Influence of Operational Parameters on Rapid Nitrate Removal Using an Electrochemical Flow Cell

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Abstract—**Nitrate contamination is a great concern all over the world. However, the conventional biological processes like the modified Ludzack-Ettinger process are time-consuming. Accordingly, a rapid process for nitrate removal is desired. We conceived an electrochemical process for rapid removal of nitrate, which contained electrochemical reduction of nitrate to ammonia and electrochemical break-point chlorination of ammonia. In this research, we investigated effects of operational parameters such as volumetric electric charge, flow rate and chloride ion concentration on electrochemical nitrate removal. A hand-made divided flow cell with a copper mesh cathode, a platinum-coated titanium anode and a cation exchange membrane as a separator was developed as well as applied to the treatment of synthetic water containing 1.42 mM of nitrate at various volumetric electric charges, flow rates and chloride ion concentrations. As a result, it was observed that the flow cell operated at a flow rate of 20 mL/min, chloride ion concentration of 800 mg/L, volumetric electric charge of 5,100 C/L and at pH 7 successfully removed nitrate from 1.42 mM to 0.43 mM without ammonia and nitrite accumulation within 1 minute contact time. Consequently, the electrochemical technique was thought to be feasible for the rapid removal of nitrate from water streams.**

Index Terms—**Break-point chlorination, biological process, electrochemical process, nitrate contamination.**

I. INTRODUCTION

A. Electrochemical Water Treatment Concepts

Literally, the electrochemical water treatment concept was first commenced in the beginning of nineteenth century in the United Kingdom (UK). After that, about a century has passed with the extensive researches by many scholars all around the world in the electrochemical field. On the other hand, the accessibility of electrical power has facilitated to enhance the electrochemical technologies to the door point of many fields [1]. Nowadays, these techniques are frequently employed elsewhere to deal with the water treatment for several nitrogenous compounds removal, including nitrate (NO_3^-), nitrite (NO_2^-) and ammonia (NH_3) [2]. However, the World Health Organization (WHO), United States Environmental Protection Agency (USEPA), and European Community (EC) set the maximum contaminant level (MCL) in drinking water to be 50 mg NO_3^-/L, 0.5 mg NO_2^-/L and 0.5 mg NH_4^+/L.

Besides, different discharge standards were demarcated based on the receiving environment such as in the fresh water body 50-100 mg NO_3^-/L, sea water 200 mg NO_3^-/L and in the sensitive areas 50-75 mg NO_3^-/L [3]. Due to elimination of nitrogenous compounds from different sources of water, many researchers have focused on the electrochemical reduction of NO_3^-, because it shows comparatively high treatment efficiency, negligible amount of sludge production, small area consumption and overall, relatively low investment costs [4]. In the last decades, numerous cathode materials were studied by several researchers in the electrochemical denitrification such as, Cu, Fe, Zn, Pt/Ir, Pd and Au [5]. Some electrodes like Cu and Fe presented quite efficient promoters for NO_3^- reduction [6].
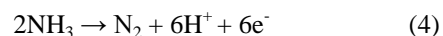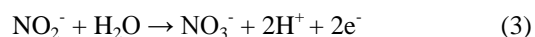
B. NO_3^- Conversion Mechanism in an Electrochemical Flow Cell

In an electrochemical cell the NO_3^- is mainly reduced to NO_2^- and NH_3 in the course of cathodic cycle (reactions (1) and (2)), and the produced NO_2^- and NH_3 are oxidized to NO_3^- and nitrogen gas (N_2) in the anodic cycle (reactions (3) and (4)) [7].

Reactions in the cathodic cycle:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \tag{1}$$

$$2NO_3^- + 12H_2O + 16e^- \rightarrow 2NH_3 + 18OH^- \tag{2}$$
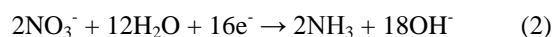
Reactions in the anodic cycle:

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \tag{3}$$

$$2NH_3 \rightarrow N_2 + 6H^+ + 6e^- \tag{4}$$

However, during electrochemical reduction of NO_3^- at a constant potential it has been demonstrated that the simultaneous electrochemical oxidation of NH_3 to N_2 seems to be difficult [8]. Therefore, it is challenging to find out the appropriate conditions to perform both cathodic reduction of NO_3^- and anodic oxidation of the produced NH_3 [9].
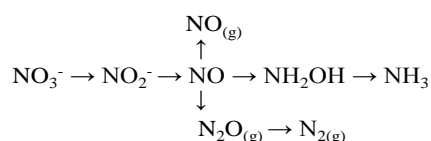
C. Nitrate Removal Using Electrochemically Produced HOCl

In general, in the course of electrolysis, water containing sufficient amount of chloride ion (Cl^-) produces chlorine (Cl_2) by an anodic oxidation, which reacts with water (H_2O) and forms hypochlorous acid (HOCl) as follows:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{5}$$

$$Cl_2 + H_2O \rightarrow HOCl + HCl \tag{6}$$

The HOCl further reacts with NH_3 and produces N_2 [10]. It has been also reported that Ti/TiO_2-RuO_2 anode can efficiently remove NH_3 with the appropriate amount of Cl^- concentration in the electrolyte [11]. The NO_3^- removal from potable water and wastewater as well as the concentrated solutions that come from the reverse osmosis (RO), electro-dialysis (ED) and ion exchange (IE) resin is a critical issue in environmental technology. Copious research works have been done for the removal of NO_3^- which include biological, catalytic, and electro-catalytic methods [12].

The electrochemical reduction of NO_3^- leads to a relatively broad spectrum of products, such as N_2, hydroxylamine (NH_2OH), nitrous oxide (N_2O), nitric oxide (NO) and NH_3 [13]. The pattern of NO_3^- reduction on catalysts and electro-catalysts can be stated as follows [14]:

$$
\begin{array}{c}
NO_{(g)} \\
\uparrow \\
NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow NH_2OH \rightarrow NH_3 \\
\downarrow \\
N_2O_{(g)} \rightarrow N_{2(g)}
\end{array}
$$

Therefore, it is likely to find out the proper conditions to perform both cathodic reduction of NO_3^- to NO_2^- and NH_3 and the anodic oxidation of the produced NH_3 with the presence of Cl^-.

D. Research Objectives

The aim of this research work was to demonstrate the NO_3^- removal by inserting a cation exchange membrane between the two-compartment electrochemical flow cell to evaluate the NO_3^- removal performances. Where, cation exchange membrane functioned as to block the flow of anions and water molecules to the anode compartment but supported only the cations to pass through the cathodic compartment. In this research, the influence of several parameters such as cathode materials, volumetric electric charges, flow rates, and Cl^- concentrations were investigated for the improvement of electrochemical denitrification process.

II. MATERIALS AND METHODS

A. Cyclic Voltammetry

The cyclic voltammetry (CV) was used to investigate NO_3^- reduction characteristics of copper cathode. Here, the saturated Ag/AgCl electrode was used as a reference electrode and a platinum-coated titanium (Ti/Pt) electrode was used as a counter electrode. Working electrode was prepared by polishing the surface with an alumina-based abrasive (#800~#100, 3M, Japan). Test solution was prepared with reagent grade chemicals (Wako Chemical, Japan) of potassium sulphate (K_2SO_4) and potassium nitrate (KNO_3) diluted with deionized water. The K_2SO_4 was used as a supporting electrolyte to ensure sufficient conductivity, since it is a strong electrolyte and fully ionized in water. The concentration of the supporting electrolyte was determined considering the similarity to general tap water conductivity. The pH and conductivity of 1 mM K_2SO_4 solution was 6.8 and 0.29 mS/cm, respectively. On the other hand, the pH and conductivity of 1 mM K_2SO_4 with 1.42 mM KNO_3 solution

was 5.3 and 0.44 mS/cm, respectively. The surface area of the working electrode was 1.0 cm^2. The potential sweep was cycled five times between +0.15 to - 1.23 V at a scan rate of 50 mV/sec from forward to backward direction for getting stable polarization using an automatic polarization electrochemical system (HSV100, Hokuto Denko, Japan).

B. Experimental Apparatus for Electrolysis

Fig. 1 (a) shows the experimental setup and (b) shows the structure of the electrolytic flow cell. The laboratory scale experimental system was composed of a hand-made electrolytic flow cell, a feed pump (RP-1000, EYELA, Japan), and a DC power supply (PW18-3AD, Kenwood, Japan). The flow cell was divided into two compartments, namely cathodic and anodic by inserting a flat sheet cation exchange membrane (Nafion NE-1110, DuPont, USA) between two compartments. Ten sheets of copper meshes (#40/36, 0.28 mm in the diameter of Cu wire) with the configuration of 50 cm^2 constituted the cathode by stacking them in the cathodic chamber. The effective cathode area amounted to 2892 cm^2. The anodic compartment was equipped with a Ti/Pt plate electrode at the outside of the compartment with the effective area of 50 cm^2 and was filled with a fluorocarbon mesh sheet. The flame of the compartment was made of a silicon sheet with 4 mm in thickness for cathodic and 1 mm in thickness for anodic one. Accordingly, the empty volume of cathodic and anodic compartment was 20 cm^3 and 5.0 cm^3, respectively. All parts of the cell were fastened tightly with 8 bolts.
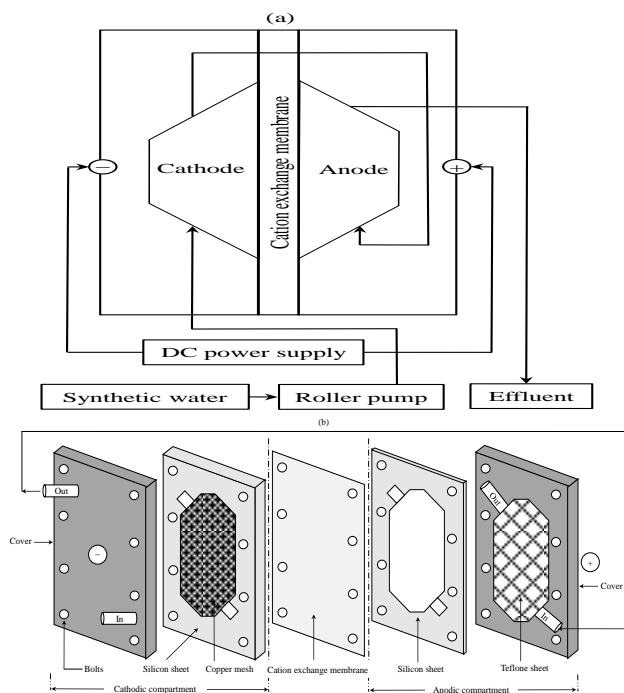

Fig. 1. (a) Experimental setup and (b) Structure of the electrolytic flow cell.

C. Experimental Procedure for Electrochemical Denitrification

Before each experimental run the positive and negative terminal of the DC power supply was perfectly connected with the anode and cathode, respectively. After that, the feed pump was switched on to feed the synthetic water into the electrolytic flow cell. Then the DC power supply was turned on for galvanostatic electrolysis. All the runs were performed

under air-conditioned room temperature at 25℃. For sampling and analysis the effluent from the anodic compartment was collected by using glass bottles. The synthetic water ingredients used for the experiments are given in the Table I. The synthetic water was fed into the cathodic compartment, and then its effluent flowed into the anodic compartment.

TABLE I: LIST OF CHEMICALS USED IN THE EXPERIMENT

Chemicals	Concentration	Function
K_2SO_4	174.25 mg/L (1 mM)	Supporting electrolyte
KNO_3	144.43 mg/L (1.42 mM)	Source of nitrate ion
NaCl	329.68 – 1318.72 mg/L (100 – 800 mg-Cl/L)	Source of chloride ion

Before each experimental operation the copper meshes were submersed into 50 mM citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) solution for 5 minutes for removing the oxide layers. Then, they were washed with deionized water for several times and used for the experiment.

D. Analytical Procedure

All the analyses were done according to the standard methods [15]. The pH and conductivity was measured by a pH meter (B-212, Horiba, Japan) and a conductivity meter (Twin cond, B-173, Horiba, Japan). The concentrations of NO_3^- and NO_2^- were determined by the ion chromatography (PIA-1000, Shimadzu, Japan) and NH_4^+ was determined by the indophenol method. Total chlorine and free chlorine was measured by a chlorine meter (HI95711, Hanna Instruments, Romania). Deionized water of conductivity less than 1 µS/cm was used for the dilution and preparation of standard solution.

III. RESULTS AND DISCUSSION

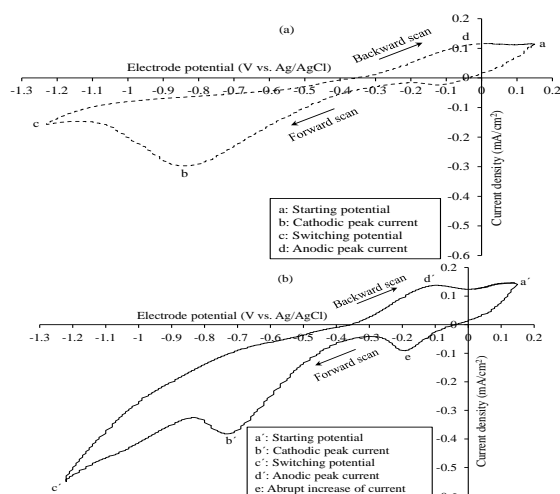### A. Cyclic Voltammetry Curve Analysis on Copper as Cathode Material

Fig. 2. Cyclic voltammograms of (a) 1mM K2SO4 and (b) 1mM K2SO4 with 1.42 mM KNO3 at the scan rate of 50 mV/s using a copper working electrode with a surface area of 1.0 cm².

Fig. 2 (a) shows the cyclic voltammogram of 1 mM K_2SO_4 at the scan rate of 50 mV/s on copper as a working electrode. The CV curve was developed in combination of the capacitive or non-faradic and faradic current. The graph in Fig. 2 (a) shows the small amount of non-faradic current which was used for the accumulation or removal of electrical charges on

the electrode and electrolyte solution near the electrode. Conversely, the faradic current higher than the non-faradic current was the result of electrochemical reactions at the electrode surface. The CV developed two peak currents at the forward and backward scan directions namely, cathodic (b) and anodic (d) peak current. On the other hand, Fig. 2 (b) shows the CV of 1mM K_2SO_4 with 1.42 mM KNO_3 under the same condition. This CV curve showed two cathodic peak currents at point e and b´. Accordingly, NO_3^- was mainly reduced by the cathodic reduction at the negative potential of -0.2 V at point e and the reduced species were thought to be stable intermediate byproducts such as NO_2^- or NH_3 [16].

Significantly, at the backward scan direction another recognizable anodic current except anodic peak current except a peak d´ was not observed, which denotes that the reduced species of NO_3^- was not reoxidized to NO_3^-. Although, Fig. 2 (a) and (b) showed the similar CV curve pattern, Fig. 2 (b) showed higher electrolytic current than Fig. 2 (a) due to higher electrical conductivity of the used electrolytic solution. In the above discussions, only one additional reduction peak (e) was observed in Fig. 2 (b). This seems to indicate one step NO_3^- reduction mechanism such as NO_3^- into NO_2^- (reaction (1)), NO_3^- into NH_3^- (reaction (2)) or NO_3^- into N_2 as follows [17]:

$$2NO_3^- + 6H_2O + 10e^- \rightarrow N_2 + 12OH^- \tag{7}$$
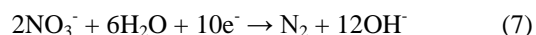
B. Influence of Volumetric Electric Charge and Flow Rate on Conversion of Nitrate to Nitrite and Ammonia

A series of electro-reduction experiments was started in the synthetic solution with 1.42 mM of KNO_3 and 1 mM of K_2SO_4 at the initial pH of about 5.5. Fig. 3 (a) shows the effect of volumetric electric charge on transformation of NO_3^- to NO_2^- and NH_3 at a constant flow rate of 20 mL/min, which was equivalent to the space velocity (SV) of 1.0 min^{-1}. Here, total nitrogen (TN) indicates the sum of NO_3^-, NO_2^- and NH_3 nitrogen concentration. The applied electrolytic current ranged from 0.10 to 2.90 A, which was equivalent to the volumetric electric charge from 300 to 8,700 C/L. At these volumetric electric charges the main reduced intermediate products were found to be NO_2^- and NH_3 [16]. The enhancement of NO_3^- reduction with the increase in volumetric electric charge was observed at 300, 1,500 and 2,700 C/L where NO_3^- concentration was measured 1.18, 0.92 and 0.71 mM, respectively. This result indicates that 17% of the initial NO_3^- was reduced at 300 C/L, 35% at 1,500 C/L and 50% at 2,700 C/L.

An increase in the reduction rate of NO_3^- at the higher electrolytic current was reasonable, since the electrochemical reduction rate depends on the electrolytic current under the electron transfer-controlled condition. In fact this assumption was true for the volumetric electric charge of 300 to 2,700 C/L and intensely supports that NO_3^- reduction increase with the increase in supplied electric charge within the specific range [18]. However, the NO_3^- reduction rate was unchanged from the volumetric electric charges of 2,700 to 8,700 C/L. In this case it can be supposed that excess electric charges applied were consumed for hydrogen evolution at the cathode and the hydrogen adsorbed on the cathode affected the NO_3^-

reduction process [19], [20]. On the other hand, NO_2^- concentration remained a constant at the volumetric electric charge from 300 C/L to 2,700 C/L, which was found to be 0.29 mM. In the higher electric charge range NO_2^- concentration gradually decreased with the increase in volumetric electric charges. It can be presumed that hydrogen evolution could play an important role in the cathodic reduction of NO_3^-. The hydrogen evolution hindered the transformation of NO_3^- to NO_2^-, though did not play any inhibition role in NH_3 formation from NO_3^- [12].
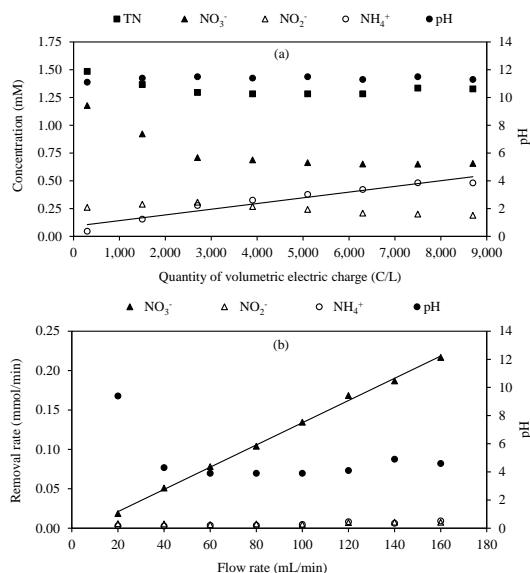

Fig. 3. Effects of (a) volumetric electric charge and (b) flow rate on transformation of NO_3^- to NO_2^- and NH_3. The flow rate was set at 20 mL/min (SV: 1.0 min^{-1}) for Fig. 3 (a) and the volumetric electric charge was fixed at 1,500 C/L for Fig. 3 (b).
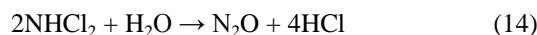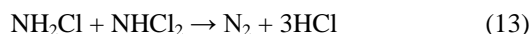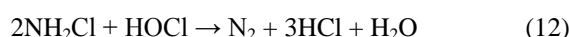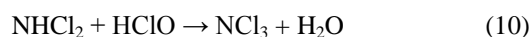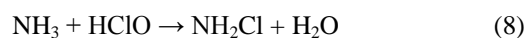
A clear linear relationship between NH_3 formation and the volumetric electric charge was observed ($R^2 = 0.934$) in Fig. 3 (a) which supports the above discussion. The pHs of all treated solutions increased from about 5.5 to about 11.5. This was happened mainly due to the reactions forming hydroxide ions (OH^-) during the electrochemical reduction of NO_3^- (equations (1) and (2)). The high pH along with almost constant TN concentration of electrolyzed effluent water recommends that NO_3^- was mainly transformed into NO_2^- and NH_3 according to the equations (1) and (2) in the cathode chamber [6].

Fig. 3 (b) shows the effect of flow rate on NO_3^- removal rate and formation rates of NO_2^- and NH_3 at the volumetric electric charge of 1,500 C/L. These experiments were also conducted using the same synthetic solution in Fig. 3 (a). From Fig. 3 (b) it is observed that the NO_3^- removal rate was linearly increased with the increase in flow rate at the R^2 value of 0.998. This phenomenon can be ascribed to the enhancement of the mass transfer processes.
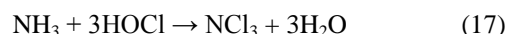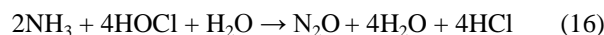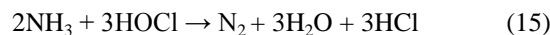
C. Influence of Chloride Ion Concentration on Reduction of Nitrogenous Compounds

Fig. 4 (a), (b), (c) and (d) shows the variation of TN, NO_3^-, NO_2^-, NH_3 and chloramines concentration after electrolysis with the presence of different dozes of NaCl (Table I). Here, TN indicates the sum of NO_3^-, NO_2^-, NH_3 and chloramines nitrogen concentration. All of these experiments were performed with 1mM K_2SO_4, 1.42 mM KNO_3 and varied Cl^-
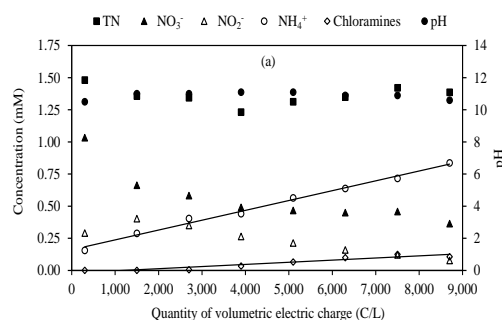
concentration of 100, 200, 400 and 800 mg/L, respectively. In addition, Fig. 5 (e) and (f) shows the NH_3 and chloramines concentration in the same effluent at Cl^- concentration of 400 and 800 mg/L at the adjusted pH 5, 7 and 9 respectively. The effluent pH was adjusted by adding the buffer solution of 100 mM sodium bicarbonate ($NaHCO_3$) with sulfuric acid (H_2SO_4). It is well known that Cl^- is converted into active Cl_2 through an anodic reaction according to the equation (5) [20]. After that, the produced Cl_2 rapidly hydrolyses to HOCl according to the equation (6) [21]. Next, the water containing NH_3 or other nitrogenous substances react with HOCl and typically formed chloramines, namely monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine or nitrogen trichloride (NCl_3) depending on the pH, temperature, reaction time and other surrounding environmental conditions according to the equations (8-10). And finally, chloramines are oxidized into N_2 or N_2O according to the equations (15) and (16) [10].

$$NH_3 + HClO \rightarrow NH_2Cl + H_2O \tag{8}$$

$$NH_2Cl + HClO \rightarrow NHCl_2 + H_2O \tag{9}$$

$$NHCl_2 + HClO \rightarrow NCl_3 + H_2O \tag{10}$$

$$2NH_2Cl \rightarrow NHCl_2 + NH_3 \tag{11}$$

$$2NH_2Cl + HOCl \rightarrow N_2 + 3HCl + H_2O \tag{12}$$

$$NH_2Cl + NHCl_2 \rightarrow N_2 + 3HCl \tag{13}$$

$$2NHCl_2 + H_2O \rightarrow N_2O + 4HCl \tag{14}$$

The above equations can be summarized as follows:

$$2NH_3 + 3HOCl \rightarrow N_2 + 3H_2O + 3HCl \tag{15}$$

$$2NH_3 + 4HOCl + H_2O \rightarrow N_2O + 4H_2O + 4HCl \tag{16}$$

$$NH_3 + 3HOCl \rightarrow NCl_3 + 3H_2O \tag{17}$$

From Fig. 4 (a) and (b) it is observable that NO_3^- was transformed into NO_2^- and NH_3 in the similar trend, where NH_3 and chloramines were accumulated with an increase in volumetric electric charge. However, addition of small amount of Cl^- (100 mg/L and 200 mg/L) did not show any significance decrease in TN. Form Fig. 4 (c) it is observable that NH_3 was enhanced with the increase in volumetric electric charge within the range of 300 to 2,700 C/L and it gradually decreased over 2,700 C/L.
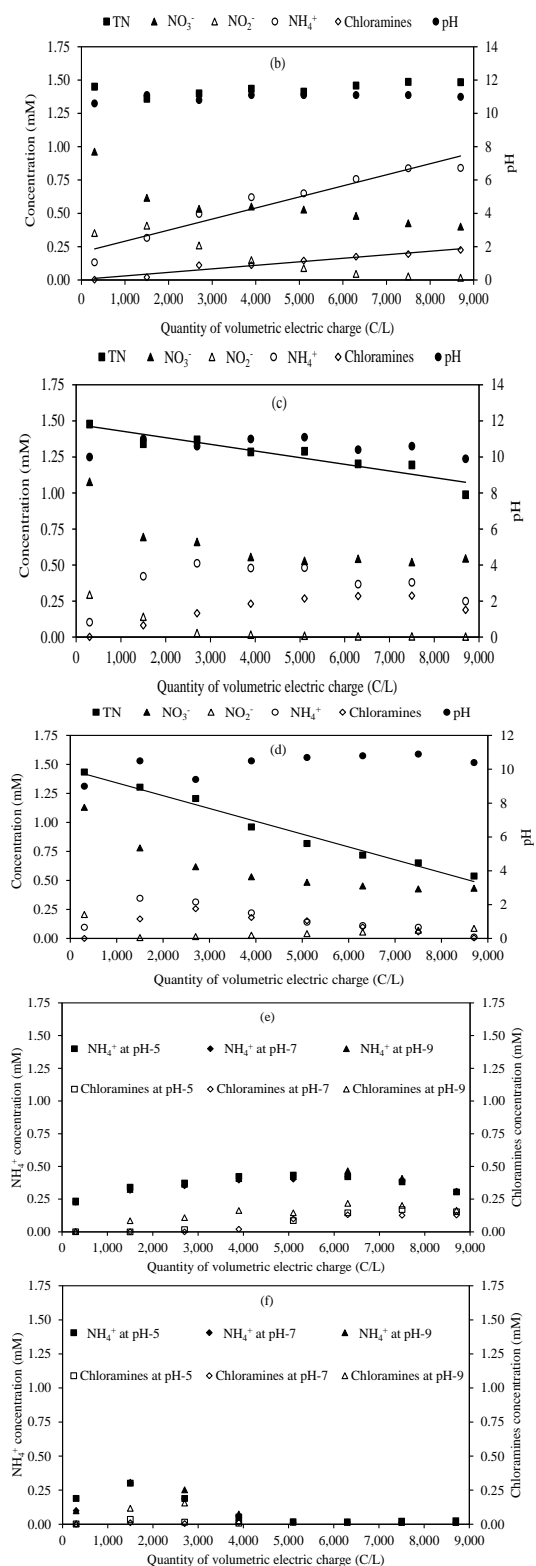
Fig. 4. Variation of TN, NO_3^-, NO_2^-, NH_3 and chloramines concentration in the effluent at (a) Cl- concentration of 100 mg/L, (b) Cl- concentration of 200 mg/L, (c) Cl- concentration of 400 mg/L and (d) Cl- concentration of 800 mg/L, (e) NH3 and chloramines concentration in the same effluent at Cl-concentration of 400 mg/L at pH 5, 7 and 9, (f) NH3 and chloramines concentration in the same effluent at Cl- concentration of 800 mg/L at pH 5, 7 and 9.

The chloramines concentration were increased gradually within the volumetric electric charge of 300 to 7,500 C/L but it decreased at the volumetric electric charge of 8,700 C/L, where TN also dropped. This result indicates that chloramines were oxidized at 8,700 C/L. From Fig. (e) it is found that when the effluent pH was adjusted at 5, 7 and 9 it showed the

similar results like Fig. (c). Here, it could be considered that the reaction rate of Cl_2 with NH_3 over 2,700 C/L exceeded the production rate of chloramines.

Then the chloramines produced was removed by the break-point chlorination mechanism and TN gradually decreased [22]. From Figure 4 (d) it is also observable that NH_3 accumulation rate was enhanced with the increase in volumetric electric charge within the range of 300 to 1,500 C/L and it gradually decreased with the volumetric electric charge over 1,500 C/L. The complete consumption of NH_3 was observed at the volumetric electric charge of 8,700 C/L. The formation of chloramines were increased from the volumetric electric charge of 300 to 2,700 C/L and it followed the similar trend like NH_3 over 2,700 C/L. Finally, TN decreased linearly with the increase in volumetric electric charge at the R^2 value of 0.978. At the volumetric electric charge of 8,700 C/L the TN was 0.54 mM that was composed of NO_3^-, NO_2^-, NH_4^+ and chloramines with the concentrations of 0.43, 0.09, 0.01 and 0.01 mM, respectively.

Moreover, from Fig. (f) it is found that when the effluent pH was adjusted at 5, 7 and 9 the NH_4^+ and chloramines were complete oxidized at the volumetric electric charge of 5,100 C/L at pH 7.These results confirm that the appropriate amount of Cl- lead sufficient amount of HOCl production, which could oxidize the NH_3 and other byproduct presumably into N_2 [9]. Also, it should be noted that the NH_3 formation rate increased with the increase in volumetric electric charges as shown in Figure 3 (a). On the other hand, the enhancement of NH_3 removal under higher current densities is that higher current density increased the anodic potential, which is favorable to electrochemical generation of Cl_2, because the standard potential of reaction [5] (1.36 V vs. SHE) is higher than that of the anodic oxidation of water (1.23 V vs. SHE). The electrode potential of anodic oxidation of Cl- can be described by the following Nernst's equation.

$$E = E^0 - \frac{RT}{2F} \ln \frac{a^2_{Cl^-}}{p_{Cl_2}} \quad (18)$$

where, E is an electrode potential [V], E^0 is the standard potential [V], R is the gas constant (8.314 J K^{-1} mol^{-1}), T is an absolute temperature [K], a_{Cl^-} is an activity of Cl- [M], and p_{Cl2} is the partial pressure of Cl- [atm]. Since, a_{Cl^-} is positively related to Cl- concentration, an increase in Cl- concentration results in a decrease in E, which can promote the anodic oxidation of Cl- into Cl_2. Thus an increase in electric charge and Cl- concentration produced a larger amount of HOCl, which enhanced the oxidization of NH_3. The initial influent pH of the electrolytic solutions were within the range of 5.5 to 6.5 but in all cases the effluent pH after electrolysis were increased into the range of 9 to 12. This result was thought to be due to the enhancement of equations (1) and (2) as already discussed using data in Fig. 3 (a) [2], [23], [24].

D. Effect of Electrochemically Produced Chlorine to Occur Break-point Chlorination on Ammonia Nitrogen Removal

Fig. 5 (a), (b), (c) and (d) shows the variation of total Cl_2, free Cl_2 and combined Cl_2 concentration after electrolysis

with the presence of different dozes of NaCl (Table I). When Cl^- is added to water, it generates HOCl. Since, HOCl is a weak acid, the following chemical equilibrium is established.

$$HOCl \leftrightarrow H^+ + OCl^- \qquad (19)$$
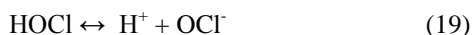
In general, HOCl and OCl^- both species altogether are known as free chlorine. These two species exist in an equilibrium condition that is pH dependent. This equilibrium situation is also slightly affected by the temperature. As the pH increases, the ratio of HOCl to OCl^- decreases. Since the pKa of HOCl is 7.5 HOCl is the dominant species below pH 7.5 and OCl^- is the dominant species above pH 7.5 [24]. The stoichiometric weight ratio of free chlorine as Cl_2 to NH_3 as N is 5.1 for NH_2Cl formation (equation (8)). After NH_2Cl formation, $NHCl_2$ forms when additional Cl_2 is added (equation (9)). The formation rates depend on pH, temperature and mixing condition [25]. Similarly, NCl_3 forms when additional chlorine reacts with $NHCl_2$ (equation (10)). The sum of the combined and free chlorine in a sample is known as total chlorine. Combined chlorine includes chloramines of NH_2Cl and $NHCl_2$. From Fig. 5 (a), (b), (c) and (d) it is clearly observable that total Cl_2 increased linearly with the increase in volumetric electric charge at the R^2 value of 0.951, 0.967, 0.917 and 0.980, respectively. At the Cl^- concentration of 100 and 200 mg/L the free Cl_2 production amount was found less than the combined Cl_2. Similarly, at the Cl^- concentration of 800 mg/L free Cl_2 was less than the combined Cl_2 from the volumetric electric charge of 300 to 2,700 C/L, but free Cl_2 gradually increased and combined Cl_2 gradually decreased over 2,700 C/L. In addition, Fig. (e) and (f) shows the total Cl_2, free Cl_2 and combined Cl_2 concentration in the effluent at Cl^- concentration of 400 mg/L and 800 mg/L at the adjusted pH 5, 7 and 9 respectively. Where free Cl_2 was found at pH 9. Fig. 6 (a) shows the production of free Cl_2 at different dozes of NaCl without KNO_3 addition. From Fig. 6 (a) it is clearly observed that the free Cl_2 production rate at the Cl^- concentration of 100, 200, 400 and 800 mg/L was linearly increased with respect to the volumetric electric charge at the R^2 value of 0.989, 0.958, 0.988 and 0.981, respectively. This results mean that the current efficiency for Cl_2 production did not depend on the volumetric electric charge. On the contrary, the current efficiency increased with the rise in Cl^- from 0.4% for 100 mg-Cl^-/L to 6.1% for 800 mg-Cl^-/L. Thus, Cl^- concentration had a strong influence on Cl_2 production at the anode. When Cl_2 consumption for TN removal is estimated by subtraction of the residual free Cl_2 and 1.5 times of chloramines in Fig. 5 from the produced free Cl_2 in Fig. 6 (a), the relationship between TN removal and Cl_2 consumption in the case of Cl^- concentration of 400 and 800 mg/L is plotted in Fig. 6 (b).
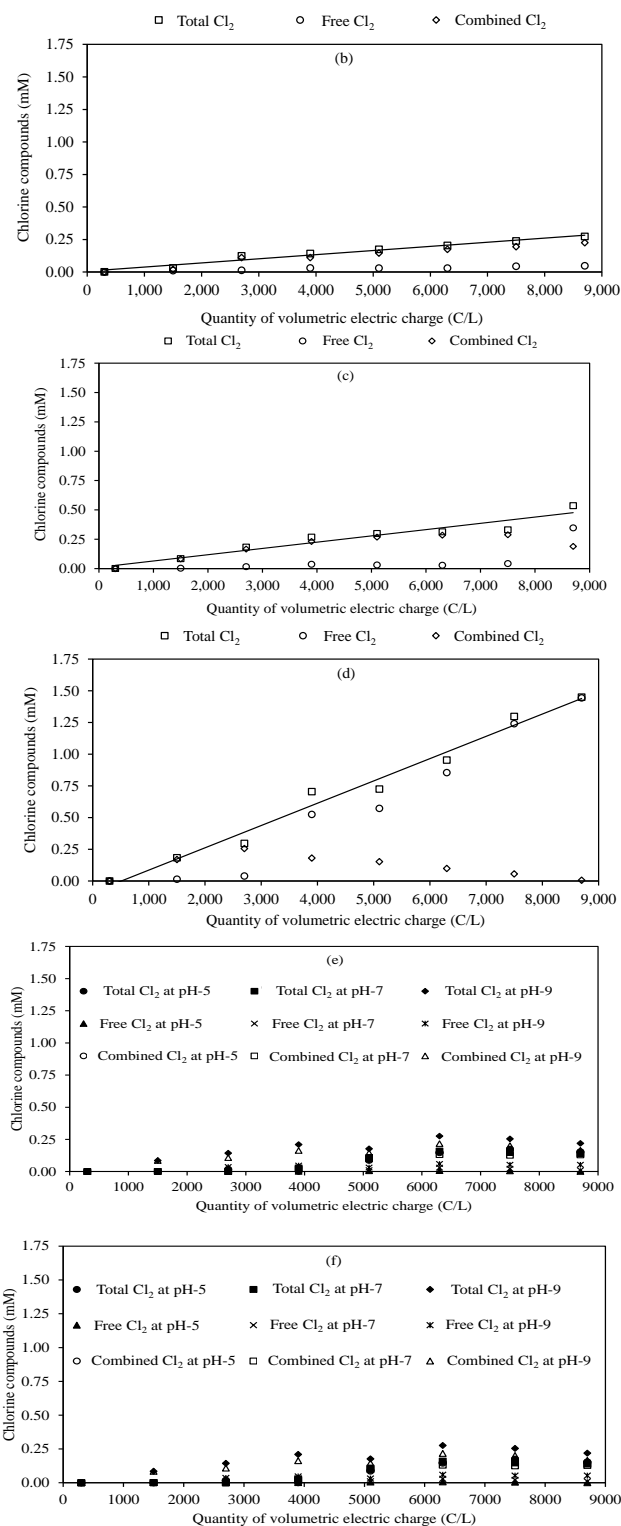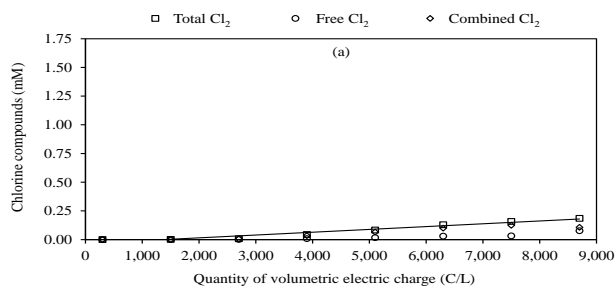

Fig. 5. Variation of total Cl_2, free Cl_2 and combined Cl_2 concentration in the effluent at (a) Cl- concentration of 100 mg/L, (b) Cl- concentration of 200 mg/L, (c) Cl- concentration of 400 mg/L and (d) Cl- concentration of 800 mg/L, (e) total Cl_2, free Cl_2 and combined Cl_2 concentration in the effluent at Cl- concentration of 400 mg/L at pH 5, 7 and 9, (f) total Cl_2, free Cl_2 and combined Cl_2 concentration in the effluent at Cl- concentration of 800 mg/L at pH 5, 7 and 9.

The slope of the regression line was 0.783 mM-N/mM-Cl_2, which is equivalent to the molar ratio of Cl_2 consumption to TN removal of 1.28. Based on the equations (15) and (16), the theoretical molar ratio of chlorine to NH_3 is projected to be 1.5 for N_2 evolution and 2 for N_2O evolution. Although the observed molar ratio was slightly smaller than the theoretical molar ratio due to the uncertainty of estimation of Cl_2

consumption for chloramine accumulation, it was close to the theoretical molar ratio for N_2 evolution. Therefore, the main TN removal pathway in this study was inferred to be the N_2 evolution as shown in equation [15].
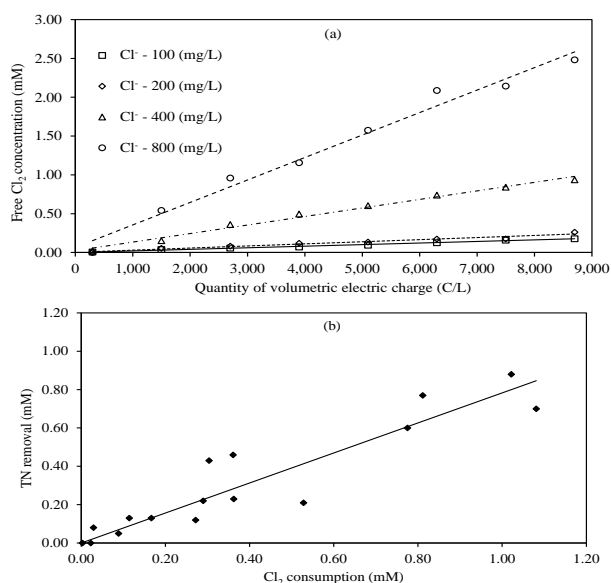

Fig. 6. (a) Production of free Cl_2 without addition of NO_3- at different Cl-concentration. The test solution contained 1mM of K_2SO_4 as a supporting electrolyte and (b) relationship between TN removal and Cl_2 consumption at Cl- concentration of 400 and 800 mg/L. The Cl_2 consumption was corrected by the residual free Cl_2 and residual chloramines.

IV. CONCLUSION

In order to develop the method of electrochemical removal of NO_3^-, a two-compartment electrochemical flow cell with copper mesh cathode and Ti/Pt anode was developed and its performances was evaluated using synthetic water containing 1.42 mM of NO_3^-. The effects of volumetric electric charge, flow rate and Cl^- concentrations were demonstrated in this study, in which the volumetric electric charge was regulated by the change in electrolytic current. The volumetric electric charge enhanced both NO_3^- reduction to NH_3 and anodic production of Cl_2, but it did not change the current efficiency. The flow rate also enhanced the electrochemical reactions due to the promotion of mass transfer process. The Cl^- concentration improved the current efficiency of Cl_2 production. As a result, TN removal was accelerated via the break-point chlorination mechanism, in which the N_2 evolution pathway was thought to be main pathway of TN removal in this study. However, the current efficiency remained a low level; only 6.1% at Cl^- concentration of 800 mg/L. In spite of the low current efficiency, 1.42 mM of initial NO_3^- was decreased to 0.43 mM without NH_3 and NO_2^- accumulation during 1.0 minute contact time for NO_3^- reduction and 15 seconds contact time for Cl_2 production at the volumetric electric charge of 5,100 C/L, flow rate of 20 mL/min, Cl^- concentration 800 mg/L at pH 7. As a consequence, this research provide a feasible foundation for the rapid removal of nitrate from water streams. However, further studies will be required for a practical application of this technique such as developing highly catalytic electrode materials and exploring the efficiency of pH control on the electrochemical denitrification.

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