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Development and optimization of Ti/Cu cathode and Ti/IrO$_2$ anode for electrochemical denitrification

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ABSTRACT

Nitrate is a known culprit behind methemoglobinemia. Long-term consumption of drinking water rich in nitrate can be carcinogenic. Electrochemical denitrification is one of the attractive technologies which can be used in denitrification. Although electrochemical nitrate removal is reported in the literature, little attention is paid towards the development of novel electrode materials considering the factors pertaining to efficient nitrate removal. In this research, attention was paid on developing novel electrode materials (i.e. anode and cathode). A novel cathode was prepared and optimized by coating Cu on Ti substrate. Applied current, plating duration, and Cu^{2+} concentration are the three parameters which were used to optimize the cathode material. Anode was developed and optimized by applying IrO$_2$ on Ti substrate. Calcination time and calcination temperature were varied in order to obtain optimum conditions to develop the anode material. Both electrodes showed promising results even in chloride-free synthetic electrolytes. Nitrate removal efficiency of the developed technology was 99% for actual groundwater. The current density was as small as 20 mA cm^{-2}. For groundwater samples, it was able to remove nitrate concentration from 176.7 to 1.34 mg L^{-1} within 2 h of reaction achieving the World Health Organization (WHO) guidelines for drinking water. Safety studies for nitrite and ammonia showed concentrations well below the WHO guidelines for drinking water. Neutron activation analysis showed no Ir was present in the treated water. Developed electrodes were successful in treating nitrate-rich water and provided potable water.

Keywords: Anode; Cathode; Electrochemical nitrate reduction; Electrode material optimization; Groundwater

1. Introduction

Nitrate is considered as one of the key water pollutants. The primary anthropogenic nitrogen source in groundwater is leaching from agro-ecosystems, although in some regions, human waste disposal can also be important. It has been discussed widely that the use of nitrogen fertilizers has increased exponentially at a global scale causing detrimental consequences on the health of different ecosystems as well

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as on humankinds [1–3]. Nitrogen in groundwater originates at the land surface as organic nitrogen, ammonium, nitrite, or nitrate. Nitrate is the primary form of nitrogen reaching the water table.

Nitrogen (N) is an essential input for the sustainability of agriculture. However, nitrate contamination of groundwater is a worldwide problem due to the excessive use of nitrogenous fertilizers [4,5]. Due to high solubility and negative charge, nitrate is highly mobile in soil [6,7]. Elevated nitrate concentrations in drinking water can cause methemoglobinemia in infants and stomach cancer in adults [8]. Drinking water which is contaminated with nitrate can be carcinogenic [9]. Above facts reveal that nitrate concentration in drinking water must be regulated. The World Health Organization (WHO) guideline for nitrate in drinking water is 50 mg L^{-1} (short-term exposure, as NO_3^-). The United States Environmental Protection Agency (USEPA) imposed a limit of 10 mg L^{-1} (measured as nitrogen, maximum contamination level) nitrate in drinking water. When it comes to nitrite, WHO and USEPA standards are 3 mg L^{-1} (short-term exposure, as NO_2^-) and 1 mg L^{-1} (measured as nitrogen, maximum contamination level), respectively.

As such, it is very important to treat nitrate-contaminated water prior to consumption. However, due to properties such as high solubility, less ability for precipitation and adsorption makes nitrate removal a difficult task. Hence, many processes including biological and physiochemical methods are used for the removal of nitrate from contaminated water. Among these processes, biological denitrification has drawn attention mainly for reducing nitrate to nitrogen. But, the need for continuous monitoring of micro-organism growth, the removal of byproducts, and long treatment durations has limited the application especially in drinking water treatment [10]. The most common treatment technologies for removing nitrate from drinking water are ion exchange, electrodialysis, and reverse osmosis, which unfortunately produce concentrated waste brine that may pose a disposal problem [11].

Compared to the other technologies, electrochemical technology has certain advantages [11,12]. Cathodic reduction provides an excellent environment for nitrate reduction. Anodic reactions produce a series of oxidants *in situ*. Besides, direct oxidation of contaminants at the anode is also possible. Thus, the potential of reduction byproduct (e.g. nitrite, ammonium ion) removal at the anode is high. Other factors such as no chemical storage or handling, low sludge generation, ease in process control, and low cost make the electrochemical technologies appealing [13]. However, sufficient conductivity is a key factor in reducing the cost of energy consumption. Since the reported value of conductivity in drinking water in troubled areas in Sri Lanka is high enough (e.g. conductivity of groundwater samples collected from 34 locations in Jaffna Peninsula is >250 μS/cm), applicability of the technology in such areas can be assured [14].

Electrochemical nitrate removal has been studied and reported in the literature [11,12,15–17]. Mechanism of electrochemical denitrification can be expressed as follows:

Reaction at cathode:

$$NO_3 \xrightarrow[\text{Reduction}]{} \text{By products}\left(\text{e.g.}\, NH_4^+,\ NO_2^-\right) + N_2 \tag{1}$$

Reaction at anode:

$$\text{By products} \xrightarrow[\text{Oxidation}]{} N_2 + NO_3^- \tag{2}$$

Most of the reported researches are focused on factors such as process parameters (e.g. effects of factors such as pH of electrolyte and applied current on nitrate removal efficiency) while using cathodes and anodes which are commercially available. Investigations into developing and optimizing novel electrode materials for electrochemical denitrification are limited in the literature. In a recent study, the optimization of cathode materials Ni, Cu, Cu_{90} Ni_{10}, and Cu_{70} Ni_{30} was accomplished by the paired electrolysis process using an undivided flow-through electrolyzer [18]. However, better efficiency would be achieved if the electrodes are developed and optimized instead of using commercial electrodes. In addition, studies on electrochemical denitrification in chloride-free electrolytes are limited [19]. It is worth noting that most of the studied electrochemical denitrification systems rely on the chloride content of the electrolyte (usually employing NaCl). Such systems may underperform if the actual contaminated water does not carry a considerable amount of chloride ion. The effect of chloride ions on NH_3 oxidation has been studied by evaluating NH_3 conversion yield with and without 0.5 mol dm^{-3} NaCl [11]. According to this study, NH_3 conversion yield was 88 and 21% in the presence and absence of NaCl, respectively, at a current density of 60 mA dm^{-3}.

As such, the main focus of this study is on developing a novel electrochemical reactor cell to treat nitrate-contaminated groundwater. In order to achieve the said goal, novel electrode materials (cathode and anode) are developed and optimized considering the electrode properties pertaining to effective nitrate removal. Among several electrode materials such as Ni, Fe, Rh, and Pb, Cu was known to be the most efficient material in nitrate electroreduction [18,20–22]. However, the use of commercially available Cu metal limited the ability of improving electrochemically active surface area of the electrode further. It is hypothesized that a Cu coating may be prepared on the same geometrical area with a higher electrochemically active surface area. As such, copper metal was electrodeposited on the pretreated titanium substrate in view of improving the electrochemically active surface area of the electrode, compared to that of commercially available Cu metal electrode. In addition, chloride-free electrolytes are employed while using synthetic groundwater samples to avoid technical limitations at the point of application. Optimized electrodes are used in treating actual groundwater samples contaminated with nitrate (or spiked with nitrate) to confirm the practical application. Safety of the treated water is confirmed by a series of laboratory investigations.

2. Materials and methods

2.1. Materials

Titanium (Ti) substrates were purchased from Sigma–Aldrich. Iridium(III) chloride trihydrate ($IrCl_3{\cdot}3H_2O$) from Acros organics (53.56%) and propan-2-ol (isopropanol, 99.9%) from Fisher Scientific were used to prepare metal precursor for the development of anode material. Copper sulfate pentahydrate, sodium nitrate, sodium perchlorate, sodium hydroxide, salicylic acid, and oxalic acid from Fluka were used. Sulfuric acid and hydrochloric acid were purchased from Sigma–Aldrich. All chemicals were of analytical grade.

2.2. Methods

2.2.1. Development of cathode material

Ti plates with the area of 1 cm × 1 cm and the thickness of 0.2 cm were used as the substrate metal. First, the Ti plates were sand blasted to improve the adhesion of the deposit on their surface by removing oxide layers. The sand-blasted Ti plates were treated by dipping in boiling 5% oxalic acid for 10 min in order to clean the surface from residuals. After that, substrates were rinsed with distilled water. Subsequently, the Ti plates were treated in boiling 37% hydrochloric acid for 10 min. At the end of the chemical treatment, Ti plates were rinsed again with distilled water. Finally, the substrates were dried in an oven to allow solvent evaporation until the weight became constant. Pretreated substrates were then coated by electro-depositing copper (Cu) on the substrate. Chronopotentiometry was the technique employed to electrodeposit copper metal on the Ti substrate. Electrochemical cell was arranged with two electrodes: a platinum rod as the anode and a pretreated Ti substrate as the cathode. The distance between the electrodes was approximately 1 cm. The current density and the plating duration were varied according to the experimental design.

2.2.2. Development of anode material

The Ti/IrO_2 anode was prepared by dip coating 0.250 mol dm^{-3} $IrCl_3{\cdot}3H_2O$ metal precursor in isopropanol on a 1-cm × 1-cm pre-treated Ti substrate followed by thermal decomposition. Thermal decomposition was carried out at 450˚C for 10 min until the final loading became 2 ± 0.05 mg cm^{-2}. Finally, the calcination was conducted at 550˚C for 60 min [23].

2.2.3. Experimental design for optimization of electrodes

A statistics-based response surface modeling methodology was used to optimize the cathode and anode materials using Minitab 16 software. After the preliminary studies, optimal conditions to develop the cathode material were studied. Three most important factors, namely applied current, plating duration, and Cu^{2+} concentration, during electrodeposition were investigated. A 3^3 design was created by the Box–Behnken design in response surface approach. Accordingly, 15 electrodes were fabricated by varying the above-stated factors simultaneously. Electrochemically active surface area and NO_3^- removal efficiency of cathodes were used as the optimization parameters. For optimizing the anode, two factors, namely final calcination duration and final calcination temperature, were considered. The weight of coating material drafted onto each Ti substrate was maintained at 2 ± 0.05 mg cm^{-2}. Central composite design in the response surface approach was used to create the experimental design. Low and high levels of each factor selected for cathode and anode were selected based on the preliminary experiments and are reported in Table 1.

2.2.4. Electrochemical analysis of electrodes

Electrochemically active surface area of the electrodes was compared indirectly using the anodic charge of prepared electrodes. This was done by

Table 1
Ranges of factors used in experimental designs for optimizing cathode and anode

	Cathode			Anode	
Level	Factor I: Applied current (mA)	Factor II: Plating duration (hrs)	Factor III: $CuSO_4{\cdot}5H_2O$ Concentration (M)	Factor I: Calcination temperature (˚C)	Factor II: Calcination time (min)
Low (−1)	20	0.5	0.2	300	60
High (+1)	80	3	1.0	800	250

evaluating cyclic voltammograms of electrodes (scan rate: 0.01 Vs^{-1}; ranges of scan voltage for cathode and anode materials were 0.8 to −0.8 V and 2 to −2 V, respectively) using Metrohm Autolab PGSTAT 128N. The electrode under study was used as the working electrode (WE), while Pt rod was used as the counter electrode (CE). Saturated calomel electrode was employed as the reference electrode (RE).

Open circuit potentials (OCP) of anodes were monitored in order to assess the stability of electrodes. Metrohm Autolab PGSTAT 128N was employed with Pt rod as CE and electrode under evaluation as WE. Saturated calomel electrode was used as the RE. Background electrolyte was 0.025 mol dm^{-3} $NaClO_4$.

2.2.5. Scanning electron microscopy

Scanning electron microscopy (SEM) of the optimized electrodes was performed using a scanning electron microscope, LEO 1420 VP.

2.2.6. Electrochemical denitrification

Electrochemical denitrification was carried out in a laboratory-customized electrochemical cell with a volume of 25 ml. After developing Ti/Cu cathode, electrochemical denitrification was carried out with it using commercially available Pt rod as the anode material. Initial NO_3^- concentration for this preliminary study was kept at about 90 mg L^{-1}, so that the initial concentration is about twice the WHO guideline value for nitrate in drinking water. For development and optimization of electrodes, denitrification studies were carried out for synthetic wastewater samples containing 100 mg dm^{-3} NO_3^- in 0.025 mol dm^{-3} $NaClO_4$. Electrochemical denitrification was accomplished by chronopotentiometry using a two-electrode system. The current density was 0.02 A cm^{-2} and the reaction time was selected based on the experiment.

For the final evaluation of the optimized electrodes using groundwater samples, denitrification was carried out. Electrolytes were the groundwater samples collected from different places of Sri Lanka (Jaffna, Anuradhapura, Puttlum, and Batticaloa). The water sample collected from Jaffna was from an agro-well in a tobacco plantation. Anuradhapura groundwater sample was collected from a well which is currently in use only for gardening purposes (owners have stopped using the water for drinking recently due to bad taste). Water samples collected from Puttlum was from drinking water wells, whereas Batticaloa water sample was collected from a tube well near a paddy field. Since this study intended to assess the feasibility of applying the developed technology for actual samples, it was decided to use these groundwater samples as electrolytes and carry out removal experiments. However, except the groundwater sample collected from Jaffna, all other samples had NO_3^- lesser than the drinking water standard. As such, those samples were spiked with NO_3^- to reach a concentration of 175 mg L^{-1} approximately. This allows studying the feasibility of developed technology to treat NO_3^- present in actual groundwater with slightly different characteristics.

2.2.7. Analysis of water samples

Nitrate in synthetic water samples was evaluated using the sodium salicylate method. However, for actual groundwater samples, nitrate was determined with nitrate ion-selective electrode to minimize interferences. Nitrite, sulfate, and phosphate were evaluated using a data logging colorimeter (HACH DR 890) with appropriate reagents. pH, conductivity, DO, fluoride, chloride, and ammonium ions were measured using Orion 5 star ISE meter with suitable ion-selective electrodes.

2.2.8. Neutron activation analysis

Neutron activation analysis is primarily a method which is used to detect trace elements. In this method, the sample was irradiated with a neutron flux of 3×10^3 neutrons cm^{-2} s^{-1}, and the generated radio nuclide was quantified depending on its decay mode and half-life. Neutrons are interacted with the nucleus of the target element via a nonelastic collision. The generated radionuclide (^{194}Ir*) is spontaneously de-exited into the more stable configuration (^{193}Ir) with the emission of one or more characteristic gamma rays. Gamma rays are detected by thallium-activated NaI detector. The duration for which the sample should be irradiated for neutron flux is five-fold the half-life of Ir. The half-life of Ir is 19 h. The sensitivity of this method to iridium is 10–100 pg.

A water sample which is subjected to electrochemical denitrification was irradiated with neutron flux for about 95 h continuously. After irradiating the sample, its gamma ray spectrum was obtained and the generation of peak at 938.63 keV was observed.

3. Results and discussion

3.1. Development of cathode

For preliminary studies, a Cu deposition density of 100 ± 5 mg cm^{-2} was achieved under the selected experimental conditions. At the end of the reaction period of two hours, percentage nitrate removal and conversion efficiency of nitrate per square centimeter of the cathode were found to be 29.24% and 0.16 mg cm^{-2} h^{-1}, respectively. In order to understand the low efficiency while using Pt as anode, the NO_3^- removal rate was evaluated every 30 min (Fig. 1). It was found that the NO_3^- removal efficiency was maintained at around 30% throughout the reaction period. This may be due to the oxidation of the reduced NO_3^- byproducts back to NO_3^- at the anode, rather than oxidizing them to N_2. High oxidation potential of Pt may have contributed to the above fact.

Since it was difficult to achieve a considerable removal of NO_3^- with Pt anode after 30 min, removal with dimensionally stable Ti/IrO_2 anode was investigated, before moving to further developments and optimization of the cathode material. Ti/IrO_2 anode was developed at the laboratory using dip coating followed by thermal decomposition. At the end of the reaction period of two hours, percentage nitrate removal and conversion efficiency of nitrate per square centimeter of the cathode were found to be 69.82% and 0.40 mg cm^{-2} h^{-1}, respectively. These findings revealed that the product formation is highly sensitive to the type of electrode materials employed in electrochemical denitrification. Accordingly, Ti/IrO_2 was used as the anode material during optimization of the cathode material.

Anodic charge indirectly represents the surface area of the electrode. The electrodes with higher anodic charge were expected to show a higher surface area leading to higher efficiencies in nitrate removal. Table 2 shows the results obtained for the anodic charge of each developed cathode. Based on the observations shown in Table 2, an increase in the applied currents has increased the anodic charge and thus the surface area of the electrodes. At high currents, the mass transfer rate of Cu^{2+} ion from bulk solution to the liquid–substrate interface is higher than that at low currents. High mass transfer rates increased the population density at the liquid substrate interface. The smallest nuclei were expected at the electrode surface with a high population density [24]. Deposition of smallest nuclei on the electrode surface formed a high surface area. At lower population densities, large nuclei tend to form at the substrate, reducing the surface area of the electrode.

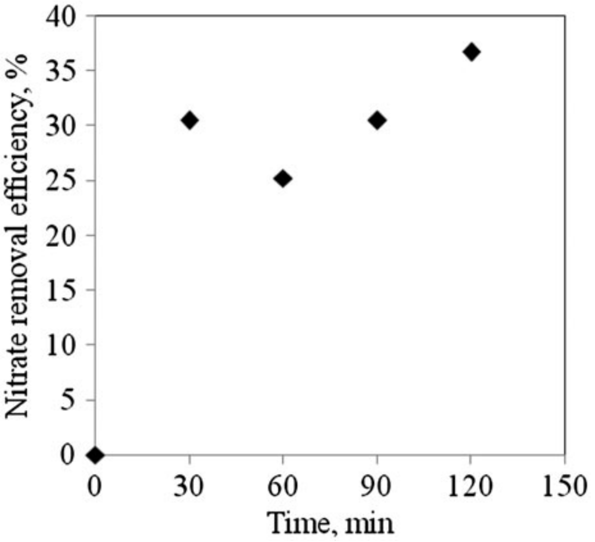


Fig. 1. Nitrate removal efficiency vs. time. Cathode: Cu/Ti, Anode: Pt.

However, it should be noted that an infinite increment in current would not be beneficial since such increment may lead to layer-by-layer deposition instead of monolayer deposition. Preliminary studies suggested that the increase in the coating current to 100 mA generated red-colored Cu_2O in the coating. Layer-by-layer deposition may have created intermediate anodic zones on cathode, leading to the generation of Cu_2O from previously deposited Cu (Fig. 2).

Anodic charge was increased with increasing plating duration (Table 2). The amount of copper deposited has increased with time, and probably the deposition may have contained several layers, rather than a single layer. As a result, the surface area may

Table 2
Anodic charge values and nitrate removal efficiencies obtained for fabricated cathodes

	Level of factors				Nitrate removal (after 30 min of reaction)	
Exp.	Applied current (mA)	Cu^{2+} concentration (M)	Plating duration (min)	Anodic charge (C)	Conversion efficiency of nitrate per square centimeter (mg cm^{-2})	NO_3^- removal (%)
1	20	0.6	30	0.9425	0.31	24.35
2	50	1.0	180	0.8534	0.17	13.20
3	80	0.6	180	0.9220	0.41	32.25
4	20	1.0	105	0.7670	0.42	33.36
5	50	0.6	105	0.7345	0.33	26.05
6	50	0.6	105	0.8567	0.33	26.09
7	80	0.6	30	0.9864	0.34	26.39
8	50	0.2	180	1.2010	0.41	32.48
9	20	0.6	180	0.7140	0.46	36.24
10	80	1.0	105	0.6004	0.31	24.36
11	50	0.6	105	0.7062	0.33	25.72
12	20	0.2	105	0.8707	0.66	51.25
13	50	0.2	30	0.7898	0.42	32.82
14	50	1.0	30	0.6274	0.09	6.90
15	80	0.2	105	1.0225	0.33	25.29

have increased. It is worth noting that the formation of spike-like features on the surface at high plating durations was observed. However, similar to coating current, an infinite increase in plating duration did not support further increase in the surface area due to the formation of Cu_2O.

Concentration of the Cu^{2+} ion showed an inverse relationship with anodic charge. At the beginning of the electroreduction, the number of copper atoms deposited at the surface was a function of initial bulk concentration. At lower Cu^{2+} concentrations, distance between two adjacent atoms can be higher compared to that of at higher concentrations. To be in the energetically favorable condition, atoms tend to form groups. This may have provided a large number of small nuclei, which provided a higher surface area at lower Cu^{2+} concentrations. Similar observations have been reported in the literature [24].

Nitrate removal efficiencies were then compared at a reaction time of 30 min and at an initial concentration of 100 mg L^{-1}. Results are reported in Table 2. Although it was initially speculated that the highest electrochemically active area would give the highest NO_3^- removal, the first observation obtained was that

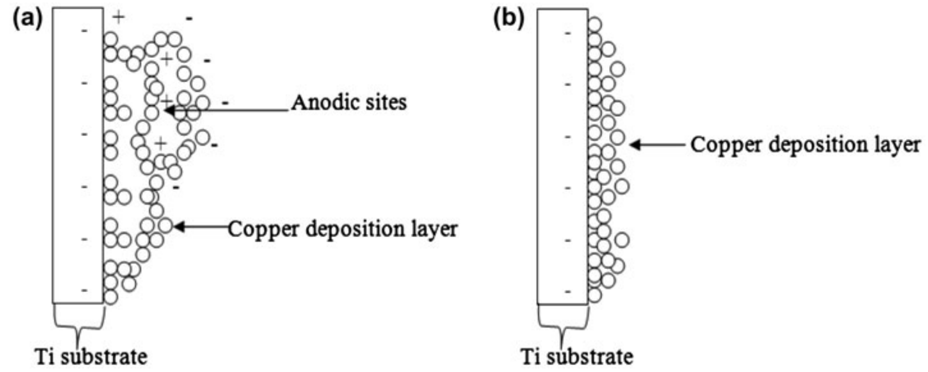


Fig. 2. Schematic diagram representing the nature of copper deposition layer under high applied currents and low applied currents: (a) deposition layer under high currents. Anodic sites formed by electrolyte leached inside the pores and (b) deposition layer under low applied currents. Compacted layer has a very low possibility of forming anodic sites.

such speculation is not valid. This may be due to the formation of anodic sites inside the deposited Cu layer. Although Cu promotes electroreduction of nitrate, Cu_2O has not been identified as a promoter in electroreduction of nitrate. At higher applied currents, Cu nuclei formed on the surface of the electrode are tending to be large. Hence, pore spaces may have formed in the deposition layer. Anodic sites could be formed when the electrolyte leached inside the pores of the deposition layer. The leached electrolyte may create individual micro-electrochemical cells by means of gaining opposite charges by adjacent layers (Fig. 2).

Oxidation of Cu atoms at the anodic sites led to the formation of Cu_2O depositions within the Cu deposition layer. Generally, these Cu_2O layers consist of coarse textures and thus of high surface area. Since the Cu_2O layers were not involved in NO_3^- electroreduction, the electrodes constructed at higher applied currents showed lower nitrate removal efficiency than that of the electrodes constructed at lower applied currents.

NO_3^- removal efficiency increased with plating duration to some extent and then showed a decrease with a further increase in plating duration. During the process of Cu deposition, nuclei started to form at the electrode surface initially. These small nuclei grouped together and started to diffuse through the surface of the electrode. The deposition of Cu atoms around these nuclei may have increased the surface area of the deposited layer. However, after a certain time period, the deposition layer became compacted due to continuous deposition of copper atoms and filled the gaps between Cu nuclei. This may decrease the surface area, and hence decrease nitrate removal efficiency after a certain time period.

Based on these findings, we evaluated the optimum coating conditions for the cathode based on NO_3^- removal efficiency. Surface plots in 3D are shown in Fig. 3. The evaluation revealed that coating duration, coating current, and Cu^{2+} concentration to obtain the optimum NO_3^- removal are 155 min, 20 mA, and 0.2 mol dm^{-3}, respectively.

It was found that the percentage NO_3^- removal of optimized Ti/Cu cathode and that of pure Cu metal of the same geometrical area was 43.23 and 24.64%, respectively (at the end of the 30-min reaction period). An analysis of the anodic charge of the optimized Ti/Cu and pure Cu metal cathodes revealed that the electrochemically active surface area was improved after coating (Fig. 4). These findings show the importance of developing and optimizing a Cu coating instead of using pure Cu metal as cathode in denitrification.

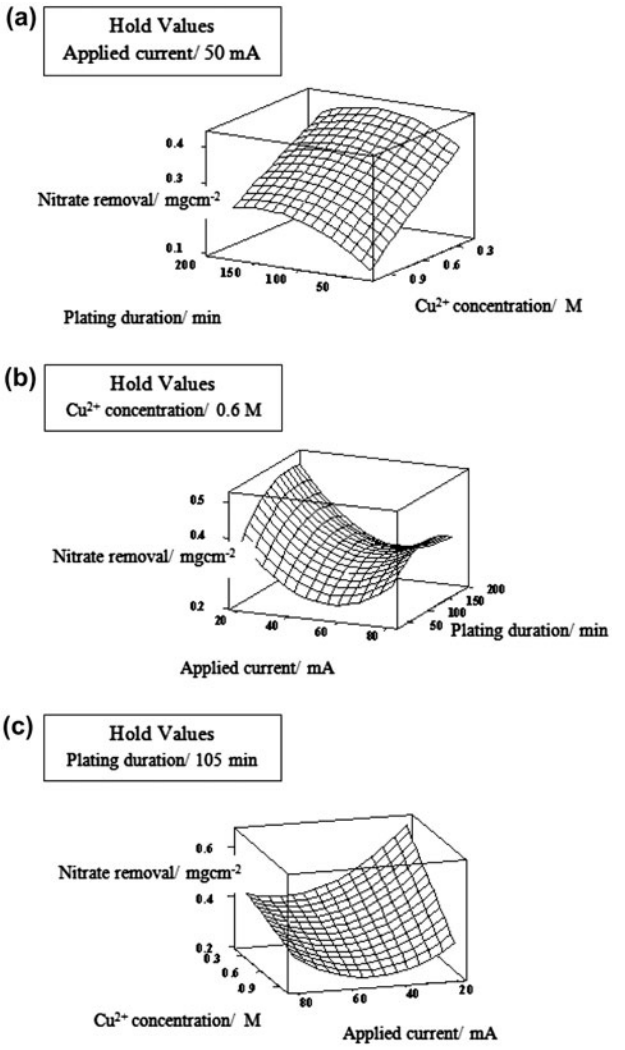


Fig. 3. Three-dimensional surface plots of nitrate removal obtained for the fabricated cathodes. (a) Nitrate removal vs. Cu^{2+} concentration and plating duration, (b) nitrate removal vs. Cu^{2+} concentration and applied current, and (c) nitrate removal vs. applied current and plating duration.

3.2. Development of anode

After optimizing the cathode, the Ti/IrO_2 anode was investigated and optimized for achieving better nitrate removal. Anodic charge was measured as an indirect measure of the electrochemically active surface area and the results are reported in Table 3. It is apparent that there was no (or minimal) charge on the surface of the electrodes which were developed at high calcination temperatures regardless of calcination time (exp. # 5, 8 and 13). This can be due to the formation of non-conducting oxide layers on the surface of the electrodes at high temperatures. In

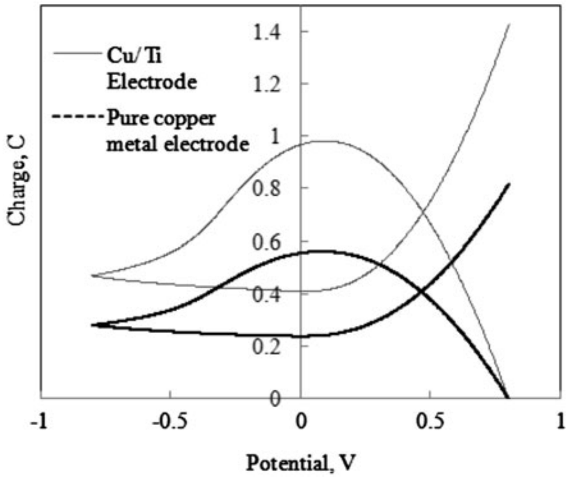


Fig. 4. Comparison of the anodic charge of Ti/Cu cathode and commercially available pure Cu cathode.

addition, anodic charge tends to increase with calcination time. This might be due to the formation of cracks on the coating layer with long exposure times at elevated temperatures. A similar finding has been reported for IrO_2 layers coated on NiTi substrates [25]. Accordingly, low calcination temperatures and long calcination times are favorable in increasing the surface area of the electrodes. Subsequently, anodes were studied for their NO_3^- removal efficiencies and it should be noted that the anodes were freshly prepared for each analysis. Results are shown in Table 3.

Table 3 shows that anodes with almost zero electrochemically active surface area (exp. # 5, 8 and 13) do not show any NO_3^- removal. This is due to the poor generation of oxidants due to very low active surface area. On the other hand, these anodes show OCP values of −1.53, −1.85, and −1.32 V compared to uncoated electrode's OCP of −1.42 V. These low OCP values indicated extremely low stability of anodes in addition to their low electrochemically active surface area [25]. As such, the coated surface may detach from the substrate very easily during the generation of oxidants, providing no visible efficiency in NO_3^- removal. The low oxidant amount generated may be consumed for the process of coating detachment. In addition, Table 3 shows that there is no clear connection between the electrochemically active surface area and nitrate removal efficiency. The stability may have reduced possibly due to the high amount of cracks on the surface at the electrodes with very high electrochemically active surface areas. Also, generated oxidants may have been used to corrode the coating

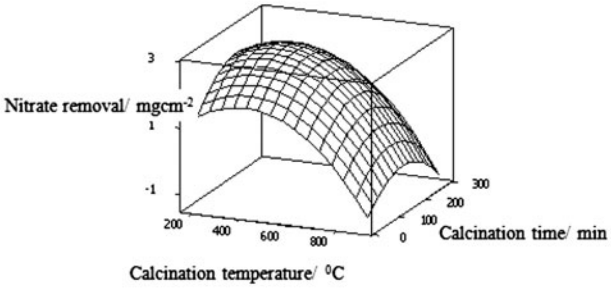


Fig. 5. Three-dimensional surface plot of nitrate removal obtained for fabricated anodes.

Table 3
Anodic charge values and nitrate removal efficiencies obtained for fabricated anodes

Exp.	Level of factors		Anodic charge (C)	Nitrate removal (reaction time = 30 min)	
	Calcination temp. (°C)	Calcination time (min)		Conversion efficiency of nitrate per square centimeter (mg cm^{-2})	NO_3^- removal (%)
1	300	60	0.2781	1.76	20.65
2	300	250	0.2782	2.04	24.05
3	196	155	0.1461	2.70	31.73
4	550	155	0.1473	2.35	27.64
5	800	250	0.0002	0.00	0.00
6	550	289	0.2321	1.90	22.41
7	550	155	0.2320	1.64	19.13
8	903	155	0.0000	0.00	0.00
9	550	155	0.2450	3.70	43.53
10	550	155	0.1513	1.94	22.79
11	550	20	0.1674	1.77	20.82
12	550	155	0.1525	2.55	30.04
13	800	60	0.0031	0.00	0.00

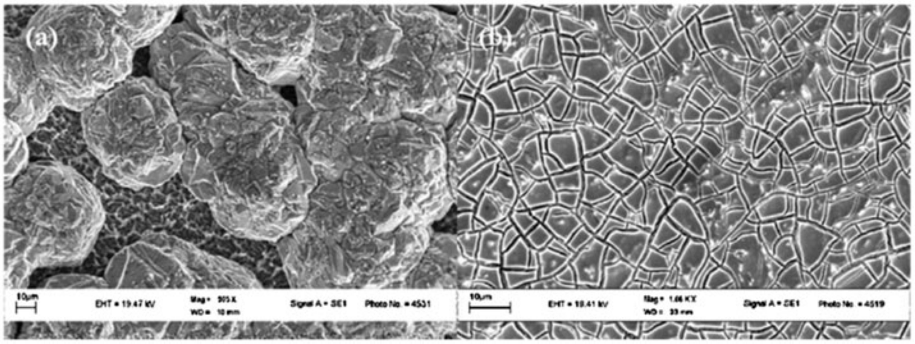


Fig. 6. Scanning electron micrographs of (a) cathode and (b) anode.

Fig. 7. Developed reactor cell. Volume of the reactor cell = 500 ml. Area of anode and cathode = 10.37 cm^2.

Table 4
Important physicochemical characteristics of collected groundwater samples

Location	Puttlum	Jaffna	Anuradhapura	Batticaloa
pH	7.39	7.53	7.74	7.32
Conductivity (μS cm^{-1})	509	717	1,297	354
DO (mg L^{-1})	7.33	7.28	5.03	6.73
NO_3^- (mg L^{-1})	2.20	175.89	0.26	31.70
Cl^- (mg L^{-1})	150	160	946	86
SO_4^{2-} (mg L^{-1})	82	66	58	61
PO_4^{3-}(mg L^{-1})	0.46	0.19	1.48	3.82
F^- (mg L^{-1})	2.80	0.74	5.50	0.66
NH_4^+ (mg L^{-1})	0.00	0.00	0.00	0.00

surface, due to low stability, reducing the available oxidants for NO_3^- removal. As such, it was decided to use NO_3^- removal efficiency as the response in optimizing two factors instead of using the electrochemically active surface area as the response.

Fig. 5 shows the 3D surface plot obtained using statistical software Minitab 16. Evaluation revealed that the calcination time and temperature of calcination to obtain optimum NO_3^- removal are 169 min and 379°C, respectively. Optimized anode was prepared

Table 5
Nitrate removal efficiency and formation of reaction byproducts in the developed reactor cell. Electrolyte: groundwater, reaction duration: 2 h, and concentration of NO_3^- ion was raised to approximately 175 mg L^{-1}

Location	Nitrate removal			Formation of reaction byproducts			
				NO_2^-		NH_4^+	
	Initial concentration (mg L^{-1})	Final concentration (mg L^{-1})	Nitrate removal efficiency (%)	Initial concentration (mg L^{-1})	Final concentration (mg L^{-1})	Initial concentration (mg L^{-1})	Final concentration (mg L^{-1})
Puttlum	176.7	1.34	99.24	0.00	0.41	0.00	0.00
Jaffna	175.9	1.84	98.95	0.00	0.43	0.00	0.34
Anuradhapura	174.1	1.30	99.25	0.00	0.39	0.00	2.52
Batticaloa	173.1	1.98	98.85	0.00	0.63	0.00	0.07

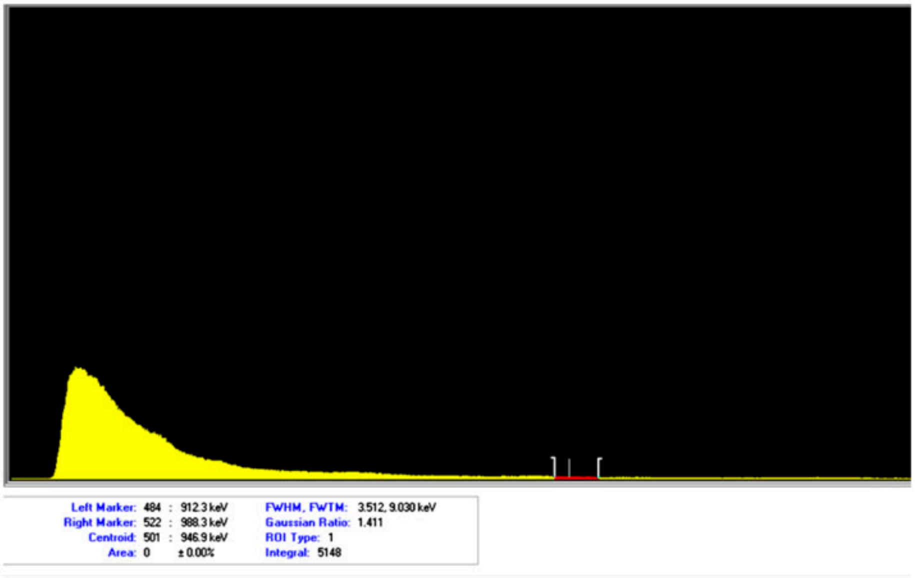
based on the above parameters. The optimized Ti/IrO_2 anode showed an anodic charge of 0.3170 C and an OCP of −0.9876 V, resulting in a high electrochemically active surface area and stability compared to that of the uncoated Ti substrate.

3.3. Developed electrodes in denitrification

Scanning electron micrographs of optimized cathode and anode are shown in Fig. 6. A reactor cell with a larger volume was fabricated employing the optimized electrodes (Fig. 7). This reactor cell was subsequently used in treating groundwater samples to analyze the applicability of technology in practical situations. Groundwater samples were collected from four different locations of the country reported with high-nitrate levels in groundwater (Puttlum, Jaffna, Anuradhapura, and Batticaloa) [26]. Results of the water analysis are shown in Table 4.

Nitrate levels of all samples were not high; however, among them the Jaffna water sample reported the highest amount of NO_3^-, which was 175.89 mg dm^{-3} which may be due to the extensive use of nitrogenous fertilizers and shallow karstic aquifers in the region [27]. The second highest nitrate level was observed in the sample from Batticaloa. Moreover, the sample from the Batticaloa district, which was collected from a tube well near a paddy field, has shown a considerably high amount of PO_4^{3-} ions. The water sample collected from Anuradhapura showed the highest conductivity and this can be due to the exceptionally high amount of dissolved ions in water. All samples did not contain any amount of ammonium ion.

Approximately 99% removal of nitrate was observed within 2 h from all actual groundwater samples, reaching WHO guideline value (Table 5). The presence of Cl^- ions may have contributed favorably to this high efficiency. At the presence of Cl^- ions, Cl_2 is generated at the anode. Generated Cl_2 subsequently may have oxidized NO_3^- reduction by products to N_2. This process plays an important role in electrochemical denitrification. A recent study, which investigated nitrate removal by paired electrolysis in alkaline media, has been able to achieve 88% ammonium conversion yield at a current density of 60 mA cm^{-2} in the presence of chloride ion. Copper was the cathode material, while Ti/IrO_2 was the anode material of the electrochemical reactor cell [11]. In another study, which has employed Cu–Zn cathode and Ti/IrO_2–Pt anode, NO_3^--N in water was removed from 100 to 9.7 mg dm^{-3} after electrolysis for 5 h at the current density of 40 mA cm^{-2} in the presence of chloride ions [16].



Left Marker: 484 : 912.3 keV
Right Marker: 522 : 988.3 keV
Centroid: 501 : 946.9 keV
Area: 0 ± 0.00%
FWHM, FWTM: 3.512, 9.030 keV
Gaussian Ratio: 1.411
ROI Type: 1
Integral: 5148

Fig. 8. Spectrum obtained by irradiating the sample for neutron flux (3×10^3 neutrons cm^{-2} s^{-1}) for five consecutive days.

3.4. Safety of treated water

^{194}Ir has its identical gamma ray emissions at 328, 640, and 938 keV. Although emission of gamma radiation at 938 keV is observed, area under the peak is 0.00% (Fig. 8). Therefore, it is apparent that there is no leaching of Ir to the solution and the Ti/IrO_2 anode is dimensionally stable.

During electrochemical denitrification, nitrate is reduced to its byproducts, mainly nitrite and ammonium ions. These byproducts are more toxic than the nitrate itself. In accordance with WHO, the maximum exposure level of nitrate is 50 mg $L^{-1}NO_3^-$, while that for nitrite is 3 mg $L^{-1}NO_2^-$. For the ammonium ion, no guideline value is proposed and can cause taste and odor problems at concentrations above 35 and 1.5 mg L^{-1}, respectively [28]. As such, it would be risky to provide treated water for drinking purposes if these agents are present in treated water. Hence, the treated groundwater samples were analyzed for the presence of NO_2^- ion and NH_4^+ ion.

As can be seen from Table 5, although there is a production of NO_2^- during denitrification, the quantities are below the WHO guideline value. In addition, it can be seen that a slight amount of NH_4^+ is remaining in the solution. The amount of NH_4^+ is not sufficient to cause odor or taste issues in treated water. These findings reveal that the developed electrochemical denitrification technology provides safe treated water for human consumption from the collected groundwater samples.

In electrochemical denitrification, reduction and oxidation processes are highly dependent on the electrolyte (provided that the electrodes are kept the same). As such, the data obtained and reported in this work may vary if a significant change occurs in the groundwater solution compared to what is reported here. Therefore, if the technology is to be employed in a different geological area, analyzing the groundwater samples before employing the reactor for drinking water treatment can be of importance.

4. Conclusions

In this study, novel cathode and anode materials were developed and optimized considering the electrode properties pertaining to effective nitrate removal in chloride-free electrolyte.

Cathode material was prepared using a Ti substrate coated with Cu by the electrodeposition technique. Three most important factors, namely applied current, plating duration, and Cu^{2+} concentration, during electrodeposition were investigated. It was found that the highest electrochemically active surface area does not guarantee the highest removal efficiency. This may be due to the formation of Cu_2O layers on Ti substrate. Unlike Cu, Cu_2O is not known to reduce nitrate in electrochemical denitrification. The evaluation further revealed that coating duration, coating current, and Cu^{2+} concentration to obtain the optimum removal are 155 min, 20 mA, and 0.2 mol dm^{-3}, respectively.

Ti substrate coated with RuO_2 was optimized for electrochemical denitrification. Dip-coating method was employed and the calcination temperature and duration of calcination of the final calcination cycle were used as the optimization factors. Higher electrochemically active surface area does not essentially provide the highest removal efficiency due to the cracked surfaces. Evaluation revealed that the calcination time and the temperature of calcination to obtain optimum NO_3^- removal are 169 min and 379˚C, respectively.

The optimized electrodes were employed in a reactor cell with a volume of 500 mL. The reactor cell was then tested for actual groundwater samples, collected from four different geographical areas of Sri Lanka. Approximately 99% nitrate removal was achieved within 2 h of reaction from all actual groundwater samples, reaching the WHO guideline value of 50 mg L^{-1} even for high initial concentrations such as ~175 mg L^{-1}. This high performance can be a result of the presence of Cl^- ion in groundwater. Treated water was analyzed for residual nitrite and ammonia. Investigation revealed that the concentrations of residual nitrite and ammonia after treatment are below drinking water standards. In addition, neutron activation analysis showed no Ir was present in treated water. With these findings, it can be concluded that the developed electrodes are successful in nitrate removal and the reactor provides safe water after treatment.

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