

Application of a bio-electrochemical reactor process to direct treatment of metal pickling wastewater containing heavy metals and high strength nitrate

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Abstract The fundamental performance of a bio-electrochemical reactor for the direct treatment of metal pickling wastewater was investigated experimentally. In the reactor, carbon anode and cathode were installed. On the cathode, denitrifying microorganisms were immobilized. Continuous experiments were carried out by feeding a synthetic wastewater containing nitrate and binary heavy metal ions, copper and lead, under different operating conditions. Acetate as well as the electric current was supplied at the minimum amount for stoichiometry of the dissimilatory denitrification reaction. The results indicated that the dissolved copper and lead removal, denitrification and neutralization could be achieved simultaneously in a single bio-electrochemical reactor. The dissolved heavy metals were removed by electrochemical deposition on cathode and by the other phenomena such as the formation of insoluble suspensions and the sorption on suspended bacterial sludge. Denitrification proceeded effectively with the utilization of both added acetate and hydrogen gas generated by electrolysis of water. The pH value increased up to around neutral due to the occurrence of denitrification in the reactor, although the influent pH was less than 3. The removal efficiencies of heavy metals and nitrate increased with increasing the current density. The applied electric current was indispensable for sustaining the stable treatment in the reactor.

Keywords Bio-electrochemical reactor; denitrification; electric current; heavy metal removal; metal pickling wastewater; neutralization

Introduction

Metal pickling wastewater is usually strongly acidic and contains some heavy metals and high strength nitrate. To say nothing of heavy metals, nitrate is a contaminant of concern since it accelerates eutrophication in closed water bodies. Therefore, both nitrate and heavy metals have to be removed sufficiently from the wastewater before the discharge. The neutralization is also necessary. These, in general, may be achieved by a sequential combination of the conventional unit treatment processes. For the nitrate removal, utilization of biological denitrification has been promising because nitrate can be easily transformed to harmless nitrogen gas when the necessary electron donor is available (Rittmann and McCarty, 2001). In the case of the metal pickling wastewater, the external addition of methanol, acetate, etc. is indispensable since it usually contains no or little internal source of electron donor to support the growth of denitrifying microorganisms. In addition, prior to the denitrification treatment, the removal of dissolved heavy metals is also needed to depress their inhibition for the bacterial activity. The chemical precipitation by adding alkali is a common unit process for removal of heavy metals in various kinds of wastewater containing them and is usually operated under strong alkaline conditions to attain higher removal efficiency (Tchobanoglous *et al.*, 2003). Therefore, before feeding the treated water into the denitrification reactor, pH adjustment may also be necessary to minimize the inhibitory effect of high pH on denitrification activity.

According to these considerations, one of the treatment processes for the metal pickling wastewater consists of chemical precipitation by adding alkali, pH adjustment, biological

denitrification with supplying organic matter and the post-treatment for the residual organic matter in this order. However, such a process is complicated and not efficient, especially in the consumption of chemicals although the contaminants in the wastewater can be successfully removed.

Recently, a bio-electrochemical reactor process in which biological and electrochemical reactions occurred was proposed for the treatment of contaminated water (Sakakibara and Kuroda, 1993). This process involved the direct immobilization of microorganisms on the cathode and the generation of hydrogen gas derived from electrolysis of water as an electron donor. It was reported that denitrification occurred efficiently in the reactor with feeding the nitrate-contaminated water (Feleke *et al.*, 1998). An enhancement method of the denitrification rate was also demonstrated by simultaneously supplying the electric current and organic matter as electron donors (Kuroda *et al.*, 1994, 1996). More recently, Skadberg *et al.* (1999) reported simultaneous heavy metal removal and biological reductive dechlorination induced by hydrogen generation in their bio-electrochemical system. Watanabe *et al.* (2001) demonstrated that the dissolved copper removal, denitrification and neutralization proceeded simultaneously in a single bio-electrochemical reactor with feeding of an acidic nitrate-contaminated solution containing copper as a reference heavy metal, indicating potential to the direct treatment of metal pickling wastewater.

The actual metal pickling wastewater often contains some kinds of heavy metals. Therefore, in this study, the influence of the present multiple heavy metals on the treatment efficiency of the bio-electrochemical reactor process was investigated experimentally. Copper and lead were chosen as reference heavy metals since they have different characteristics for electrochemical reduction and the impact on the bacterial activity. In addition, the fundamental performance of the bio-electrochemical reactor for the dissolved heavy metals removal, denitrification and neutralization were examined under different operating conditions by feeding a synthetic metal pickling wastewater.

Materials and methods

Apparatus and experimental procedures

A schematic of the experimental apparatus is shown in Figure 1. A cylindrical vessel made of acrylic resin with 14.5 cm inner diameter and 37 cm high was used as the reactor. The effective working volume was about 5 L. The cathode was expected to play important roles for denitrification and heavy metals removal in the system. Therefore, to enlarge the contact area of the cathode with the solution, one carbon rod 16 mm in diameter was installed along the axial center of the reactor as the anode and was surrounded by twelve carbon rods 8 mm in diameter used as the cathode. In order to support biofilm attachment, the cathodic carbon rod was pasted with carbon fiber felt about 5 mm thick by means of electroconductive glue. Total external surface area of the twelve cathodes was about 1,800 cm². The distance between the anode and the cathode was about 5 cm.

The reactor liquid was mixed sufficiently by a magnetic pump. The temperature was kept at 35°C by immersing the reactor in a temperature-controlled water bath. The procedure for cultivation of denitrifying microorganisms and the development of the biofilm on the cathode surface was described elsewhere (Kuroda *et al.*, 1994, 1996).

The experiments were carried out by feeding synthetic wastewater to the reactor at different hydraulic residence times (HRT) and applied electric currents. The synthetic wastewater contained 200 mg-N/L of nitrate, 30 mg/L of copper ion and other trace inorganic nutrients required for the growth of denitrifying microorganisms. Lead concentration in the solution varied from 0 to 20 mg/L in a stepwise manner. Acetate was also added at 1.0 of C/N mass ratio as an external energy/carbon source to support denitrification. The final pH value of the synthetic wastewater was adjusted in the range from 2.6 to 3.0. The operational

range of the electric current was chosen so that the current density at the cathode was below 0.1 mA/cm^2 . Sakakibara *et al.* (1994) reported that the current density beyond this value was not effective for the bio-electrochemical denitrification treatment. The deficiency of the electron donor for denitrification was partly compensated by the acetate addition mentioned above.

Analytical methods

All samples for the analyses of the dissolved constituents were filtered through membrane filters with $0.2 \mu\text{m}$ of nominal pore size. Nitrate and nitrite were analyzed by an ion chromatograph (Yokogawa Analytical Systems, IC-7000). Acetate was measured by means of a steam gas chromatograph equipped with a flame ionization detector (Ohkura GC103FP). The total copper, the total lead and their dissolved fractions were determined through preliminary treatments of the samples according to Standard Methods (APHA, 1998). The concentrations of copper and lead were measured by a flame atomic absorption spectrophotometer (Hitachi, A-2000).

Results and discussion

Tendency of contaminant concentrations in effluent

Figure 2 shows an example of the change in the concentrations of nitrate, nitrite and dissolved heavy metals and pH value in the effluent at different conditions. The concentrations of dissolved copper and lead in the effluent reached very low levels. Nitrate decreased sufficiently without accumulating nitrite. The nitrate removal was caused by biological denitrification since no acetate and hydrogen gas were detected in the effluent and in the produced gas, respectively (data not shown). The pH value in the reactor was kept at around neutral although an acidic solution below pH 3.0 was fed continuously. In the reactor, the following reactions were assumed to occur as the electrolysis on the cathode and anode and the denitrification by utilizing acetate and hydrogen gas, respectively (Watanabe *et al.*, 2001):

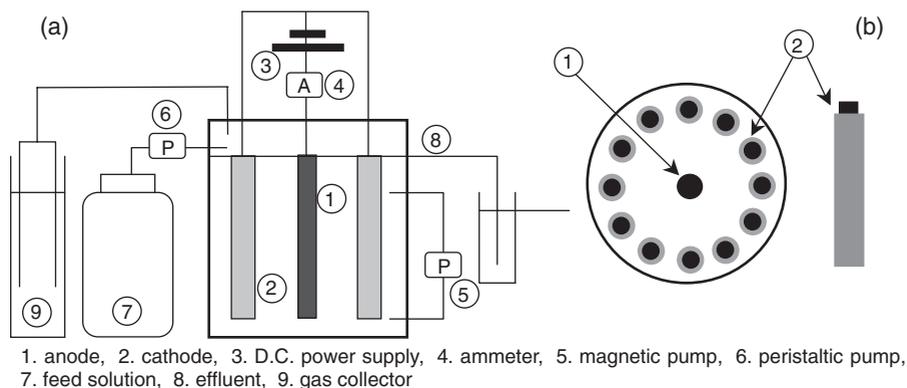


Figure 1 Schematic diagram of experimental apparatus; (a) overview of experimental apparatus and (b) configuration of electrodes in the reactor



As a result of these reactions depending on the operating conditions, pH in the reactor seemed to reach around neutral value. The generation of hydroxyl ions could increase the pH, whereas dissolution of carbon dioxide generated by reaction Eqs (2) and (3) may act as buffer. Actually, Claus and Kutzner (1985) reported that an acidic wastewater containing high nitrate concentration was neutralized by denitrification by utilizing organic matter in their complete mixing reactor. The results shown in Figure 2 indicated that the binary heavy metals removal, denitrification and neutralization could be achieved simultaneously in a single bio-electrochemical reactor. Therefore, the effect of operational conditions was further examined.

Effect of lead loading

Figure 3 shows the effect of lead loading on denitrification, pH value and heavy metals removal at constant HRT and electric current. Nitrate concentration in the effluent increased gradually with increasing lead concentration in the influent. Concomitantly, the pH value in the effluent slightly decreased. Nitrite began to be detected when the lead concentration in the influent increased to 20 mg/L. According to these results, it was suggested that denitrification may be inhibited by increasing lead loading. Further investigation will be necessary to make the inhibition effect of lead on denitrification clear.

The dissolved copper and lead in the effluent were kept at low levels regardless of lead loadings in the experimental range, whereas the total lead concentration in the effluent tended to increase with increasing lead loading. The total lead and copper concentrations in the effluent were always lower than those in the influent, respectively. This indicates that copper and lead were deposited on the cathode due to the electrochemical reduction. Moreover, the fact that there was the difference between total and dissolved concentrations

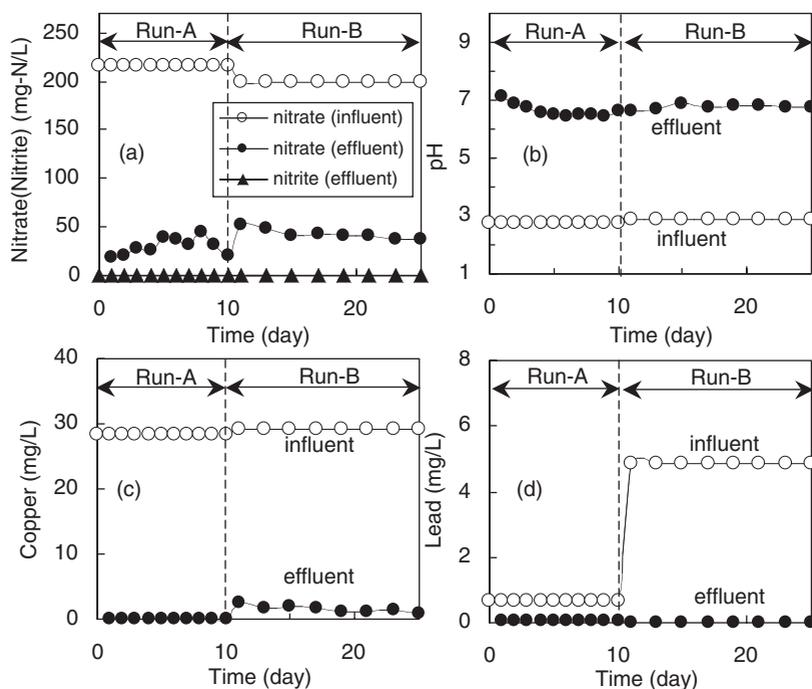


Figure 2 Change in the concentrations of nitrate, nitrite and dissolved heavy metals and pH value in the reactor effluent (HRT of 18 h and electric current of 108 mA); (a) nitrate and nitrite, (b) pH value, (c) copper and (d) lead

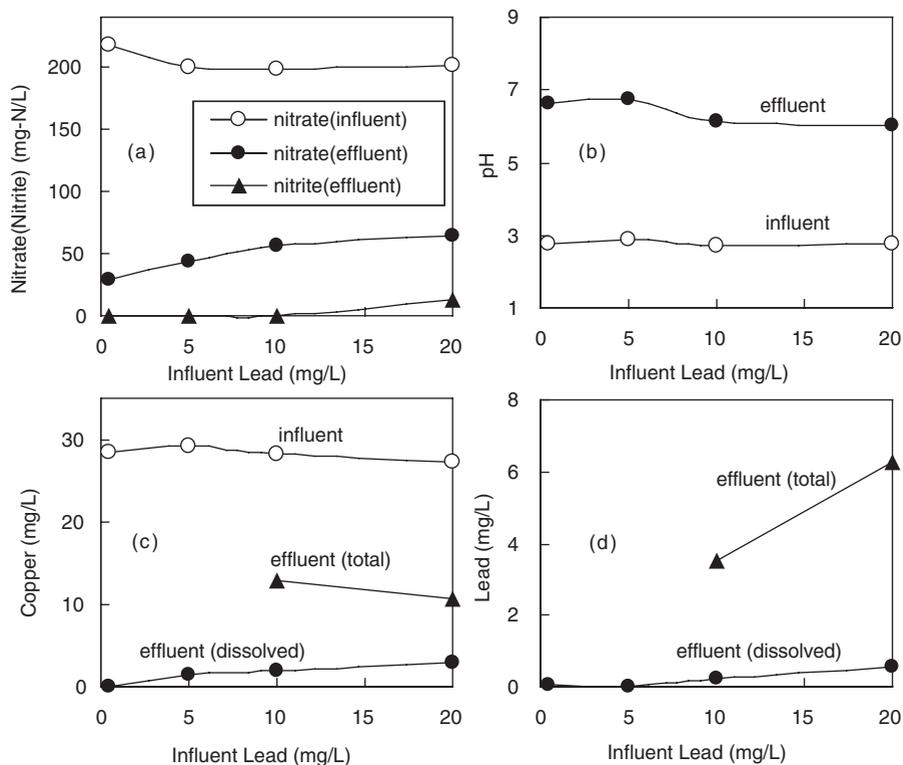


Figure 3 Effect of lead loading on denitrification, pH value and removal of heavy metals at HRT of 18 h and electric current of 108 mA; (a) nitrate and nitrite, (b) pH value, (c) copper and (d) lead

of heavy metal in the effluent suggested that the heavy metals were partly transformed into insoluble suspensions and/or adsorbed on the bacterial sludge suspended in the reactor (Costley and Wallis, 2001; Pagnanelli *et al.*, 2003).

Figure 4 shows the influence of the presence of heavy metals in the influent on the denitrification rate at constant HRT and electric current. When no copper and lead were contained in the influent, nitrate concentration in the effluent was about 30 mg-N/L (Case I). This approximately corresponded to the theoretical value estimated on the basis of the operating condition and the stoichiometry for the denitrification reaction included the assimilation and Faraday's law for hydrogen generation (Watanabe *et al.*, 2001). The slight decrease in the denitrification activity was observed when copper was present in the influent as sole heavy metal (Case II). The existence of both copper and lead led to the further decrease in the activity of denitrifying microorganisms (Case III). This may be due to the relatively high inhibition effect of lead.

Effects of HRT and electric current

As the HRT shortened at a constant electric current, nitrate concentration in the effluent increased (data not shown). The reason was because hydrogen gas generation rate did not change under the constant electric current condition, although nitrate loading increased with shortening HRT. Similarly, the total copper and lead concentrations in the effluent rose by shortening HRT, whereas the dissolved concentrations did not vary clearly, indicating that the contribution of electrochemical reduction for the removal of the dissolved heavy metals diminished due to the operation at a constant electric current (data not shown).

The effect of applied electric current on denitrification and removal of heavy metals at a constant HRT is shown in Figure 5. The denitrification efficiency increased with an

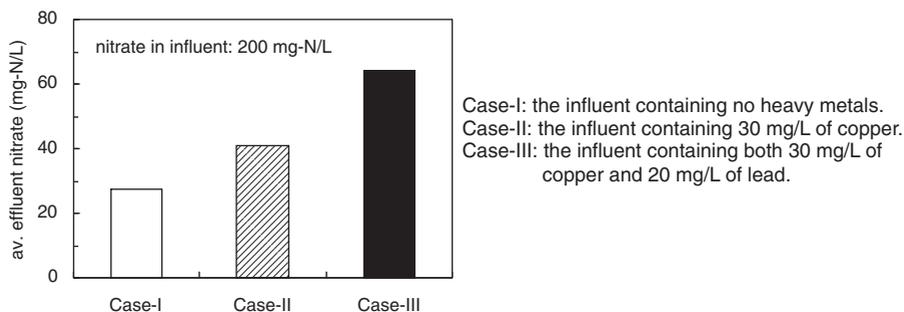


Figure 4 Influence of the presence of heavy metals in the influent on the denitrification at constant HRT (18 h) and electric current (108 mA)

increase in the applied electric current. The difference in the denitrification rate between Cases A and B approximately corresponded to that in the hydrogen gas generation rate based on Faraday's law. For the removal of dissolved heavy metals in the reactor, the relative fraction of the deposition on the cathode increased significantly with increasing electric current, indicating the clear contribution of the electrochemical reduction to overall heavy metal removal. In addition, the overall removal efficiency slightly increased. These results suggested that the removal of nitrate and heavy metals in the bio-electrochemical reactor could be easily controlled by applying electric current.

Significance of electric current

To investigate the importance of the electric current in the bio-electrochemical reactor, the experiment without applying electric current was carried out after about one year of operation under various conditions. The synthetic wastewater was continuously fed at constant HRT of 10 h and the nitrate and copper concentrations and pH in the effluent were monitored. The variation of these values with time is shown in Figure 6. After stopping the electric current, the nitrate concentration in the effluent gradually increased. Although the influent contained acetate at a C/N mass ratio of 1.0, the denitrification ceased after the first 3 weeks. In this period, pH value in the effluent lowered gradually due to the decrease in denitrification rate, and finally approached the influent level. The total and dissolved copper concentrations in the effluent increased and the difference between them tended to zero in the first 2 weeks, indicating that no suspended form of copper was practically contained in the effluent. After the dissolved copper concentration exceeded the influent level and reached a peak about 180 mg/L, it decreased finally down to the influent level.

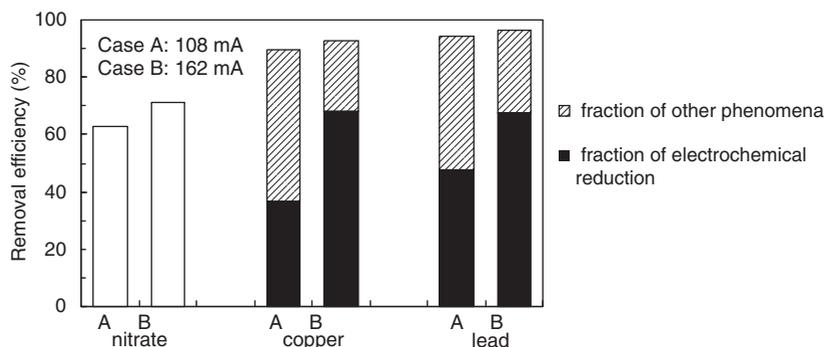


Figure 5 Effect of the applied electric current on denitrification and removal of heavy metals at a constant HRT (12 h)

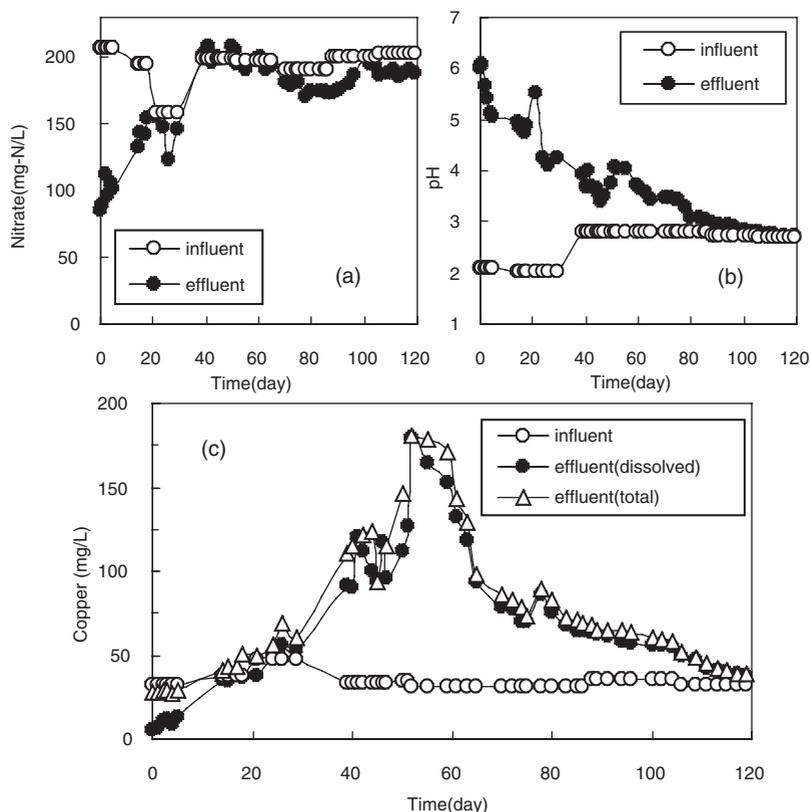


Figure 6 Variations of the nitrate and copper concentrations and pH in the effluent after stopping the electric current; (a) nitrate concentration, (b) pH value and (c) copper concentration

This was caused by the dissolution of copper deposited on the cathode during one year of operation before stopping the electric current. It was presumed that the tendency of the change in the lead concentration was similar to copper, although it was not monitored in this experimental run.

The significant decrease in the denitrification rate may have been caused by the inhibition of heavy metals rather than the cessation of hydrogen gas generation after stopping the electric current. In addition, pH lowering and increase in dissolved heavy metal disturbed the recovery of the denitrification activity. The fact that the removal of nitrate and heavy metals ceased by stopping the electric current indicated the indispensability of the electric current for the direct treatment of metal pickling wastewater by the bio-electrochemical reactor process.

Conclusions

The experimental results indicated that the removal of dissolved binary heavy metals and nitrate from a synthetic metal pickling wastewater could be attained simultaneously by means of a single bio-electrochemical reactor. In the reactor, the dissolved heavy metals were removed by electrochemical deposition on the cathode. The other phenomena such as the transformation into insoluble suspensions and the sorption on suspended bacterial sludge also contributed. Denitrification occurred with effective utilization of added acetate and hydrogen gas derived from the electrolysis of water. Concomitantly, the strongly acidic influent was neutralized due to the occurrence of denitrification. Although the increase in heavy metal loading slightly inhibited the denitrification activity in the reactor, the higher

electric current led to the increase in the removal of dissolved heavy metals and nitrate within the experimental range. The cessation of the nitrate and heavy metals removal after stopping the electric current indicated the indispensability of the electric current for the treatment of metal pickling wastewater by the bio-electrochemical reactor process.

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