Nitrogen removal from the saline sludge liquor by electrochemical denitrification

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Abstract Sludge liquor from the sludge dewatering process has a high ammonia content. In the present study, a lab-scale electrochemical (EC) system with a pair of Ti electrode plates was used for treating the sludge centrate liquor of digested wastewater sludge with a $NH_4^+ - N$ content of around 500 mg/L. The sludge liquor had a high salinity due to seawater being used for toilet flushing in Hong Kong. The results show that the EC process is highly effective for denitrification of the saline sludge liquor. Complete nitrogen removal could be achieved within 1 hr or so. The rate of EC denitrification increased with the current intensity applied. The best current efficiency for nitrogen removal was obtained for a gap distance between the electrodes at 8 mm. Electro-chlorination was considered to be the major mechanism of EC denitrification. The formation of chlorination by-products (CBPs) appeared to be minimal with the total trihalomethanes (THM) detected at a level of 300 μg/L or lower. The power consumption for EC denitrification was around 23 kWh/kg N. Additional electro-flocculation with a pair of iron needle electrodes could enhance the flocculation and subsequent sedimentation of colloidal organics in the sludge liquor, increasing the organic removal from less than 30% to more than 70%. Therefore, the EC process including both electro-denitrification and electro-flocculation can be developed as the most cost-effective method for treatment of the saline sludge liquor.

Keywords Denitrification; electrochemical; sludge liquor treatment; wastewater treatment

Introduction

Secondary biological wastewater treatment produces a large volume of sludge wastes. The sludge collected from primary and secondary clarifiers is usually processed with anaerobic digestion followed by dewatering prior to its final disposal. The sludge liquor out of the dewatering unit is then returned to the inlet of the treatment system. Although the flow rate of the sludge liquor is low, accounting for about 1% of the influent, it contains a high nitrogen content in $NH_4^+ - N$ between 500 to 800 mg/L. The ammonia loading from the sludge liquor contributes to 10–20% of the influent nitrogen loading. Removing this ammonia input will either improve the performance or increase the capacity of the mainstream wastewater treatment process for nutrient removal (Jetten *et al.*, 1997). In addition, separate treatment of the sludge liquor can take advantage of the high NH_4^+ concentration in the liquor, and hence increases eventually the overall cost-effectiveness of a municipal wastewater treatment plant (Arnold *et al.*, 2000; Kolisch and Rolfs, 2000).

The electrochemical (EC) method can be considered for treatment of the sludge liquor. An EC system is simple and robust in structure and operation. During EC treatment the sludge liquor will be forced through a reactor of electrolysis, in which electro-chlorination and the subsequent ammonia oxidisation are expected. Due to the shortage of freshwater supply in recent years, seawater has been increasingly used for domestic purposes, such as toilet flushing, in Hong Kong and a few coastal cities in China. Seawater

in sewage increases its salinity content, which would largely improve the performance of the EC process (Li *et al.*, 2002; Diao *et al.*, 2004). Moreover, the effluent from EC denitrification should be more reliable in quality due to its simple working conditions compared to other nitrogen removal processes. In the present study, laboratory experiments were carried out to investigate the effectiveness of EC treatment of saline sludge liquor for denitrification and organic removal.

Methods

Electrochemical treatment system

The EC experiment system included an EC reactor on a magnetic stirrer, two potentiostats as the DC power suppliers, a pair of titanium electrode plates for electro-denitrification, and sometimes a pair of needle iron electrodes for additional electro-flocculation (Figure 1). The EC reactor was a 1-L beaker filled with the raw sludge liquor. The electrode plates were made of Ti mesh rectangular in shape with a dimension of $5 \times 4 \, cm^2$. The electrode surface was coated with RuO_2, TiO_2 and ZrO_2 by thermal deposition to improve its corrosion resistance. The gap distance between the two electrode plates could be varied for different testing conditions. The two power sources, when both were used, could charge the pair of Ti plates and the pair of Fe needles separately. The DC input from any of the power suppliers was adjustable by varying both the current, I, and the voltage, V. Because of different treatment purposes, the power input to the Ti plates for denitrification was much greater than that to the Fe needle electrodes for dissolving iron and electro-flocculation.

Electro-denitrification and electro-flocculation experiments

The EC treatment experiments were carried out in batch mode. The electrodes were immersed into the sludge liquor in the EC reactor. Three gap distances between the Ti plates, 3, 8 and 15 mm, were tested. For each electrode setting, the experiment was conducted at different current input, including 0.5, 1.0, 1.5, 2.0 and 2.5 A, resulting in different current intensities. For each test run which lasted from 1 hr to more than 2 hrs depending on the current intensity, samples were withdrawn from the reactor at various
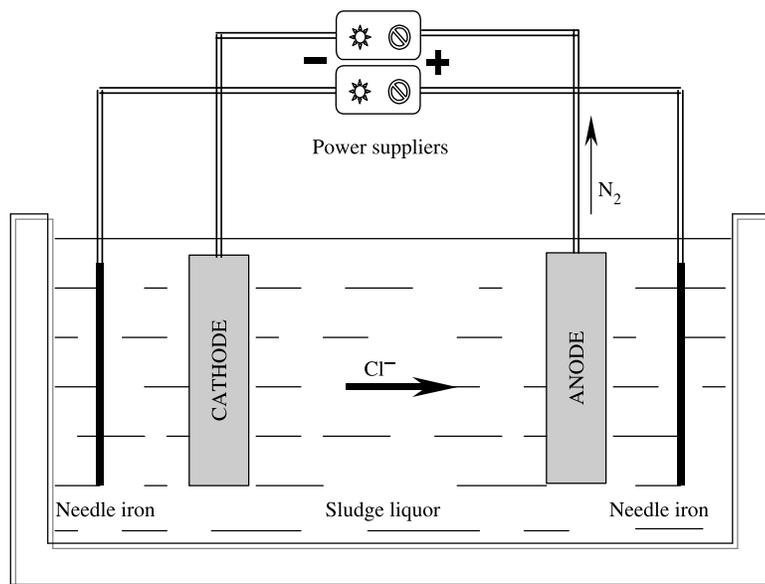

Figure 1 Experimental set-up: EC denitrification + EC flocculation

time intervals for evaluation of the treatment result, particularly the removal of total inorganic nitrogen (TIN). The current efficiency of electrolysis for denitrification can be estimated (Prentice, 1991) by

$$\eta = \frac{3F\Delta N}{14It} \tag{1}$$

where: ΔN is the amount of TIN removed from 1 L of the sludge liquor within a treatment time of t at the current I, and F is the Faraday constant (96,500 coulombs).

Electro-chlorination is believed to be essential to EC denitrification of the saline sludge liquor. In the presence of Cl^-, NH_4^+ and other impurities, electro-chlorination for nitrogen removal is a complex process. The reaction of Cl^- electrolysis can be written (Parsons, 1959; Casson and Bess, 2003) as

$$Cl^- + 2H_2O \rightarrow HOCl + OH^- + H_2 \uparrow \tag{2}$$

The principle chlorination reaction in the presence of NH_4^+ (Metcalf and Eddy, 2003) is

$$2NH_4^+ + 3HOCl \rightarrow N_2 \uparrow + 3H_2O + 5H^+ + 3Cl^- \tag{3}$$

Combining equations (2) and (3) produces the overall reaction of EC denitrification:

$$2NH_4^+ \xrightarrow{Power} N_2 \uparrow + 3H_2 \uparrow + 2H^+ \tag{4}$$

In combination with EC denitrification, electro-flocculation was tested for additional organic removal. The pair of iron needles placed 65 mm apart were charged at a low current. With the DC charged, iron dissolved into the solution at a controlled rate by adjusting the current input. Fe^{2+} was expected to function as a flocculant for particulate organics in the sludge liquor, according to the following reactions.

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \uparrow, \tag{5}$$

$$4Fe^{2+} + 8OH^- + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \downarrow \tag{6}$$

By the end of EC treatment the sludge solution was flocculated for 30 min followed by sedimentation of 120 min. In addition to the change in nitrogen content, the supernatant was analysed for organic and SS reductions and the amount of sludge in the sediment.

Characteristics of the sludge centrate samples

Sludge liquor was collected from a local municipal sewage treatment works, Shatin Sewage Treatment Works (STW) in Hong Kong, in which the conventional activated sludge process is used. Sludges from both primary and secondary sedimentation tanks are mixed and treated with anaerobic digestion of around 10 days. The digested sludge is then dewatered by centrifugation to a solid content of around 30%, while the sludge centrate is returned to the main stream of sewage flow for treatment. The raw sludge centrate

Table 1 Sludge centrate

Parameter	Value
NH_4^+-N (mg/L)	518 ± 137
BOD (mg/L)	160 ± 40
COD (mg/L)	224 ± 84
TOC (mg/L)	62 ± 11
Cl^- (mg/L)	5278 ± 422
pH	7.70 ± 0.21

collected from the dewatering unit was dark-yellow in colour with a $NH_4^+ - N$ content of around 500 mg/L (Table 1). Due to the use of seawater for toilet flushing in Hong Kong, seawater accounts for around 20% of the sewage influent to the Shatin STW. As a result, the sludge liquor samples had a high salinity with a Cl^- concentration of more than 5000 mg/L.

Analytical methods
The input of DC current and voltage could be read directly from the power suppliers. All analyses of conventional water quality parameters, such as the biological oxygen demand (BOD), chemical oxygen demand (COD) and the suspended solids (SS), were performed following *Standard Methods* (1998). Free chlorine and chloride (Cl^-) in a solution were measured with a portable datalogging spectrophotometer (DR/2010, HACH) following the methods defined by the manufacturer. The NH_3-N concentration was measured by the electrochemical method using an ammonia electrode and a potentiometer (920A, ORION). Chloramines of NH_2Cl, $NHCl_2$ and NCl_3 were determined for their concentrations by the titration method in accordance with the Standard Methods (1998). A UV-visible spectrometer (Lambda 12, Perkin Elmer, 1 cm path length) was used for NO_3 and NO_2 measurements following the Standard Methods (1998). The total organic carbon (TOC) was determined by a TOC analyser (TOC-5000A, Shimadzu) based on the combustion-infrared method. The solution pH and turbidity were measured by a pH meter (420A, ORION) and a turbidimeter (2100N, HACH), respectively. A jar-test device (PB700, Phipps & Bird) with a flat paddle mixer ($3.8 \times 1.25\,cm^2$) was employed for the flocculation and experiment test. Formation of trihalomathanes (THM) after the EC treatment in a sample was also assessed following the extraction with pentane. The extracted sample was then analysed for the THM concentration by a gas chromatograph (GC6890, Hewlett Packard) equipped with a capillary column ($30.0\,m \times 320\,\mu m \times 1.0\,mm$ nominal, DB-5, Agilent J&W), an autosampler and a linearised electron capture detector (ECD) (Li and Chu, 2003).

Results and discussion
Electrochemical denitrification of the sludge centrate liquor
The EC treatment was demonstrated to be highly effective for denitrification of the saline sludge liquor. Nitrogen measured as TIN was removed continuously from the sludge centrate samples by electrolysis. With a sufficient duration of the EC treatment, complete denitrification could be achieved (Figure 2). An increase in the current intensity resulted
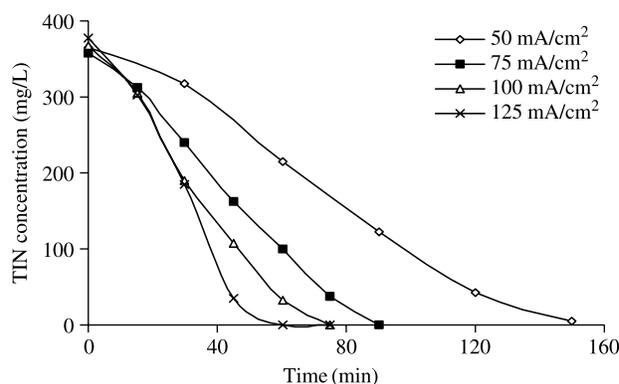
Figure 2 Nitrogen removal as a function of the contact time and current intensity with a gap distance of 8 mm between the electrodes

in a faster rate of TIN reduction. For example, at a current intensity of $50 \, \text{mA/cm}^2$ for sludge liquor with a NH_4^+-N of more than $350 \, \text{mg/L}$, denitrification could be completed within 150 min. This treatment time was shortened to around 60 min at an elevated current intensity of $125 \, \text{mA/cm}^2$. Thus, higher current input favoured the kinetics of EC denitrification.

As anticipated, electrolysis of the ammonia solution formed intermediate products of chloramines prior to the completion of denitrification. However, there did not appear to be significant accumulation of chloramines, including NH_2Cl, $NHCl_2$ and NCl_3, during the EC treatment (Figure 3a). NH_2Cl-N could reach a concentration of around $20 \, \text{mg/L}$, which disappeared from the solution by the end of EC denitrification. Formation of NO_3^- and NO_2^- were hardly detectable during the EC process. Thus, NH_4^+ was the predominant TIN species throughout the EC treatment.

Chloride in the sludge liquor was electrolysed to chlorine, which was believed to be essential to EC denitrification. While both free chlorine and combined chlorine were present in the solution, free chlorine accounted for the major fraction of total chlorine in the reactor (Figure 3b). The combined chlorine of NH_2Cl and $NHCl_2$ was found in a low and rather stable concentration level. Upon complete $NH_4^+ - N$ removal, the combined chlorine was gradually eliminated, while free chlorine was found to increase with time by continuous electrolysis.

The importance of chloride to EC denitrification was also demonstrated with a model water of $(NH_4)_2SO_4$ solution. Without salt (Cl^-) addition, electrolysis of the model solution did not result in any effective nitrogen removal. While Cl^- was dosed into the solution at a level of $4000 \, \text{mg/L}$, the same denitrification result that was obtained for the actual sludge centrate was reproduced. Thus, electro-chlorination can be considered as the major mechanism responsible for EC denitrification of the saline sludge liquor (Stoner and Cahen, 1982; Casson and Bess, 2003).

One of the major concerns in use of the EC treatment process is the formation of chlorination by-products (CBPs). As an indicator, trihalomethanes (THMs) were used for assessing the potential CBP problem in EC denitrification of the sludge liquor. The total THM in the treated sludge liquor was found to range only from 200 to $300 \, \mu\text{g/L}$. The low THM formation during the electro-chlorination was likely due to the short contact time of 1 hr or so used. Since the sludge liquor will be returned to the main stream of sewage flow, the low level of THMs in the denitrified liquor will be degraded by the downstream biological treatment. Hence, it is predictable that the accumulation of THMs and other CBPs during EC denitrification will be insignificant, which is not supposed to cause any deterioration in the quality of treated effluent.
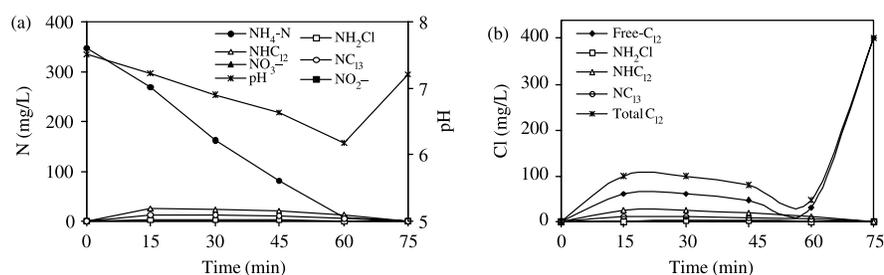

Figure 3 (a) Nitrogen removal as a function of treatment time and (b) chlorine compounds during the EC process at a current intensity of $125 \, \text{mA/cm}^2$ with an electrode gap of $3 \, \text{mm}$

Operational conditions for EC denitrification

According to the electro-chlorination and denitrification reactions (2–4), electrolysis of NH_4^+ would lead to an accumulation of H^+ ions and thus a pH decrease. This was observed during the EC treatment tests (Figure 3a). After the completion of nitrogen removal, reaction (3) became dominant. Thus, a turn point of the pH value was expected, after which the pH would increase with time. This pH change during the EC process was well demonstrated by the test results (Figure 3a).

For a given EC system, parameters such as the current intensity, the gap distance between the electrodes and treatment time regulate the effectiveness and performance of EC denitrification. As shown in Figure 2, an increase in the current input would accelerate the nitrogen removal process by electrolysis. However, for the same gap distance between the electrodes, a higher current intensity might not improve the efficiency of the current used for denitrification. Instead, a too high current input would decrease the current efficiency (Figure 4). In the EC treatment, in addition to NH_4^+ electrolysis to nitrogen gas, current input was also consumed for electrolysis reactions of H_2O, Cl^- and other compounds, as well as for heat generation. It is apparent that the fraction of current used for denitrification did not increase with the current intensity, although a higher current favoured the nitrogen removal kinetics.

The gap distance of the electrodes had a more profound effect on the current efficiency for EC denitrification. Among the 3 distances examined, a gap of 8 mm gave the best current efficiency as high as 65% or more. Increasing the gap to 15 mm resulted in a large reduction of the current efficiency to around 55%. More electricity was likely wasted for heat generation as the gap distance increased, as evidenced by the temperature rise observed. However, when the gap was reduced to only 3 mm, the current efficiency dropped more dramatically to around 40%. Bubbles trapped between the narrow gap could have a negative effect on the EC nitrogen removal process. Possible short circuit between the electrodes would considerably lower the current efficiency for NH_4^+ electrolysis. Thus, an appropriate gap distance between the electrodes should be adopted in the EC system to ensure a high current efficiency for denitrification.

For a batch operation of NH_4^+ electrolysis, the amount of nitrogen removal from the sludge liquor depended directly on the power input into the EC treatment system. It was estimated that the power consumption rate for nitrogen removal from the sludge liquor was about 23 kWh/kg N under the optimum operation conditions. This cost is comparable with other denitrification processes (Teichgraeber and Stein, 1994). In addition, EC denitrification is simple in structure and easy in operation. It has the potential to be developed as a robust and cost-effective technology for separate treatment of saline sludge liquor.
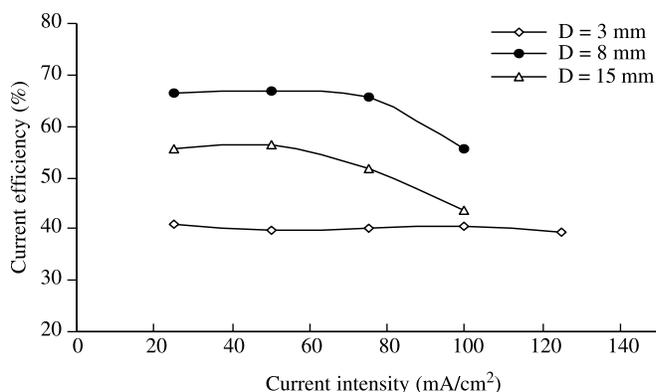

Figure 4 Current efficiency as a function of current input for different electrode gaps in EC denitrification
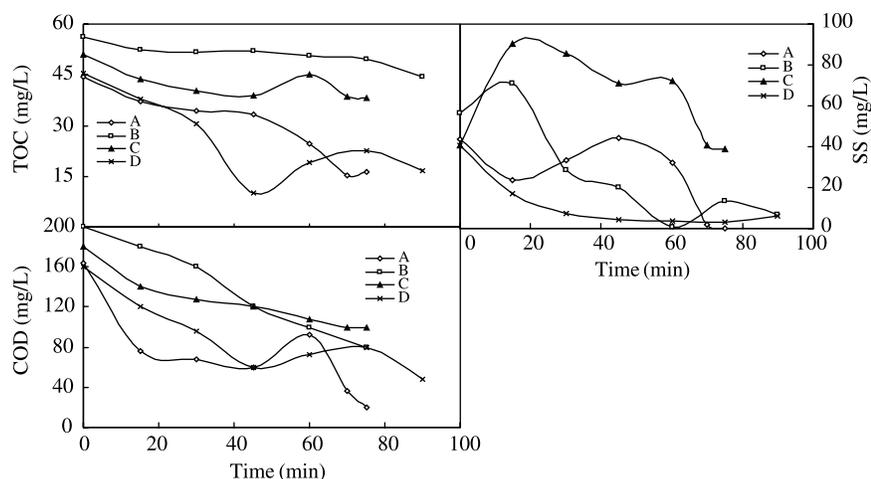
Figure 5 Comparison in the removals of TOC, COD and SS for conditions of (A) EC-denitrification + EC-flocculation, (B) EC-denitrification only, (C) EC-flocculation only and (D) EC-denitrification + chemical flocculation

Electro-flocculation for organic reduction

The EC process did not appear to be highly effective for the removal of organic materials from the sludge liquor, although a certain extent of reduction in the organic content was observed (Figure 5). Some organic molecules could likely be oxidised by EC reactions or the oxidising products of the EC process. However, EC oxidisation was not expected to be highly efficient for large organic molecules and particulate organics. With the electro-flocculation examined in this study, organic removal of the sludge liquor was improved considerably (Table 2, Figure 5).

Electrolysis with the iron electrodes would dissolve Fe^{2+} into the sludge solution. Fe^{2+} and its hydrolysis products are excellent flocculants. They are capable of destabilising the colloidal solution of large organic molecules, particulate organics and other impurities. In the present tests, Fe^{2+} compounds produced by the EC process functioned as a flocculant to promote flocculation of organic materials. Large flocs formed by electro-flocculation were effectively removed in the subsequent sedimentation. With the EC system, the rate of Fe^{2+} dissolving into the sludge liquor from the iron anode could be well controlled by regulating the current input. Electro-flocculation did not have any adverse effect on EC denitrification. Instead, the combined action of electro-denitrification with electro-flocculation had better treatment results in organic and SS removals (Figure 5). The electrolysed effluent after flocculation and sedimentation was transparent and colourless with a rather low turbidity (Table 2). It should be noted, however, over-dosage of Fe^{2+} by the EC reaction did not result in more organic and SS reductions from the sludge liquor, while sludge production was largely increased.

In comparison, electro-flocculation without EC denitrification only removed a portion of organic and SS and had no function of nitrogen removal. Chemical flocculation using $FeCl_3$ in combination with EC denitrification had a similar treatment result as the coupled

Table 2 Effect of electro-flocculation on the result of EC sludge liquor treatment

Electro-flocculation	$NH_4^+ - N$ (mg/L)	TOC (mg/L)	COD (mg/L)	SS (mg/L)	Sludge (mg/L)	Turbidity (NTU)
No	0.18	44.4	100	6.74	0.22	17.8
Yes	0.12	17.2	44	2.89	441	0.57

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process of EC denitrification and electro-flocculation. However, chemical flocculation lowered the solution pH to around 3 and produced more sludge sediment. In actual application, chemical flocculation would require more facilities and operation attention. Therefore, electro-denitrification together with electro-flocculation appears to be the best treatment approach for nitrogen removal and organic reduction of the sludge liquor.

Conclusions

The experimental results show that the EC process is highly effective for denitrification of the saline sludge liquor with a $NH_4^+ - N$ concentration of around 500 mg/L. Complete nitrogen removal could be achieved within a treatment time of 1 hr or so. The best current efficiency for nitrogen removal was obtained with a gap distance of 8 mm between the electrodes, followed by a gap of 15 mm and then 3 mm. Electro-chlorination was considered to be the main mechanism for EC denitrification. Nonetheless, there was not significant accumulation of chloramines during the EC reactions. The formation of chlorination by-products appeared to be minimal as the concentration of total THMs was only 300 μg/L or lower. The power consumption rate for nitrogen removal from the sludge liquor was around 23 kWh/kg N. Additional electro-flocculation with a pair of iron needle electrodes could enhance the flocculation and subsequent sedimentation of colloidal organics in the sludge liquor, which increased the organic removal from less than 30% to more than 70%. Therefore, the EC process including both electro-denitrification and electro-flocculation could be developed as the most cost-effective method for the separate treatment of the saline sludge liquor.

Acknowledgements

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