer.

Effect of C/N ratio on denitrification in bio-electro reactor system

Fig. 3 shows the time course change of nitrate and acetate concentrations under the conditions of C/N=0.7 and 100 mA of applied electric current (Run B-2). Hydrogen gas was not detected in the gas collector when nitrate was remained in the reactor. Nitrate and acetate concentrations were decreased linearly with the elapse of time. After whole amount of acetate was consumed, the denitrification rate decreased and approached to that with hydrogen gas produced by electrolysis of water shown in Fig. 2. These results indicate that nitrate reduction to nitrogen gas occurred with simultaneous utilization of acetate and hydrogen gas in the cathodic denitrifying biofilm. Nitrate can be removed continuously by hydrogen gas even if the amount of organic matter used as hydrogen donor is present in less quantity than the minimum stoichiometric value (C/N=1.07) to remove nitrate.

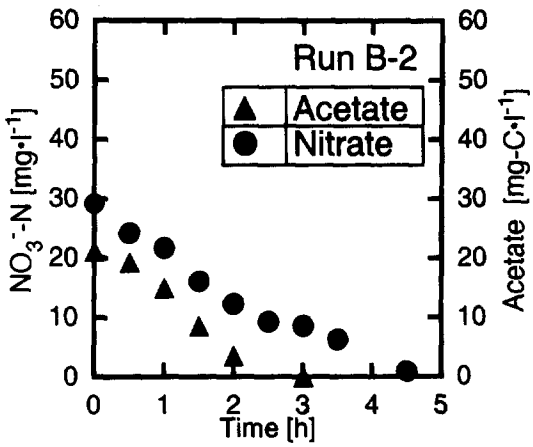

Fig. 3 Nitrate and acetate concentrations at Run B-2 (C/N=0.7, 100 mA of applied electric current)

Fig. 4 shows the time course change of nitrate and acetate under the condition of C/N=4.7 and 100mA of electric current (Run B-5). Fig. 5 shows the result of control experiment without applying electric current. As can be seen in both figures, nitrate and acetate decreased linearly with the elapse of time and nitrate was removed completely. Acetate remained when whole amount of nitrate was removed. The denitrification rate when electric current was applied(Fig.4), was clearly higher than that without applied electric current(Fig.5). Hydrogen gas was not detected in gas collector in the reaction period when nitrate was remained in the reactor. These results indicate that denitrification supported by the hydrogen gas produced by electrolysis of water occurred efficiently even the organic matter present in the system could be enough to remove nitrate biologically. The contribution of hydrogen gas to the denitrification in this bio-electro reactor was smaller than that of organic substrate used as hydrogen donor, however, higher contribution could be obtained if a higher electric current is applied.

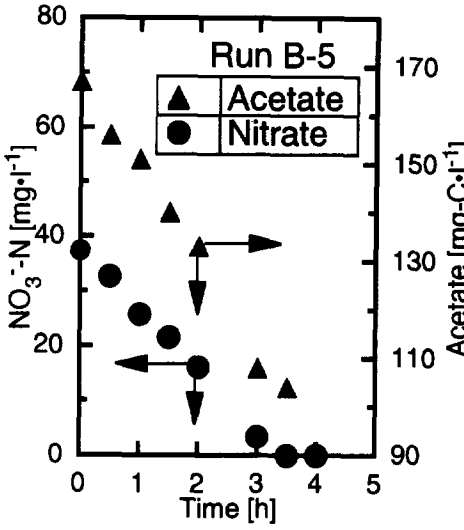

Fig. 4 Nitrate and acetate concentrations at Run B-5 (C/N=4.5, 100 mA of applied electric current)

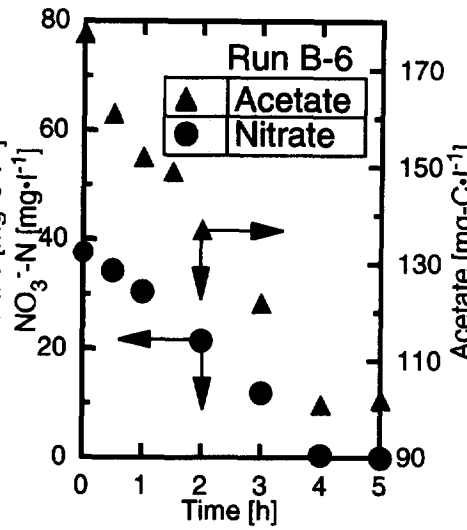

Fig. 5 Nitrate and acetate concentrations at Run B-6 (C/N=4.7, without appling electric current)

Fig. 6 shows acetate and nitrate concentrations with the elapse of time under the condition of C/N=1 and 100mA of electric current. Nitrate was removed completely with simultaneous utilization of acetate and hydrogen as electron donor and residual acetate was not observed. These results suggest that denitrification without residual organic matter may be occurred if the applied electric current is controlled in function of the influent C/N ratio. For example, denitrification occurred without residual acetate under the condition of C/N=1 when 100 mA of electric current was applied (Fig. 6).

Table 2 lists overall denitrification rates obtained in the batch experiments. The denitrification rate increased with an increase of C/N ratio. As mentioned above, the denitrification with efficient utilization of the hydrogen gas produced by electrolysis of water occurred even through organic matter which acted as hydrogen donor was in the bulk solution of the reactor. The results obtained by batch experiments suggested that the bio-electro reactor system was applied to denitrify of wastewater as an efficient and simple process.

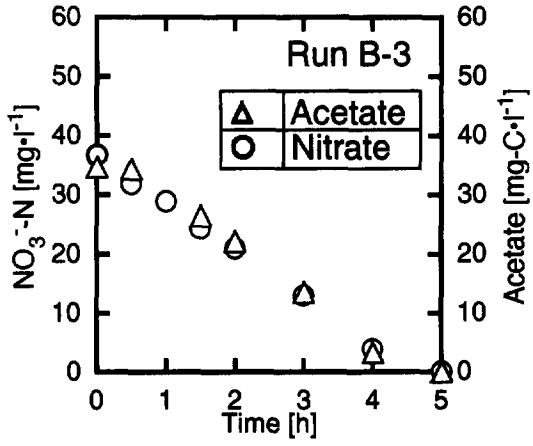

Fig.6 Nitrate and acetate concentrations at Run B-3 (C/N=1.0, 100 mA of applied electric current)

Table 2 denitrification rate and residual acetate concentration in batch experiments

run No.	initialC/N ratio	denitrification rate[mg-N/(L•h)]	residual acetate [mg-C/L]
B-1	0	2.9	-
B-2	0.7	9.4	0
B-3	1.0	8.6	0
B-4	1.5	13.7	8.0
B-5	4.5	12.1	97.4

Denitrification of prepared synthetic wastewater under continuous operation

Fig. 7 shows nitrate concentration of the reactor effluent under the condition of 40 mA of applied electric current without organic matter in the continuous operation (Run 1). The denitrification rate was maintained nearly constant by the hydrogen gas produced by electrolysis of water. About 80% of the influent nitrate load was removed by the applied electric current.

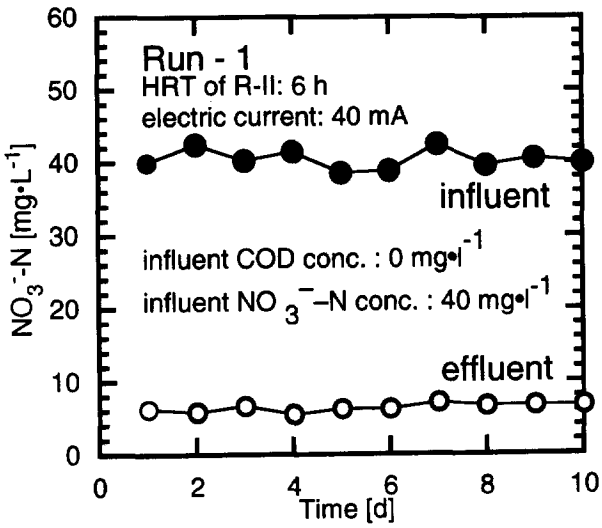

Fig. 7 Nitrate concentration of effluent from Reactor-II under the condition of 100 mA electric current without feeding organic matter

Fig. 8 shows nitrate and COD concentration of reactor effluent under the conditions using prepared synthetic wastewater containing organic matter and appling 40 mA of electric current (Run 3). The result of the control experiment without applied electric current is also shown in the figure (Run 2). Removal efficiency of nitrate was increased by the applied electric current. This confirmed that denitrification occurred by simultaneous utilization of the organic matter in wastewater as hydrogen donor and the hydrogen gas produced by electrolysis of water. COD of the wastewater was also removed by the applied electric current. Denitrification and COD removal can occur simultaneously in the bio-electro reactor system developed in this study, though further investigations are necessary to determinate clearly the mechanism of COD removal by applied electric current.

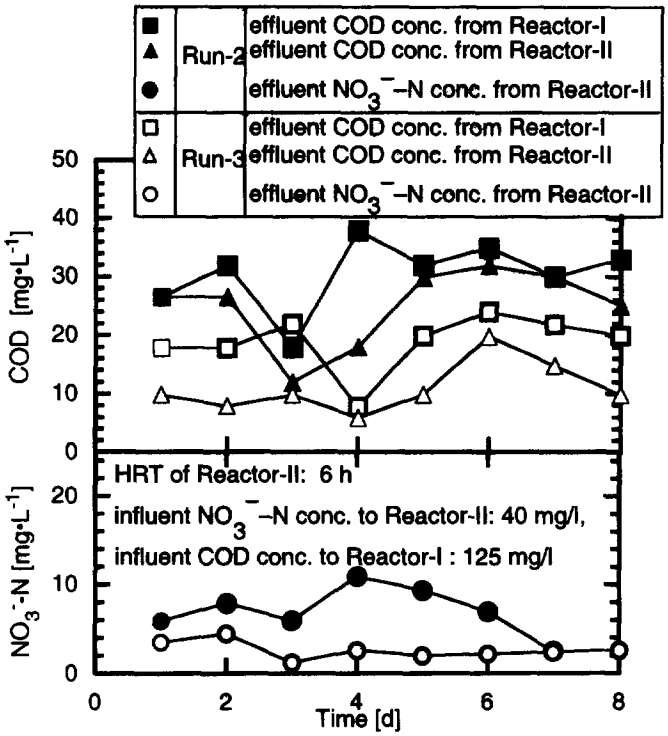

Fig. 8 Effect of applied electric current on nitrate and COD removal under continuous operation

CONCLUSION

A feasibility of denitrification treatment of wastewater containing nitrate and organic matter was investigated using a bio-electro reactor system. Nitrate reduction to nitrogen gas occurred biologically with simultaneous use of organic matter as internal source of hydrogen donor in the wastewater and hydrogen gas by electrolysis of water. Hydrogen gas produced by electrolysis of water was utilized efficiently for denitrification even if excess amount of organic hydrogen donor was existed in wastewater. Denitrification rate was increased by applied electric current. So, the bio-electro reactor process may be applied to denitrify various kinds of wastewater. From the continuous experiment, it was confirmed that removals of nitrate and COD occurred simultaneously. COD as well as nitrate was removed from the tested synthetic wastewater by applied electric current, though further investigation are necessary to analyze the phenomenon of COD removal in detail and to determine the treatment performance under various conditions.

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