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Fabrication and Characterization of Cu/Ti Bilayer Nanoelectrode for Electrochemical Denitrification

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A novel Cu/Ti bilayer nanoelectrode was fabricated to improve electrochemical nitrate removal rate. The Cu/Ti bilayer nanoelectrode was fabricated by plating Cu on Ti nanoelectrode. In the Cu/Ti bilayer nanoelectrode, Ti nanostructure of the electrodes surface can increases the specific surface area, meanwhile Cu present high electrocatalytic activity for nitrate reduction. Using the Cu/Ti bilayer nanoelectrode, the nitrate concentration decreased from an initial concentration of 50.0 mg/L to 14.1 mg/L in the presence of 0.50 mg/L Na_2SO_4 after 90 min electrolysis (nitrate removal efficiency of 71.8%). Under the current conditions, the removal efficiency of the Cu/Ti bilayer nanoelectrode was 254.6% compared with that of the Ti nanoelectrode for electrochemical denitrification. SEM images illustrated the Cu/Ti bilayer nanoelectrode is a honeycomb structure with Sponge deposit on it. The XRD results showed the Cu/Ti bilayer nanoelectrode were dominated by Ti, Cu and O. For the same initial nitrate concentration, the nitrate removal rate increased sharply with increasing current density. In the presence of NaCl, especially with IrO_2 anode, a novel condition for performing both cathodic reduction of nitrate and anodic oxidation of the nitrite and ammonia by-products was achieved with high removal efficiency. Using the IrO_2 anode nitrate could be completely removed. In the treated solution, little amount of ammonia was detected

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Keywords: Nanoelectrode, Nitrate reduction, Electrochemical denitrification, removal rate, electrolytic reduction

1. INTRODUCTION

Pollution of water resources by nitrate is a serious and wide spread problem [1]. Major anthropogenic sources of nitrate are associated to industrial wastewater, domestic sewage, waste liquid infiltration as well as animal wastes and nitrogen fertilizer [2-4]. Nitrate in potable water may cause methemeglobmenia in infants, and it is a possible cancer risk with long-term exposure [5]. The maximum contaminant level in drinking water and wastewaters is 45 mg/l in the United States, while in the European Union this level is 50 mg/l for adults and 15 mg/l for infants [6,7]. Various technologies and methods for removal of nitrate from drinking water have been proposed, such as physicochemical, biological and chemical [8-12]. Biological method has various disadvantages such as it need a long time to react, difficult to control, react incomplete will release of NO_2, N_2O and NO_x, produced a large number of biological sludge, requires a constant supply of the organic substrate. This limits the biological removal of nitrate application [13-17]. The physicochemical processes mainly include distillation, reverse osmosis [18-21], electrodialysis, ion exchange [22-23], it would produce secondary wastes, because the nitrates are just separated but not destroyed [8]. The chemical methods produce toxic byproducts, such as ammonia and nitrite and require either large quantities of metals or hydrogen as reducing agent, which is a difficult and unsafe to handle gas [4].

Among these methods electrochemical reduction of nitrate is a promising route. The electrochemical methods are superior due to the use of clean reagents i.e., electrons [11]. Generally, electrochemical methods offer such advantages as short of the requirement for chemicals before or after the treatment, environmental compatibility, energy efficiency [24], no sludge production, small area occupied by the plant and relatively low investment costs [25]. The commercial application of nitrate reduction by electrochemical techniques is underway. The mechanism for the nitrate removal is complex, from the current-voltage curve the steps were developed, and shown below [5]:

$$NO_3^- + H_2O + 2e^- = NO_2^- + 2OH^- \quad (1)$$

$$NO_3^- + 3H_2O + 5e^- = (1/2)N_2 + 6OH^- \quad (2)$$

$$NO_2^- + 5H_2O + 6e^- = NH_3 + 7OH^- \quad (3)$$

$$NO_2^- + 4H_2O + 4e^- = NH_2OH + 5OH^- \quad (4)$$

$$2NO_2^- + 4H_2O + 6e^- = N_2 + 8OH^- \quad (5)$$

$$2NO_2^- + 3H_2O + 4e^- = N_2O + 6OH^- \quad (6)$$

$$NO_2^- + H_2O + e^- = NO + 2OH^- \quad (7)$$

$$N_2O + 5H_2O + 4e^- = 2NH_2OH + 4OH^- \quad (8)$$

$$2H_2O + 2e^- = H_2 + 2OH^- \text{(sidereaction)} \quad (9)$$

However, electrochemical methods have some disadvantage such as slow reaction rate, high running costs [26]. Overall nitrate reduction efficiency depends on the active surface area of the working electrode, flow rate, operating voltage, etc [27]. As the electrode material plays an important role in nitrate reduction [8], we have to improve the electrode or invent a more efficient electrode. The electrode material must be readily available and should have sufficient electrocatalytic activity, suitable mechanical properties, and selectivity to N_2 as the final product [28]. Various electrodes [29-33] including metals, alloys, adatoms, metal complexes and diamond, have already been discussed for nitrate reduction [23]. Among these, Cu was found to have a significant effect on the electrochemical reduction of nitrate ions, and it was shown to be the high efficient electrocatalyst concerning the rate of the nitrate reduction [23]. Ti is a nontoxic metal and so is suitable for groundwater water treatment [34].

Nanostructured materials often exhibit unique performance compared to the bulk materials [35-36]. Nanomaterials have received much attention because of their high activity and large specific surface area. The use of high reduction activety elements such as Cu with nano structure as electrodes may therefore be efficient for the reduction of nitrate. To our knowledge, use of bilayer nanoelectrodes for electrochemical reduction of nitrate has not been reported previously.

In this study, we prepared Cu/Ti bilayer nanoelectrodes and investigated their performance for the reduction of nitrate. We developed a fabrication method for the nanoelectrode and optimized this method. The removal mechanism and experimental conditions were also investigated. The aim of this study is to achieve highly efficient removal of nitrate using non-toxic nanomaterials.

2. MATERIALS AND METHODS

2.1. Materials and chemicals

A cylindrical electrochemical cell was designed with a networking volume of 100 mL. The electrolysis cell was manufactured by acryl plates with two outer flakelet for the electrodes assembled.

Chemicals used in this study include: HCl, Acetic acid, HF, H_2SO_4, NH_2SO_3H, $CuSO_4•5H_2O$, NaSO4. Solutions were prepared with reagent grade chemicals and deionized water. Fresh electrolyte was parepared for each electrolysis [37]. Solutions and chemicals identical in the present study. All solutions were prepared using deionised water (AR2-100L-P00, Aquapro International Company LLC., USA).

2.2. Electrode

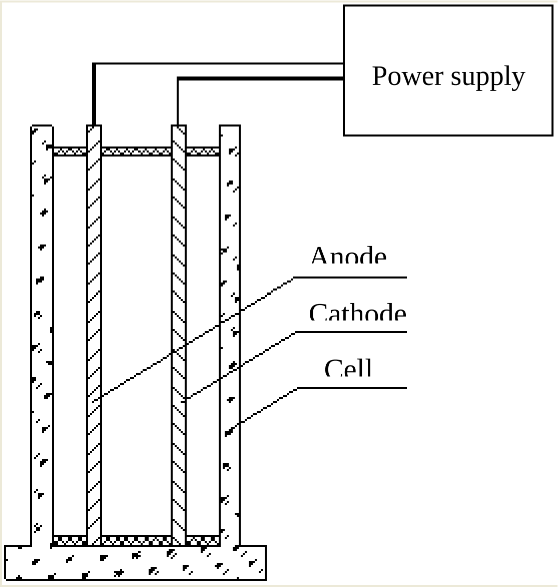


Figure 1. Schematic diagram of electrochemical apparatus.

A 100-mL electrolysis cell (Fig. 1) was fabricated using acryl material. To fabricate the nanoelectrode, graphite was used as the cathode and Ti was used as the anode. To fabricate the double-layer nanoelectrode with Cu plated on Ti, Ti was used as the cathode and Cu was used as the anode. For reduction of nitrate in aqueous solution using the double-layer nanoelectrode, Ti was used as the cathode and Pt was used as the anode. All of these electrodes were with a dimension of 2.5 cm wide, 2 mm thick and 10 cm high.

2.3. Methods

2.3.1. Electrode fabrication

The typical roughness factor of the electrode surface was in the range 1.3–1.6. Prior to the experiment, the surface of the anode was mechanically polished with 800–1200 SiC metallographic paper and washed several times with deionized water. The fabrication is divided into two steps.

Step a: 100 mL solution which contains acetic acid (1:10) and 0.05 wt.% HF were poured in 100 mL electrolysis cell. The process was performed at room temperature. Voltage was set to 25 V and the experiment lasted for 2 h. 2 hours later, Ti nanoelectrode was completed.

Step b: The middle layer is Cu catalytic layer. Cu catalytic layer were deposited on the surface of the Ti nanoelectrode, which is completed in step a. It was necessary to ensure that only Cu was present on the nanoelectrode surface. To load Cu on the Ti nanoelectrode, Cu was electrodeposited from a 180 g/L $CuSO_4$ solution in 60 g/L H_2SO_4 at a deposition current of 0.15 A and quiescent conditions for 10 s. After these, Cu/Ti bilayer nanoelectrode is completed.

2.3.2. Nitrate Removal

In our study, the initial concentration of 50 mg/L of nitrate were prepared in advance. 100mL nitrate solution was poured into electrolytic cell, reaction started with the current density of 30 mA/cm^2. In order to raise the conductivity, 0.5 g/L Na_2SO_4 was added into all the experiments. At different intervals, 1.0mL of sample was drawn from the electrolytic cell. The sample is monitored and analyzed as a function of time. The sample is monitored and analysed as a function of time. Before sample analysis, added 0.5 ml of HCl and 0.05 ml of amino sulfonic acid, and then use spectrophotometer to analyse samples.

The electrolysis was ceased when 90 min elapsed. The desired pH using dilute NaOH (0.1 and 0.01 N)/H_2SO_4 (0.1 and 0.01N) solutions.

Effect of different current densities were investigated at 10, 20, 30, 50mA/cm^2. In order to investigate the effect of temperatures, experiments were performed at 0 ◦C kept on ice bath and at 25, 40 and 60 ^{0}C kept on water bath.

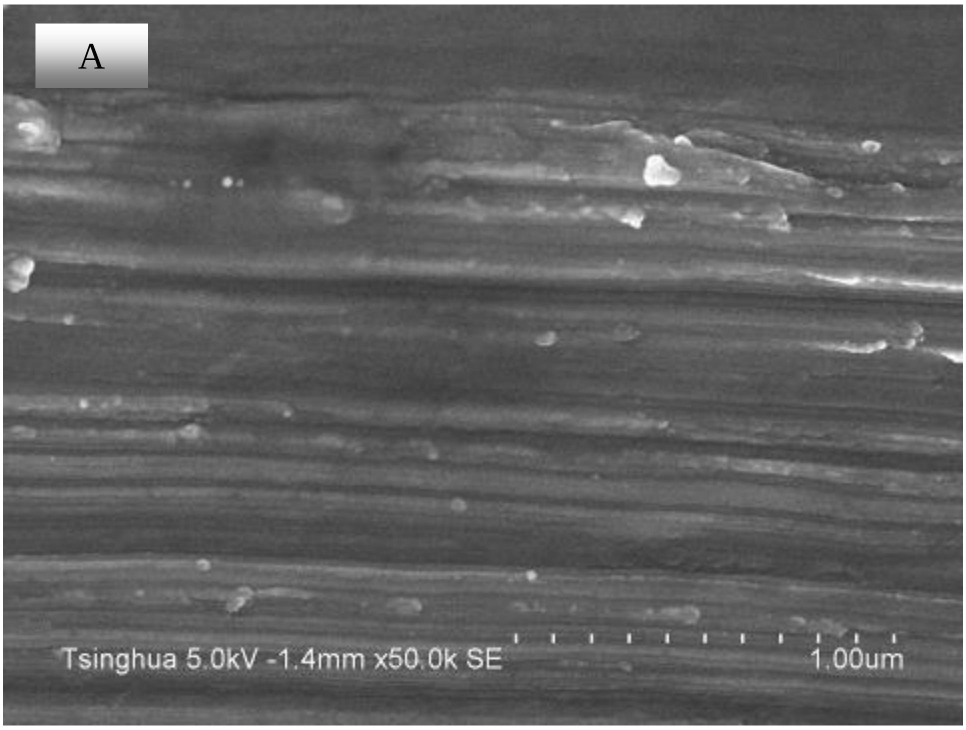
2.3.3. Analysis method

The determination of nitrate, nitrite and ammonia were based on its light absorption at 220-275 nm. Samples were absorbance of solution was measured by spectrophotometer (HACH DR/6000, USA). The microstructure and morphology of electrodes are analysed by field-emission scanning electron microscopy (SEM) (Hitachi S5500, Japan) and energy dispersive spectroscopy (EDS) (Hitachi S5500, Japan).

3. RESULTS AND DISCUSSION

3.1. Cu/Ti bilayer nanoelectrode fabrication

Fig. 2 show scanning electron microscopy (SEM) images of the Ti electrode, Ti nanoelectrode, and Cu/Ti double-layer nanoelectrode, respectively. Fig. 2 (A) shows that the Ti surface is smooth. Fig. 2 (B) shows that the Ti nanoelectrode is a loose honeycomb configuration with numerous micropores. Fig. 2 (C) shows that the Cu/Ti double-layer nanoelectrode is a multi-hole structure with thick and smooth hole walls. In order to verify the three different electrode for nitrate removal rate, we use three different kinds of electrodes to do experiment under different conditions. Fig. 3 shows the nitrate removal rate for the different electrodes. It can be seen from Fig.3 that the lowest removal rate of nitrate was Ti electrode, the removal rate of the Ti nanoelectrode was slightly increased, the highest removal efficiency was attained using the Cu/Ti double-layer nanoelectrode with I = 0.15 A and t_P = 10 s. The nitrate removal rate increased with treatment time in all cases, the rate was 21.3%, 28.3% and 71.8% in 90min by Ti, Ti nano, and Cu/Ti bilayer cathodes, respectively.



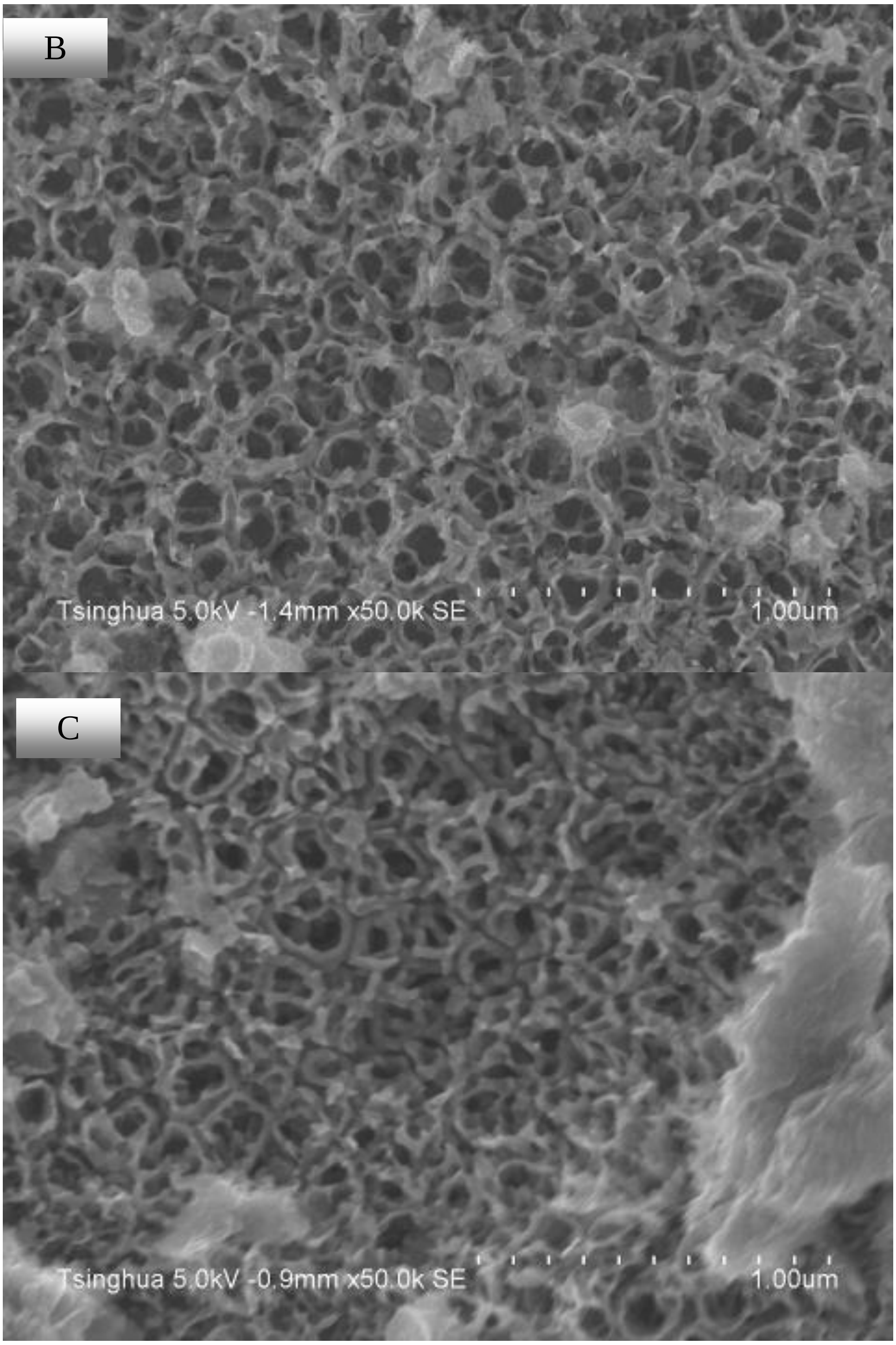


Figure 2. Scanning electron microscopy images of the (A) Ti electrode surface, (B) Ti nanoelectrode surface, and (C) Cu/Ti bilayer nanoelectrode surface

According to the results obtained by Dash et al. [38], using aluminum and iron as electrodes, it showed 70 – 97% nitrate reduction, while with graphite electrode the removal was only 8%. All electrodes were made to maintain an immersed electrode face area of 16 cm^2 inside the cell. All reactor dimensions were 12 cm long, 10 cm wide and 19 cm high. It also has been reported [4] that with alloy Sn85Cu15, Zn, Al, and Pb electrode, the nitrate reduction was 35.3%,61.0%, 88.6% and 55% , respectively. In this study, applied voltage was -2.0 V, -1.5V, -1.8V and -2.0V and electrolysis time is 12 h.

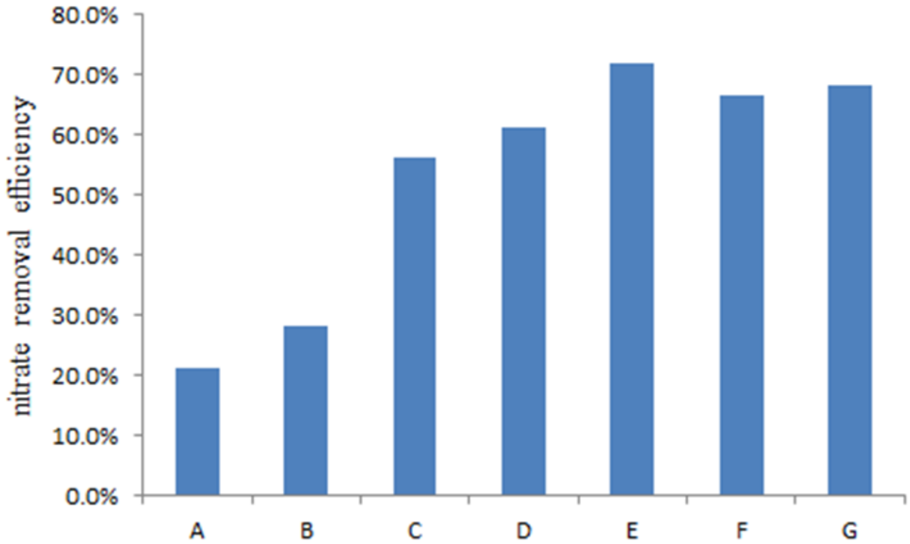
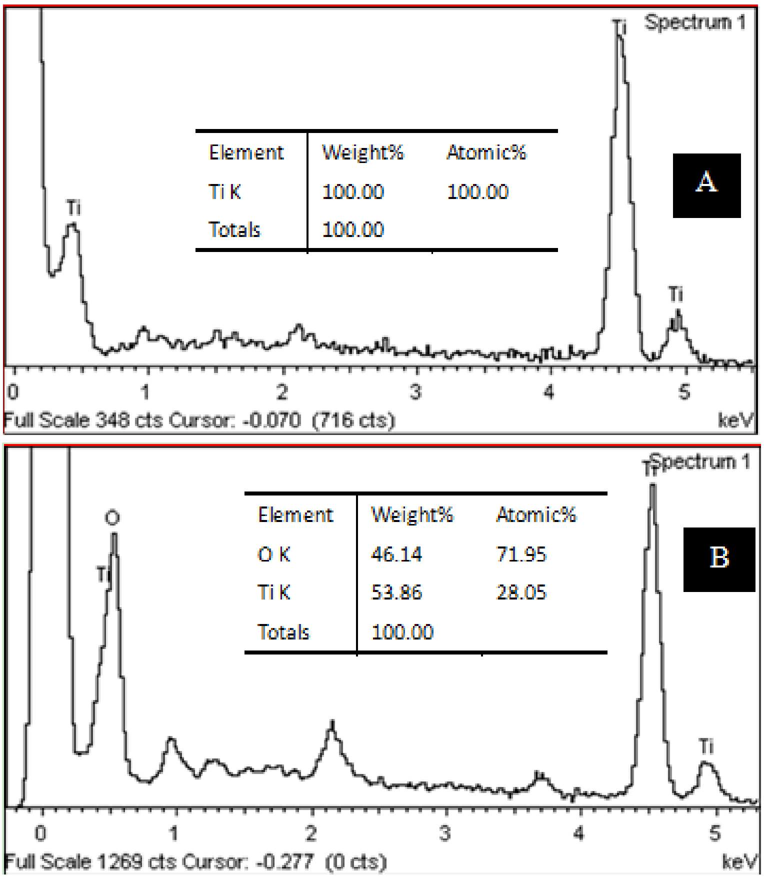
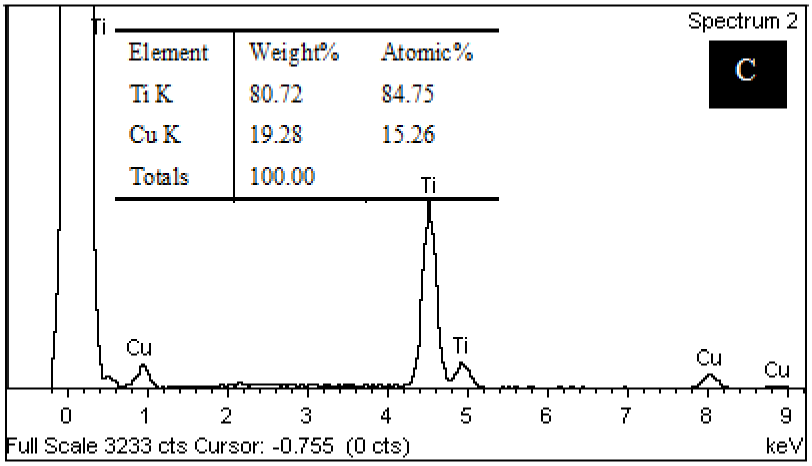


Figure 3. Removal rates achieved using (A) the Ti electrode, (B) the Ti nanoelectrode, and (C) the Cu/Ti nanoelectrode (plating Cu: 0.10 A for 90 s), (D) the Cu/Ti nanoelectrode (plating Cu: 0.15 A for 30 s), (E) the Cu/Ti nanoelectrode (plating Cu: 0.15 A for 10 s) , (F) the Cu/Ti nanoelectrode (plating Cu: 0.20 A for 60 s), and (G) the Cu/Ti nanoelectrode (plating Cu: 0.30 A for 30 s).



Element	Weight%	Atomic%
Ti K	100.00	100.00
Totals	100.00	

Element	Weight%	Atomic%
O K	46.14	71.95
Ti K	53.86	28.05
Totals	100.00	



Element	Weight%	Atomic%
Ti K	80.72	84.75
Cu K	19.28	15.26
Totals	100.00	

Figure 4. Energy dispersive spectra showing the elemental compositions of the (A) Ti electrode, (B) Ti nanoelectrode, and (C) Cu/Ti bilayer nanoelectrode

We found that the Cu/Ti bilayer electrodes actually had the very big enhancement for nitrate removal rate, in order to verify the presence of Cu element, we further do the EDS (energy dispersive spectroscopy) analysis. Fig 4 show EDS spectra of the Ti electrode, Ti nanoelectrode, and Cu/Ti bilayer nanoelectrode, respectively. From Fig. 4 (A), the Ti electrode contains 100 wt.% Ti. From Fig. 4 (B), the Ti nanoelectrode contains 53.86 wt.% Ti and 46.14 wt.% O. From Fig. 4 (C), the Cu/Ti double-layer nanoelectrode contains 80.72 wt.% Ti, and 19.28 wt.% Cu.

The reason why the Cu/Ti bilayer nanoelectrode with $I = 0.15$ A and $t_P = 10$ s has highest nitrate removal rate in all of these electrode was assuming to be as follows: Ti shows little activity for reduction of nitrate. The first series of experiments was performed using a nitrate solution without the addition of a copper layer to the Ti nanoelectrode. However, nitrate reduction proceeded with low efficiency.

Cu was added in the experiment, which results in increase the desired catalytic properties of constituent material for nitrate reduction. Cu is known to be a better promoter for electrochemical nitrate reduction compared with other coinage metals like gold and silver. Nitrate ions are able to adsorb on the surface of the Cu cathode and Cu can rapidly provide the electrons for nitrate reduction, so nitrate is rapidly reduced on the cathode.

The existence of a limiting value of the nitrate concentration is because of gradual deactivation of the cathode surface. Only a few compounds can decrease the electrocatalytic activity by forming on the electrode surface during cathodic polarization of the Ti electrode in the solution used in this study. It is thought that active sites on the cathode surface are preferentially occupied by adsorbed hydrogen molecules, which inhibits nitrate reduction. This does not correspond to our view of the formation of a thick layer of particles on the cathode surface. The addition of Cu ions to the treated solution in the form of $CuSO_4 \cdot 5H_2O$ was found to be more suitable to prevent deactivation of the cathode. The effect of Cu ions can be explained by slow continuous Cu deposition on the cathode surface. The deposited copper forms new active sites on the cathode surface, and thus maintains the electrocatalytic activity independently of the electrolysis duration. To verify that the increase in the current efficiency of cathodic nitrate reduction by Cu ion addition is caused not only by the formation of a porous surface layer but also by a corresponding increase in the surface area, a series of experiments with aqueous solutions without Cu addition was performed using a cathode that was previously activated by electrolysis in an electrolyte with added Cu ions.

3.2. Performance of nitrate reduction with Cu/Ti nanoelectrode

3.2.1. Influence of current density

Increasing the current density is a simple way of speeding up the reduction reaction, but it also accompanied by a decrease in current efficiency and the selectivity. The effect of current density in batch electrolysis using a Cu/Ti electrode for the nitrate removal is shown in Fig. 5. The nitrate reduction rate increased with increasing current density in the range 10–50 mA/cm^2, especially when increasing the current density from 30 to 40 mA/cm^2. We found that the current efficiency decreased with increasing current density. The decrease in the current efficiency is probably because of higher hydrogen gas generation in the structure of the electrode.

At current densities of 10, 20, 30, 40, and 50 mA/cm^2, the potentials were in the ranges 7.8–9.0, 10.9–15.0, 12.3–20.5, 14.2–26.5, and 14.8–30.4 V, respectively. In practical use, selection of the most suitable current density depends on the treatment conditions. Zhang et al. [39] reported that with an applied current of 40 mA, the denitrification rate in reactor was 55.1%. At 75 mA, the denitrification rate was just 33.5%. The reason why the result is better in our experiment than that of Zhang's was due to Ti nanostructure has large specific surface area and Cu exhibit high electrocatalytic activity.

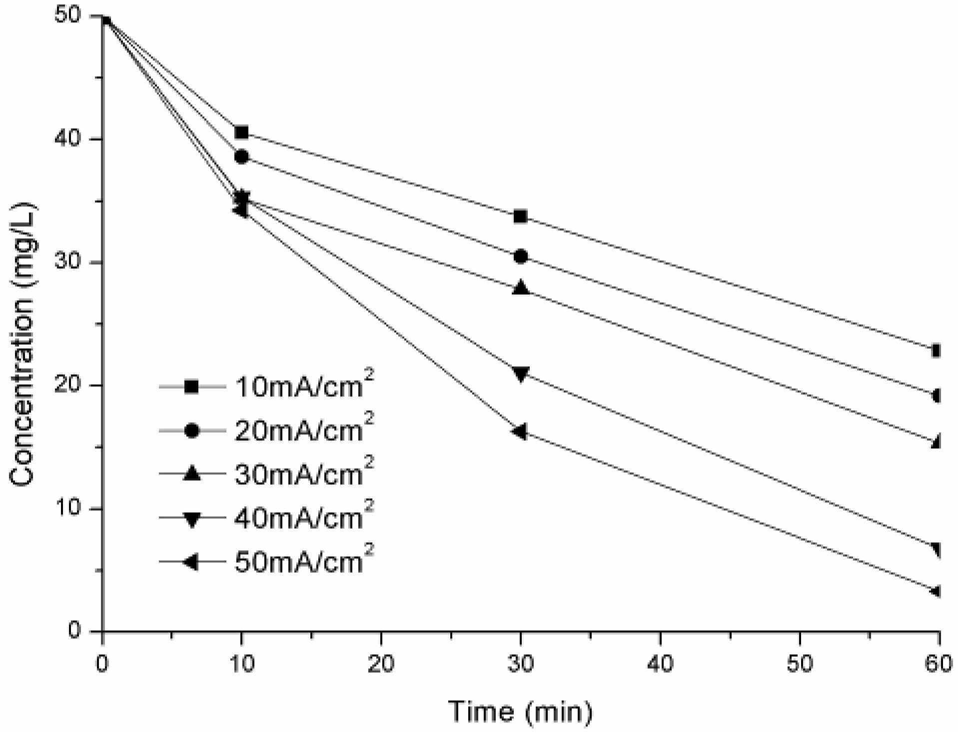


Figure 5. Effects of the current density on changes in the nitrate concentration over time (0.50 g/L Na_2SO_4)

3.2.2. Influence of initial pH

The pH was adjusted by adding HCl or NaOH through a pH meter. The effect of the pH on nitrate reduction is shown in Fig. 6. Good nitrate reduction performance was achieved in all of the solutions. The nitrate removal rate was the highest at pH 3, whereas the nitrate reduction rate was the lowest at pH 11. The trends of reduction of nitrate are similar at the different initial pH values. The nitrate concentration decreased from 50.0 mg/L to 4.04–8.41 mg/L in 60 min. At initial pH values of 3.0, 5.0, 9.0, and 11.0, the concentration of nitrate sharply decreased to 31.8, 37.4, 35.6, and 40.2 after 10 min, and then to 15.2, 21.0, 22.4, and 22.3 after 30 min, respectively.

The formation of a film on the surface of the material inhibits the reaction. In acid conditions, H^+ reacts with this film, which ensures complete contact between the nitrate nitrogen atom and Cu, and thus accelerates the reaction. In neutral and alkaline conditions, the film on the surface of the material cannot be removed, so the reaction slows down. The presence of the Cu surface above Ti is necessary for an effective denitrification process. Koparal et al. [40] and Chen et al. [34] found that higher removal rates have been observed at lower pH values. Aaccording to Eq. (1) the smaller the pH, the conversion of nitrate becomes greater. This does correspond to our observation.

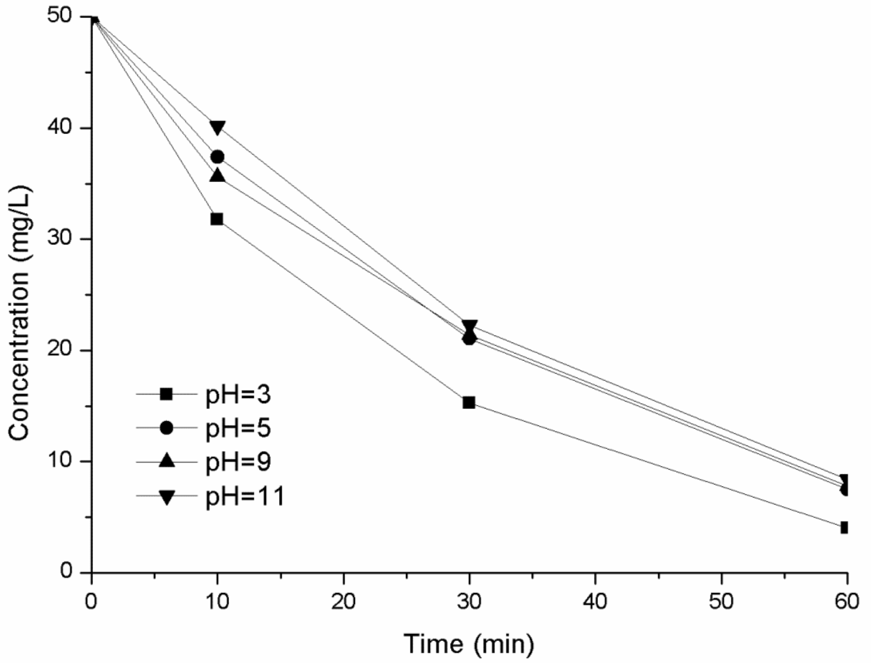


Figure 6. Effects of the pH on changes in the nitrate concentration over time (I = 30mA/cm^2, 0.50 g/L Na_2SO_4)

3.2.3. Influence of initial nitrate concentration and temperature

Fig. 7(A) shows the concentration of nitrate during constant current electrolysis in the electrolytic cell using a Cu/Ti double-layer cathode at 30 mA/cm^2 for solutions with different initial nitrate concentrations. For each solution, the reaction rate, selectivity, and efficiency of nitrate reduction rapidly decreased after the electrolytic started. With increasing initial nitrate concentration, the removal rate of nitrate decreased. When the concentration of $NaNO_3$ was 20 mg/L, the removal efficiency was 90.82% (i.e., the nitrate concentration decreased from 20.00 to 1.86 mg/L). With increasing initial concentration of $NaNO_3$, the removal efficiency decreased.

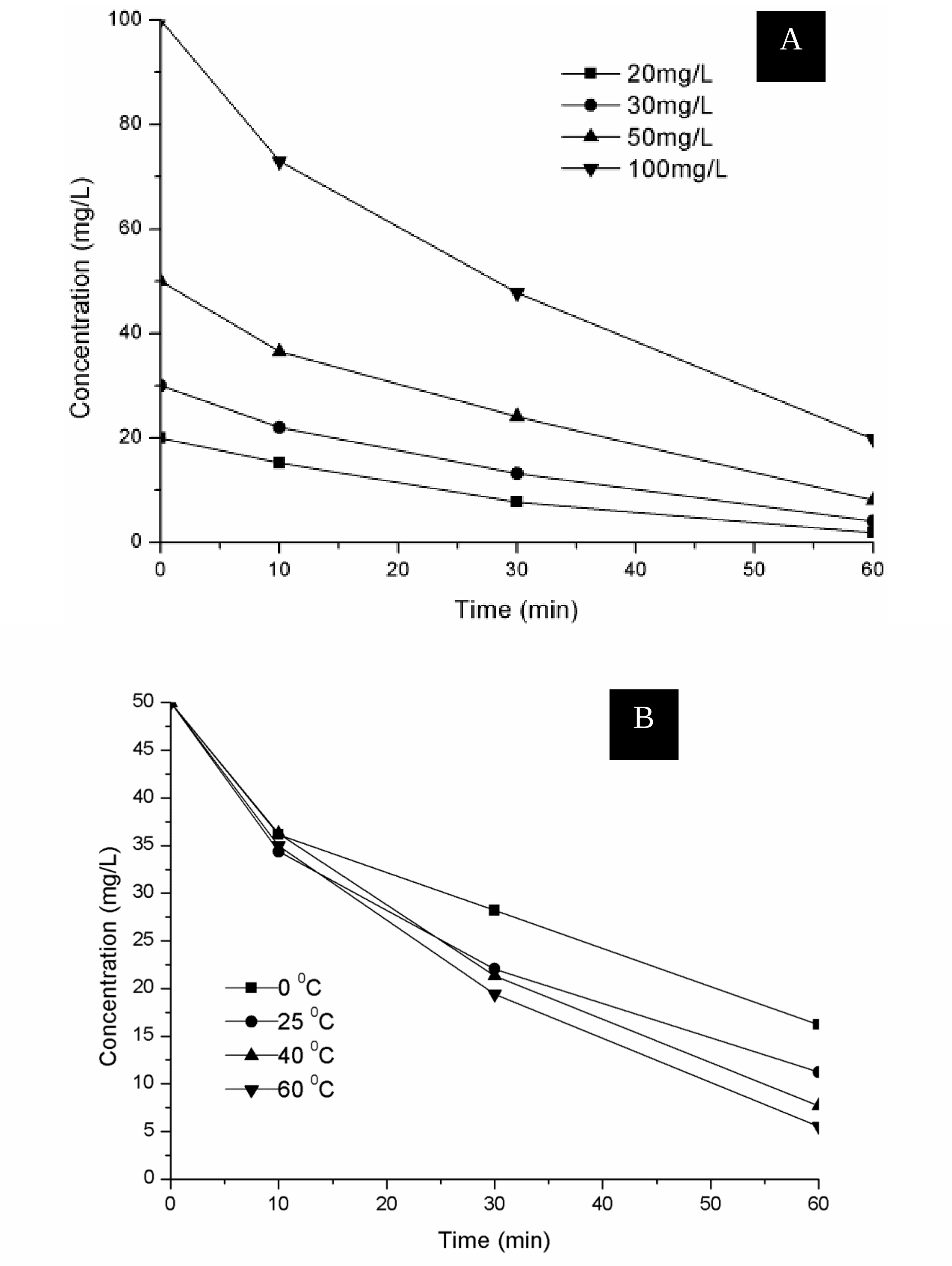


Figure 7(A). Effects of the (A) initial nitrate concentration and (B) temperature on temporal changes in the nitrate concentration (I = 30 mA/cm^2, 0.50 g/L Na_2SO_4)

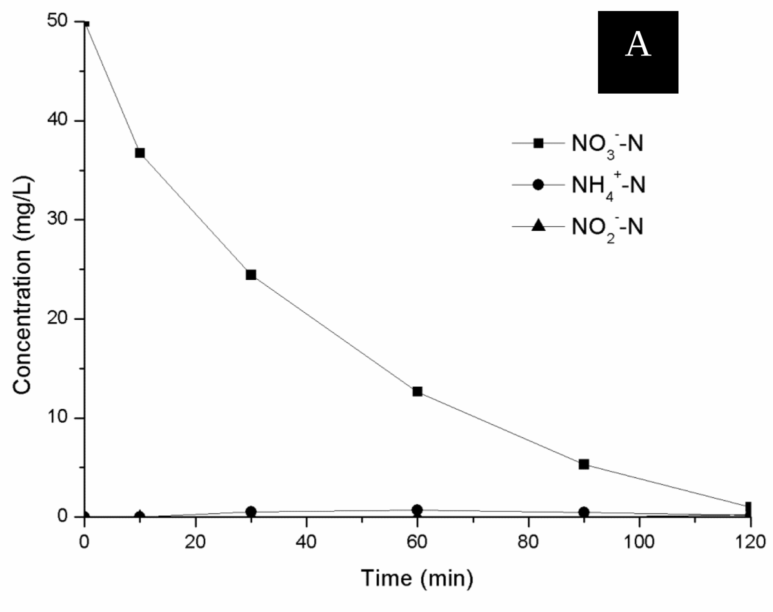
The removal efficiencies were 86.45%, 83.98%, and 80.21% for 30, 50, and 100 mM $NaNO_3$ solutions, respectively. It has been reported [40] that as initial concentration decreases, the removal rate has increased as expected. This does not correspond to our observation, the reason for this might be that a high concentration inhibits mass transfer of nitrate to the electrode and thus reduces the removal of nitrate.

Fig. 7(B) shows the influence of reaction temperature on nitrate reduction. The previous experiments were performed under the condition of room temperature. This time the electrolytic cell were kept in a water bath or ice bath with the constant temperature at 25 ◦C, 40◦C, 60◦C, 0◦C, respectively. Most of the experiments were performed without deliberate stirring, although stirring eventually occurred because of bubbles of hydrogen or oxygen formed at the cathode and anode, respectively.

Generally, increasing temperature can increase the nitrate removal rate by increasing the rate of diffusion and increasing the intensity of adsorption. The nitrate removal efficiencies at 40 and 60 °C were slightly higher than at 25 °C (from an initial concentration of 50.00 mg/L to 11.38 mg/L at 25 °C and 7.71 and 5.53 mg/L at 40 and 60 °C, respectively). As previously reported [37, 41], with the increase of electrolyte temperature, removal rate is also increased. This is because of increasing the temperature favored ammonia formation and reduced nitrogen formation. This is because at different temperatures, the pH of the electrolyte will change.

3.2.3. Influence of NaCl dose

As mentioned, the electrochemical activity of Cu for nitrate reduction is good, but the reduction leads to NH_3 as the main final product.



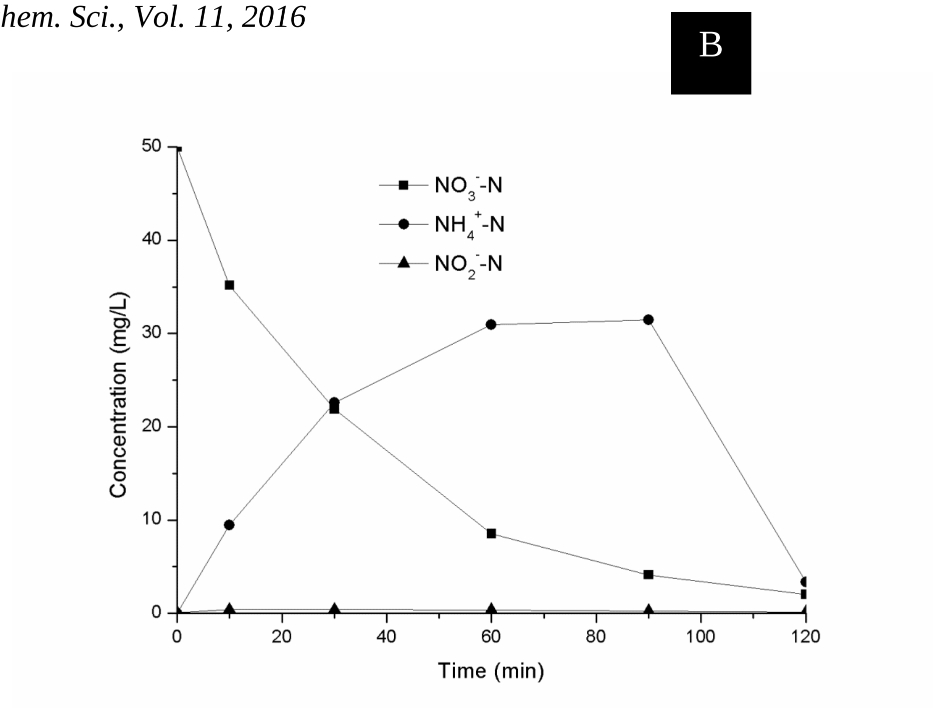


Figure 8(A) Temporal changes in nitrate, nitrite, and ammonia concentrations using an IrO_2 anode and a NaCl concentration of 0.3 g/L and (B) Temporal changes in nitrate, nitrite, and ammonia concentrations using an Pt anode and a NaCl concentration of 0.3 g/L

This will make the groundwater processing become more complicated. During the other methods, the nitrate are mainly reduced to nitrite, ammonia and nitrogen, which is further electrochemically inactive. We used Pt and Ir as anode, meanwhile added 0.1 g/L, 0.15 g/L, 0.3 g/L, 0.5 g/L and 1.0 g/L NaCl in order to find a proper condition to produce less nitrite and ammonia. Through lots of experiments, we find that use IrO_2 as anode and add 0.3 g/L NaCl, the removal rate of nitrate is 97.99% and generated the minimum amount of by-products. This may be because compared with the Pt, IrO_2 have stronger oxidizing, so it will produce less ammonia nitrogen and nitrite nitrogen in the process of electrolysis, meanwhile sodium chloride is added to the solution and chlorine ion can dissolve in water to form a hypochlorite, hypochlorous acid can produce hypochlorous acid root, ionization which have strong oxidizing hypochlorous acid root, nitrite and ammonia oxidation, can be transformed into nitrate or nitrogen removal.

According to Ning et al. [42], adding Cl^- in supporting electrolyte is contributed to nitrate removal. That is consistent with our study. In the solution of sodium chloride added to too little, hypochlorite produced will be less, can't all the formation of nitrite and ammonia nitrogen oxide, adding excess sodium chloride, will produce the competitive adsorption, inhibition of nitrate removal.

4. CONCLUSIONS

A novel Cu/Ti nanoelectrode was fabricated to improve electrochemical nitrate reduction efficiency. The nitrate removal efficiency of the Cu/Ti electrode was investigated in an undivided and unbuffered cell under different conditions. This study demonstrates the applicability of the electrochemical process for the removal of nitrate from aqueous solution. The conclusions drawn are as follows:

(1) The electrode played an important role in the nitrate reduction products. Using the Cu/Ti double-layer nanoelectrode, the nitrate concentration decreased from 50.0 to 14.1 mg/L (nitrogen removal efficiency 71.8%) in the presence of 0.50 mg/L Na_2SO_4 after 90 min electrolysis at the current density of 30 mA/cm^2.

(2) For the same initial nitrate concentration, the nitrate removal efficiency increased sharply by increasing the current density. For the same current density, the nitrate removal efficiency decreased slowly by increasing the initial nitrate concentration from 20 to 100 mg/L. The temperature had a great effect on nitrate reduction. The pH in the range 5–11 had little effect on nitrate reduction. However, the removal rate greatly improved for pH = 3. In the presence of 0.3 g/L NaCl, Nitrate could be completely removed using the IrO_2 anode, with little amount of ammonia detected in the treated solution.

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