Electrochemical denitrification of metal-finishing wastewater: Influence of operational parameters

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Abstract−Experimental results are presented for the electrolytic ChemDen (Chemical-Denitrification) process which was designed to investigate the effect of operational parameters on the nitrate (NO_3^-) removal from metal-finishing wastewater. The parameters included electrode materials, electrode gap, reducing agent, hydraulic retention time (HRT) and recycle ratio in the single electrolytic ChemDen reactor for lab-scale tests. The removal efficiency of nitrate is based upon a non-biological process which consists of chemical and electrolytic treatment. Results showed that removal efficiency of nitrate was highest when the zinc (Zn) electrodes were used for both anode and cathode. In the case of insoluble electrode, combining Pt anode with Ti cathode provided great improvement of nitrate removal. For the Pt-Ti electrode combination, increasing electrode gap tended to increase removal efficiency of nitrate significantly. However, no further increase in the nitrate removal was observed when the electrode gap was longer than 10 mm. Using sulfamic acid and Zn metal powder as reducing agents for the electrolytic ChemDen reaction, highest nitrate removal was achieved when the mole ratio of Zn : sulfamic acid : nitrate was 1.2 : 1 : 1. Remarkable improvement in the nitrate removal was also observed with increasing HRT from 10 to 30 min, while the effectiveness was limited when HRT was increased to 60 min. Recycling in electrolytic ChemDen reactor affected nitrate removal positively because it could improve both dispersion and reuse of Zn metal powder as reducing agent in the reactor. Recycling effects were thought to be associated with increasing surface reactivity of the Zn metal powder in the electrolytic ChemDen reactor.

Key words: Electrolytic ChemDen Process, Electrodes, Nitrate Removal, Metal-finishing Wastewater

INTRODUCTION

Metal industries generate high concentration of nitrate waste, and water sources contaminated by the nitrate can be serious environmental problems because of adverse effects on public health [1-3]. High nitrate level causes methemoglobinemia, a disease of newborns which can result in brain damage and even death. Nitrate pollution also suggests a potential risk between nitrate ion and stomach cancer in humans. In addition to the health considerations, nitrate pollution is responsible for poisoning lakes and rivers with resulting harm to fish and other aquatic life, and algae growth due to nutrient function of nitrogen [4-6].

For the removal of nitrate, biological denitrification has been established well by reducing nitrate to the gaseous nitrogen [6-8]. However, the biological treatments require a large holding tank with slow reaction time and continuous monitoring, such as addition of carbon source for microorganisms, pH control and temperature maintenance [9]. In addition, high level of total dissolved solids (TDS) presenting in metal-finishing wastewaters can affect activity of microorganisms negatively, which can lead to inhibiting the nitrate removal from the wastewater [6].

Traditionally, physicochemical denitrification includes air sparging, breakpoint chlorination and ion exchange. However, air stripping through a sparging system is always associated with high operating and maintenance costs. Ammonia nitrogen is also oxidized by applying breakpoint chlorination with proper control, but industrial wastewater can contain a variety of chlorine-demanding substances [10]. Most of all, breakpoint chlorination may not be suitable particularly for the treatment of metal-finishing wastewater because the pH in wastewater is changed widely from 4.5 to 8.0. For the removal of nitrogen by applying ion exchange, additional pretreatment needs to be considered because of the accumulation of suspended solids within the ion exchange resins [5,10].

Recently, interest in applying electro-chemical denitrification technique, which we call electrolytic ChemDen process, has been growing for the treatment of nitrate-contaminated wastewater [7,8,11]. The electrolytic ChemDen process was invented originally by Los Alamos National Laboratory (LANL) to treat nitrate-containing waste [12]. In the electrolytic ChemDen process, wastewater contaminated by nitrate is added in the electrolytic reactor and treated by contacting with two chemical reagents such as Zn metal powder and sulfamic acid (NH_2SO_3H) to reduce nitrate to harmless nitrogen gas which can be released to the atmosphere [7,8,10]. This non-biological method has been proven to remove nitrate effectively for a wide range of nitrate concentrations in various wastewaters containing up to 100 g/L from a few parts per million of nitrate [11]. Both Zn metal and sulfamic acid reduce nitrate to gaseous nitrogen according to following overall reaction [7,8,12].

$$NO_3^- + Zn + H^+ + NH_2SO_3H \rightarrow N_2 + SO_4^{-2} + Zn^{+2} + 2H_2O \qquad (1)$$
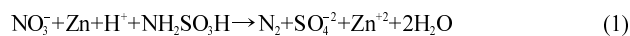
The Zn^{+2} ions generated in reaction (1) can be reduced further on cathode back to the Zn as metallic status by applying electrolysis. As a result, the Zn metal is not consumed reagent, but it can be reused

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subsequently as a metal catalyst while the sulfamic acid (NH₂SO₃H) is consumable [7,8].

According to results obtained by Sabzali et al., the solution pH and agitation had great effect on denitrification from groundwater when both Zn powder and sulfamic acid were used as reducing agents in the electrolytic ChemDen reactor [8]. In this study, stainless steel plate and graphite were applied as anode and cathode, respectively, to recover Zn metal from the electrolytic unit. Lee et al. also reported that the removal rate of nitrate increased with increase in Zn concentration, while the effect of sulfamic acid on the nitrate removal was relatively small. Although several studies have been performed to observe nitrate removal in electrolytic ChemDen process, the extent to which nitrate removal is understood should vary greatly depending upon operational conditions.

The objective of this work was to observe nitrate removal by varying operational conditions in single electrolytic ChemDen reactor treating metal-finishing wastewater. Previous studies focus mostly on the effect of reducing agents such as Zn metal powder and sulfamic acids on nitrate removal. However, nitrate removal by physical parameters including electrode gap, HRT and recycling ratio in electrolytic ChemDen process is still largely unknown. Furthermore, in previous studies, the ChemDen reactor and electrolytic recovery reactor were operated in a separate unit. In this study, however, we combined these two reactors into single unit to reduce footprint and study nitrate removal systematically with the single electrolytic ChemDen process.

MATERIALS AND METHODS

A schematic diagram of bench-scale, electrolytic ChemDen unit used in this study is given in Fig. 1. The electrolytic ChemDen unit was made of plexiglass and consisted of four reactors. Each reactor had the dimensions of 10 cm×10 cm×20 cm (length×width×height) and 1 L of working volume. The reactors were developed in consecutive pattern as multi-step reactor in which electrodes were installed. The removal efficiency of nitrate was observed by measuring it in the effluent from the electrolytic unit. Electrodes tested in this study were purchased from ACE Science (Korea). Six electrode materials including Ti, stainless steel, Ni, Fe, Cu and Zn were tested as anode and cathode. Plate-type electrodes (8 cm×8 cm) were used and installed in each reactor under 10 mm electrode gap (Fig. 1).

Throughout all experimental works, current density was maintained constant during the operation of electrolytic ChemDen unit by using IPS-30B10 and IPS-60B03DD (VUPOWER, Inc., Korea), which are programmable with DC power supplies. The current density for each reactor was 100, 50, 25 and 25 A/m², consecutively. Each power supply was also connected to a multimeter (Multimeter model 2700, Keithley) to monitor conductivity, solution pH and electric voltage of the bulk solution in the reactor. Experimental works were performed at room temperature of 25 °C.

Sulfamic acid (OCI Inc., Korea: Extra pure) and Zn metal powder (Deajung Chemical Inc., Korea: Extra pure) were purchased as reducing agents and used as received. Feed solutions having different concentrations of Zn metal and sulfamic acid were prepared to find the optimum mole ratio of Zn:sulfamic acid for nitrate removal. Since nitrate (NO₃-N) concentrations discharged from metal-finishing industries in the Incheon metropolitan city in South Korea ranged from 70 to 100 mg/L, the NO₃-N concentration was fixed as 100 mg/L in this study. The Zn and sulfamic acid concentrations were
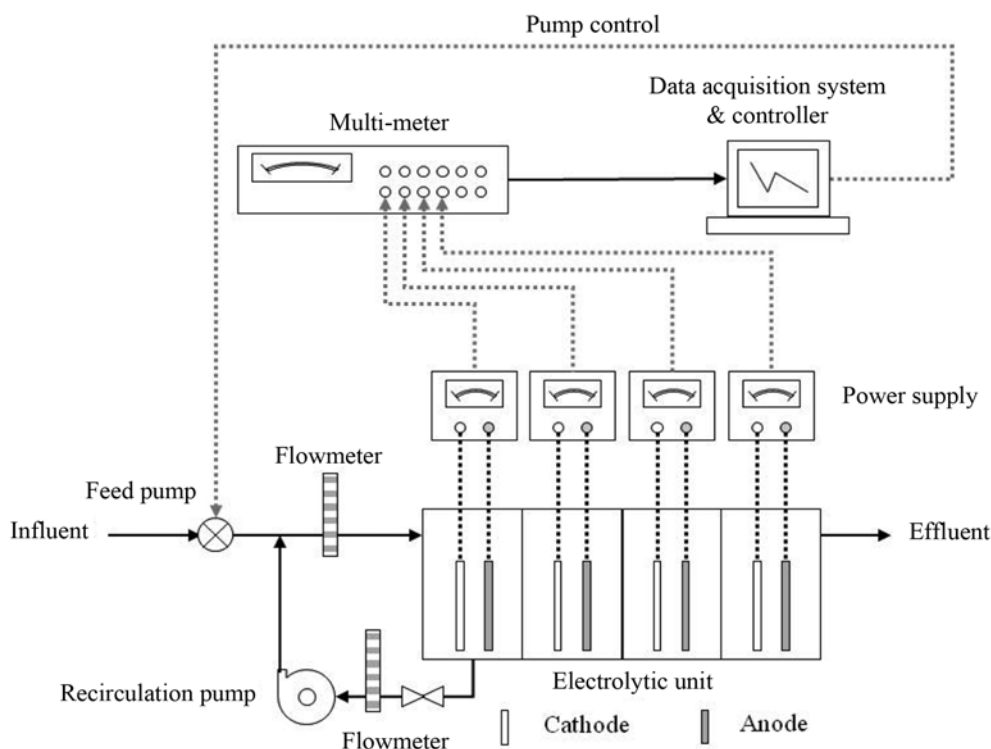

Fig. 1. Schematic diagram of electrolytic-ChemDen experimental set-up.

467 and 720 mg/L, respectively, when the mole ratio of Zn : sulfamic acid : nitrate was 1 : 1 : 1. The pH of the feed solution was adjusted to about 2.0 by using sulfuric acid solution.

During the operation of electrolytic ChemDen unit, effluent samples were collected periodically from the unit to measure nitrate concentrations under various operational conditions. The nitrate concentration was measured by using an automatic water analyzer (AWA, TRAACS2000, Bran+Luebbe). The automatic water analyzer can measure the concentration of nitrate in the effluent by quantifying N-(1-Naphtyl) ethylenediamine which is produced by the reaction with nitrite (NO_2^-) reduced from nitrate (NO_3^-) through Cd-Cu coil and sulfamilamide. The concentration of red-colored N-(1-Naphtyl) ethylenediamine was measured by UV spectrometer under 540 nm of wavelength [13].

RESULTS AND DISCUSSION

1. Effect of Electrode Materials on Nitrate Removal

Experimental results on the removal efficiency of nitrate with different electrode (anode+cathode) materials are given in Fig. 2. The removal efficiencies of nitrate were compared for different electrode materials including Ti, Stainless Steel (SUS) 304, Ni, Fe, Cu and Zn. The HRT was 60 min, and the mole ratio of reducing reagents and nitrate was 1 : 1 : 1 (Zn : sulfamic acid : nitrate). Among these six electrode materials, the Zn-Zn electrodes (anode+cathode) provided highest removal efficiency of nitrate. The order of electrode materials for both anode and cathode increasing in the removal efficiency of nitrate was Ti (1.5%), SUS304 (2.1%), Ni (5.1%), Fe (8.6%), Cu (18%) and Zn (56%). An increase in nitrate removal may have resulted from highest electrocatalytic activity of the Zn metal in the transformation of nitrate into nitrogen [14,15]. However, releasing Zn^{+2} from the Zn anode via electron transfer consumed the anode. As a result, the Zn anode may need to be replaced more often than other anode materials.

Because of soluble characteristics of Zn anode, a Pt anode which is insoluble was selected and tested with various cathode materials. Fig. 3 shows the effect of cathode materials on the removal efficiency of nitrate as the Pt electrode is utilized as anode. The removal efficiency of nitrate was found to be greatest as the Pt anode was accompanied with Ti cathode. However, using Zn cathode rather

Fig. 3. Effect of cathode materials on the removal efficiency of nitrate (anode: Pt electrode, HRT=60 min, mole ratio of Zn : sulfamic acid : nitrate=1 : 1 : 1, electrode gap=10 mm, pH= 2, no recycling).

than Ti cathode decreased the removal efficiency of nitrate significantly ($p<0.05$). Changing Zn cathode to Fe cathode had no significant difference in the removal efficiency of nitrate ($p>0.05$). The order of cathode materials combined with Pt anode increasing in the removal of nitrate was SUS304 (14.7%), Ni (16.2%), Cu (18%), Zn (25. 4%), Fe (27.5%) and Ti (37.1%).

Figs. 2 and 3 also compare the removal efficiency of nitrate between Pt-Zn electrode (anode+cathode) and Zn-Zn electrode. It can be seen that with Pt anode there is a reduction of nitrate removal (25.4%), while the use of Zn anode increases the nitrate removal significantly (56%). Highest removal efficiency of nitrate was achieved by applying Zn-Zn electrode in this study. However, it was expected that using Pt anode could prevent releasing Pt ions from the anode during electrochemical reaction because it was insoluble material. Thus, the use of Pt anode can not only reduce the total costs pertaining to the replacement of the electrode, but also increase the recovery of the Zn metal powder from the electrolytic ChemDen reactor [15]. Using Pt anode, the residual concentration of Zn ion in the treated effluent from the reactor was not detected, implying that most of the Zn ions produced by the oxidation of Zn metal should be transported to the Pt anode.

2. Effect of Distance between Anode and Cathode on Nitrate Removal

Removal efficiencies of nitrate observed at different distances between anode and cathode (electrode gap) are shown in Table 1. The Pt-Ti electrode (anode+cathode) was used in the first stage of electrolytic ChemDen unit under 30 min of HRT and the mole ratio of Zn : sulfamic acid : nitrate was 1 : 1 : 1. Four electrode gaps (1, 5, 10 and 15 mm) were tested in this experiment. Table 1 shows
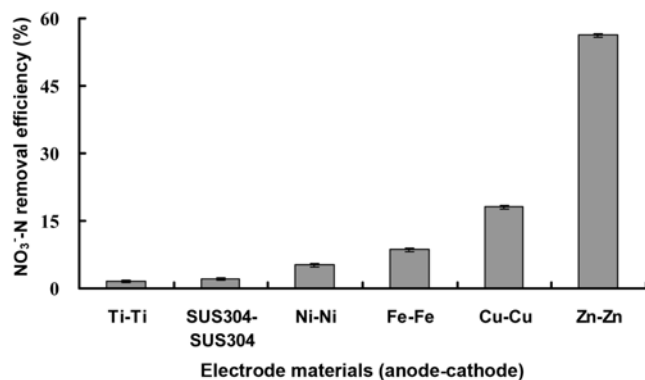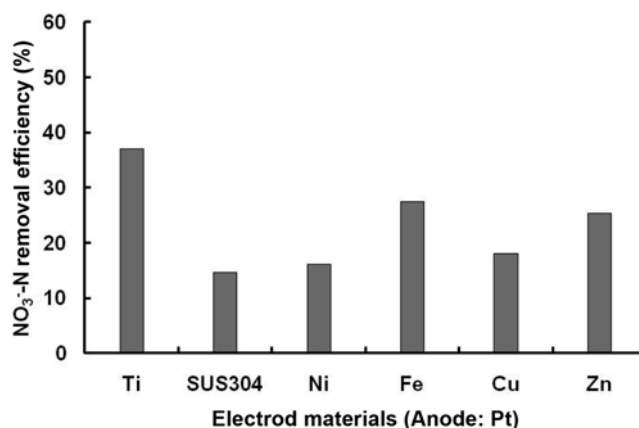

Fig. 2. Effect of electrode materials on the removal efficiency of nitrate (HRT=60 min, mole ratio of Zn : sulfamic acid : nitrate=1 : 1 : 1, electrode gap=10 mm, pH=3.0, no recycling).

Table 1. Effect of electrode gap between Pt anode and Ti cathode on the removal efficiency of nitrate and energy consumption (HRT=30 min, Zn : sulfamic acid : nitrate=1 : 1 : 1, pH=2.0)

Electrode gap (mm)	1	5	10	15
Removal efficiency of nitrate (%)	25.2	30.0	36.1	22.9
Energy consumption (kJ)	23.3	18.1	16.3	26.9

that increasing electrode gap increases the removal efficiency of nitrate. However, the nitrate removal started decreasing when the electrode gap was longer than 10 mm. Gradual deactivation of electrode during nitrate reduction was reported and the surface of the used soluble electrode became rougher over operating time [9,16,17]. Chiang et al. [14] also found that the current efficiency decreased when the electrode gap increased from 15 mm to 30 mm.

The fact that the removal efficiency of nitrate becomes highest under 10 mm of the electrode gap suggests that an optimum distance between anode and cathode should exist. Possible explanation for our observed results is that increasing electrode gap increases electric resistance which is against current flows between anode and cathode [16,18]. As the electrode gap becomes shorter, the extent of mixing in the fluid between electrodes can also be insufficient, and this may lead to increase concentration-polarization layer on electrode surface. As a result, these effects can increase electric potential or resistance of electrode, thereby diminishing nitrate removal efficiency subsequently [7,19,20].

3. Effect of Reducing Agents on Nitrate Removal

The effects of sulfamic acid and Zn metal powder by varying mole ratios of these two reducing agents on nitrate removal efficiency are shown in Fig. 4. In this test, the distance between anode and cathode was 10 mm and the Pt-Ti electrode was utilized under 30 min of HRT. Results showed that 80% of nitrate was removed by 20% increase in the amount of Zn metal powder. However, the effectiveness was less pronounced with sulfamic acid, which is similar to the finding in other study [7]. Differences in nitrate removal efficiency were statistically insignificant from that obtained by 20% increase in sulfamic acid ($p>0.05$). Regarding the mole ratios tested in this study, highest efficiency of nitrate removal was achieved when the mole ratio of Zn : sulfamic acid : nitrate was 1.2 : 1 : 1. Although we found that nitrate removal depended strongly upon electrode materials and the distance between the electrodes, as evident in Figs. 2, 3, and Table 1, the effect of concentration of reducing agent on nitrate removal was not overlooked from the single electrolytic ChemDen reactor. Higher efficiency in nitrate removal may be caused by the fact that excess addition of Zn metal increases its catalytic reactivity, and this leads to facilitate conversion of nitrate to the gaseous nitrogen.

Considering energy consumption required to remove nitrate from

Fig. 5. Effect of mole ratios of reducing agents (Zn : sulfamic acid) on the energy consumption using Pt-Ti electrode (HRT=30 min, electrode gap=10 mm).

electrolytic ChemDen unit, however, Fig. 5 shows that 20% increasing in sulfamic acid reduces energy consumption considerably ($p<0.05$) while nitrate removal is not that significant (Fig. 4). Reaction of sulfamic acid with nitrate during electrochemical process produces hydrogen ions generally due to ionization of sulfamic acid. Therefore, conductivity of bulk solution can be increased, and this effect can reduce both electric potential of electrode and thus energy consumption required to remove nitrate [7,11].

4. Effect of Hydraulic Residence Time on Nitrate Removal

The removal efficiencies of nitrate at different HRTs are compared in Fig. 6. The Pt-Ti electrode (anode-cathode) was used in this test and the mole ratio of Zn : sulfamic acid : nitrate was 1 : 1 : 1. Fig. 6 shows that nitrate removal is greatest (88%) when HRT is 30 min above which no significant improvement in the nitrate removal is observed ($p<0.05$). However, Fig. 6 also indicates that shortening HRT to 10 min from 30 min under similar conditions fails to increase removal efficiency of nitrate because of wash-out effect of bulk solution from the reactor.

The effects of HRTs on the nitrate removal observed for each stage in the single electrolytic ChemDen unit are also shown in Fig. 7. It was found that most of the nitrate removal was achieved in the first stage of the reactor in electrolytic ChemDen unit for all HRTs
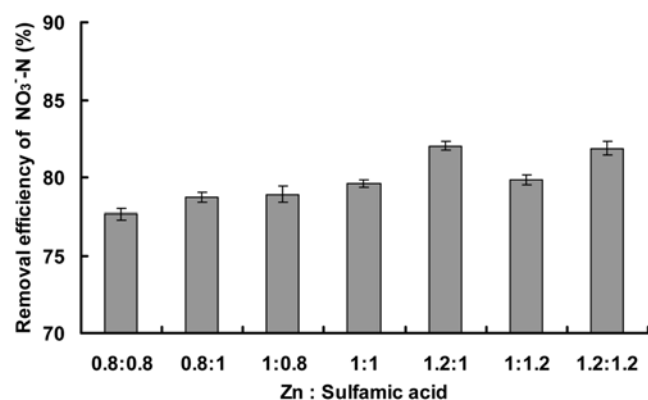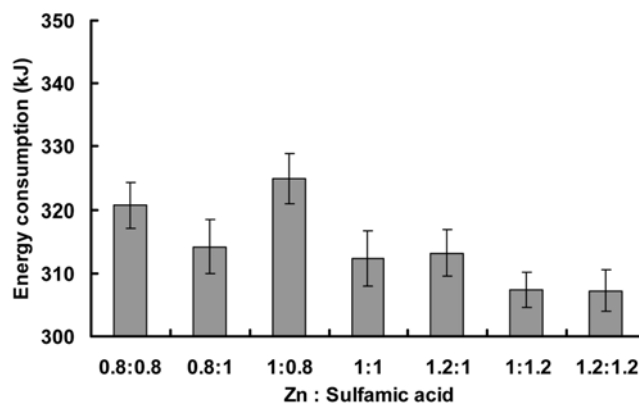
Fig. 4. Effect of mole ratios of Zn and sulfamic acid for 1 mole of nitrate on the removal efficiency of nitrate using Pt-Ti electrode (HRT=30 min, electrode gap=10 mm).
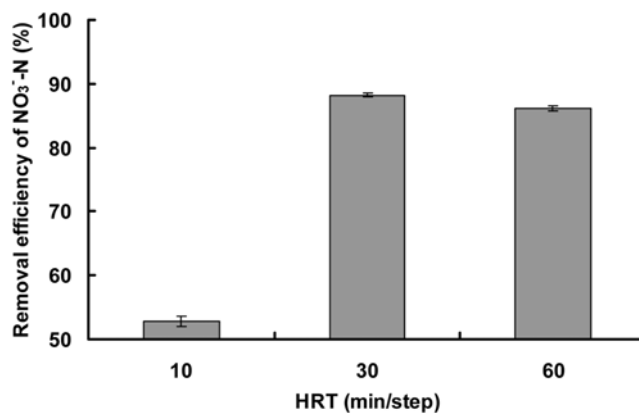
Fig. 6. Effect of HRT on the removal efficiency of nitrate using Pt-Ti electrode (mole ratio of Zn : sulfamic acid : nitrate=1 : 1 : 1, electrode gap=10 mm).
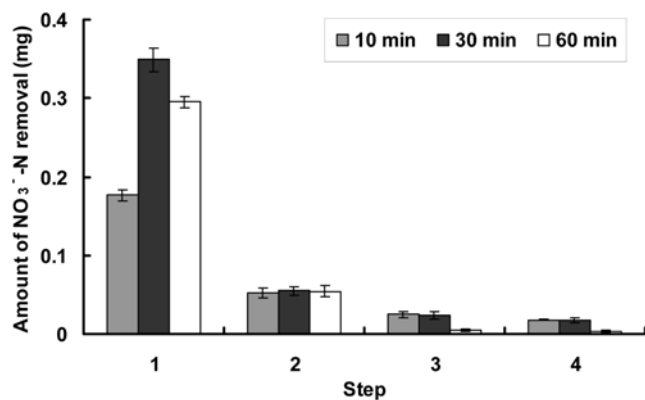
Fig. 7. Effect of HRT on the removal of nitrate at each stage of reactor using Pt-Ti electrode (electrode gap=10 mm, mole ratio of Zn : sulfamic acid : nitrate=1 : 1 : 1).

Fig. 9. Effect of recycle ratio on the removal efficiency of nitrate (electrode: Pt anode and Ti cathode, mole ratio of Zn : sulfamic acid : nitrate=1 : 1 : 1, pH=2.0).
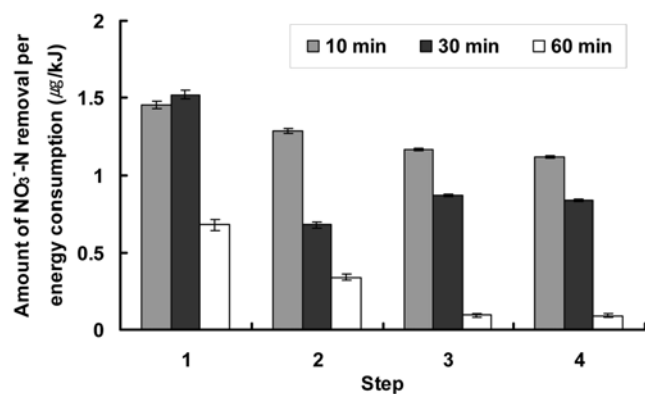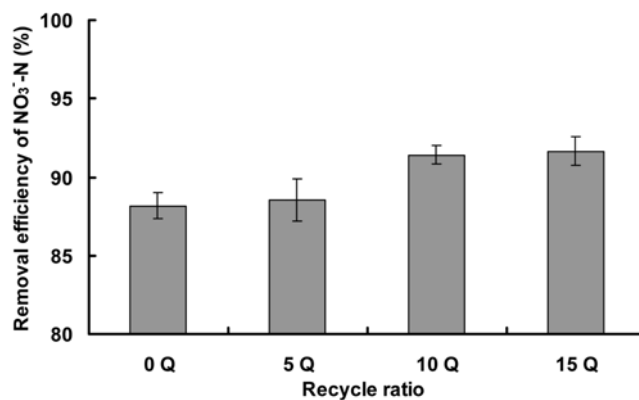

Fig. 8. Effect of HRT on the amount of nitrate removed per energy consumption at each step of reactor using Pt anode and Ti cathode (electrode gap=10 mm, mole ratio of Zn : sulfamic acid : nitrate=1 : 1 : 1).
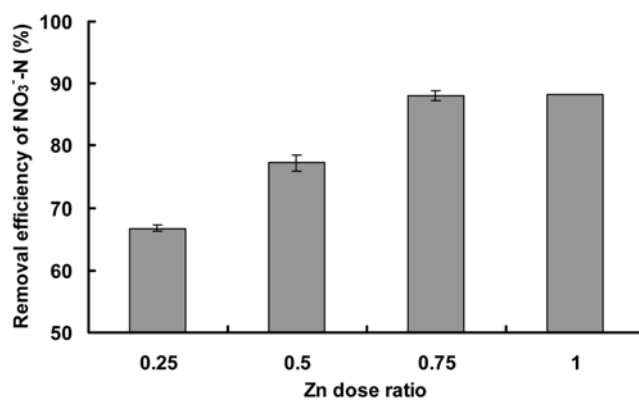

Fig. 10. Effect of Zn dose ratio on the removal efficiency of nitrate under recycling (recycle ratio=10Q, electrode: Pt anode and Ti cathode, mole ratio of Zn : sulfamic acid : nitrate= 1 : 1 : 1).

tested. In particular, more than 97% of nitrate was removed in first (88.2%) and second stage of the reactor (8.8%) at 30 min of HRT. Therefore, reaction rate of nitrate removal from last stage in the electrolytic ChemDen unit should be determined by its exit concentration from the first stage of the reactor.

However, the difference in the amount of nitrate removed from each stage was reduced when energy consumption to remove nitrate was considered under all HRTs tested (Fig. 8). Since the amount of nitrate fed from the first stage to the following stages in electrolytic ChemDen unit is reduced, thus the energy consumption required to remove the nitrate in following stages is relatively small. This effectiveness was greatest at 10 min of HRT. Possible explanation is that shortening HRT can reduce concentration polarization layer on electrode surface due to wash-out effect of feed solution from stages. Shortening HRT also can provide insufficient reaction time, and thus reducing amount of nitrate removed from the electrolytic ChemDen reactor while kinetic studies are further needed [14].

5. Effect of Recycle Ratio on Nitrate Removal

Since most of the nitrate was removed in the first stage of the single electrolytic ChemDen unit (Fig. 7), the first stage of the reactor was selected to observe the effect of recycle ratio on nitrate removal. The mole ratio of reducing agents (Zn : sulfamic acid) and

nitrate was 1 : 1 : 1, and Pt-Ti electrode (anode-cathode) was installed under 30 min of HRT. Fig. 9 shows the removal efficiency of nitrate is more pronounced with recycling than without recycling. Recycling may improve not only the mixing condition of the reducing agent of Zn metal powder in bulk solution but also its detachment from electrode plates by shear effect. In addition, increasing recovery of Zn metal powder can also improve its surface reactivity for the nitrate removal from metal-finishing wastewater. However, no significant difference in nitrate removal was observed when recycle ratio was changed from 10 Q to 15 Q ($p>0.05$) where Q is the influent flow rate to first stage, suggesting that an optimum recycle ratio should exist.

From Fig. 10, it was found that about 88% of nitrate removal could be achieved under the condition of recycling even at 25% reduction in the amount of Zn metal powder as reducing agent. This result indicates clearly that recycling should reduce the amount of Zn metal powder required to achieve the same efficiency of nitrate removal without recycling. The importance of recycling with effluent on the functionality of reducing agent such as Zn metal powder should be related to the manner in which the mixing effect of bulk solution can reduce the concentration-polarization layer from the electrode surface and improve surface activity of the Zn metal powder as re-

ducing agent.

CONCLUSIONS

This study showed that the single electrolytic ChemDen reactor treating metal-finishing wastewater could increase the removal efficiency of nitrate under appropriate operational conditions. Nitrate removal was strongly dependent upon electrode materials, electrode gap, amount of reducing agent, HRT and recycling ratio. Highest removal efficiency of nitrate was observed as the Zn electrode plates were applied for anode and cathode. Although the removal efficiency of nitrate was relatively small, more benefits were expected by utilizing insoluble electrode because exhausting anode could be reduced. The efficiency of a single electrolytic ChemDen reactor was controlled by varying the electrode gap. Increasing electrode gap increased nitrate removal, but no further increase in it was observed when the gap was longer than 10 mm. Increasing the amount of Zn powder also increased nitrate removal, while there was more beneficial effect in terms of energy consumption when the excess sulfamic acid was used. The HRT was found to be an important parameter to control nitrate removal in the electrolytic ChemDen process. Shortening HRT reduced energy consumption to operate the electrolytic reactor, but it could induce a wash-out effect, thereby reducing nitrate removal efficiency. Removal efficiency of nitrate was higher with recycling than without recycling, implying both mixing effect around electrodes and reuse potential of Zn powder by mitigating concentration-polarization layer from the electrode.

ACKNOWLEDGEMENT

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