

# An-Najah National University Faculty of Graduate Studies

# ELECTROCHEMICAL REDUCTION OF NITRATE ION BY MODIFIED ALUMINUM SHEETS AS ELECTROCATALYSTS: A NOVEL WATER TREATMENT METHOD

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### Dedication

To my father

To my mother

To my brothers and sister

And to my dear husband

#### Acknowledgments

I would like to express sincere gratitude to my supervisors Prof. Hikmat S. Hilal for all his guidance, understanding, support and sound advice in all aspects of my research and Dr. Heba Nassar for her support, guidance and constructive advice. I would also thank technical staff at An-Najah National University labs especially Mr. Nafith Dweikat for his endless help.

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The warmest acknowledgment is for my dear family for their endless support, love and encouragement.

#### Declaration

I, the undersigned, declare that I submitted the thesis entitled:

#### ELECTROCHEMICAL REDUCTION OF NITRATE ION BY MODIFIED ALUMINUM SHEETS AS ELECTROCATALYSTS: A NOVEL WATER TREATMENT METHOD

I declare that the work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

سروی عبد محمد عبر Student's Name:

Signature:

inger and

Date:

27/4/2022

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### ELECTROCHEMICAL REDUCTION OF NITRATE ION BY MODIFIED ALUMINUM SHEETS AS ELECTROCATALYSTS: A NOVEL WATER TREATMENT METHOD

By Shorooq Eid Mohammed Eid Superviosor Prof. Hikmat Hilal

#### Abstract

**Background:** Nitrate contamination of surface and ground water has been an issue in many places of the world, which has harmful effects on human health and the environment, were wrong human practices, whether it is industrial or agricultural, have contributed in raising the percentage of pollution allowed according to the World Health Organization (WHO) in water, which we have to find a solution to this problem.

**Aims:** Our main goal of this study was to develop a simple, practical, and cost-effective method for reducing nitrate concentrations in aqueous solutions.

**Methods:** In this study we tested Al electrode and different Al modification electrodes: Al-graphite, Al-graphene, Al-Cu, Al-Cu-graphite, Al-graphite-Cu to remove nitrate from water, by using nitrate electrochemical reduction experiments.

**Results:** The products in these cases were  $NO_2^-$ ,  $NH_4^+$  and it's expected to produce  $N_2$ . The most efficient electrode was Al-Cu that can convert  $NO_3^-$  to  $N_2$  and the removal efficiency of nitrate 73.73%. The experiment of all electrodes was conducted on -1.8 volt.

**Conclusion:** By studying the kinetics of reduction for Al-Cu, the results indicate that the nitrate electro-reduction is approximately first order with respect to nitrate. XRD was conducted for Al-Cu, Al-graphite and Al-Cu-graphite. Effects of several parameters on Al-Cu electrode efficiency in nitrate ion reduction, such as time and initial nitrate concentration, have been studied. Stability and the electrode material were also studied under experimental conditions. The possibility of reusing Al-Cu electrode again was investigated as well.

**Keywords:** water pollution, WHO, nitrate concentration, Al modification electrodes, electrochemical reduction experiments

### Chapter One Introduction

#### 1.1 Overview

Pollution is one of the most critical problems facing human communities in the all world, particularly in developing countries. As environmental pollution is a global problem because of its harmful effects on human environments, resources and the health of the population on a large scale, thus we should pay more attention to this environmental problem [1-4].

Urbanization and industrialization increase human activities and industrial discharge of nitrate-containing waste into rivers and lakes without sufficient treatment [5]. Human practices, including agricultural and industrial activities, contributed to the pollution of the environment greatly, which affected the water quality that is considered a necessity for life. Therefore, pollution is considered one of the greatest bad practices that man commits against himself and his health [6].

Water is considered polluted if there are specific hazardous substances that make it unusable for certain purposes. Water pollution is the presence of high amounts of a hazardous substance or pollutant in water that renders it unfit for drinking, cooking, bathing, or other activities. [7].

#### 1.2 The nitrogen cycle

Nitrogen is an important element and has a vital role in the production of amino acids, whose function is to build amino acids as a building unit for the cell [8]. Nitrogen naturally exist in atmosphere, marine and soil. However, the increase in human wrongful practices against the environment unnaturally raise the amounts of nitrogen, which led to a change in the fixed balance of the nitrogen cycle [9]. An imbalance in the nitrogen cycle leads to negative effects on the environment, such as acid rain and global warming as a result of population growth and human activities [10].

Nitrogen chemistry is characterized by the multiplicity of oxidation states, which made it more complex. The oxidation states include -3, 0, +3 and +5, which make it of special

importance for chemists and environmental engineers. Common examples are ammonia (NH<sub>3</sub>) ions, nitrate (NO<sub>3</sub><sup>-</sup>) and nitrite (NO<sub>2</sub><sup>-</sup>) [11].

There nitrogen occurs inside organic compounds in animal waste. The urine in form of urea (NH<sub>2</sub>)<sub>2</sub>CO contains nitrogen. Bacteria are able to decompose this organic matter and release ammonia. Nitrosomonas may oxidize this resulting ammonia to nitrite, and it may be oxidized to nitrate by Nitrobactor bacteria. The set of these biological reactions is called nitrification [11].

#### 1.3 Nitrate in drinking water

#### 1.3.1 Nitrate and its derivatives uses

In the laboratory industry, nitrate is commonly used as a precursor to manufacture valuable chemicals such as ammonia, hydroxylamine, hydrazine, nitrous oxide, and many others. This chemical agent adaptability allows a wide range of applications not only in the industrial sector, such as the creation of fireworks, explosive materials and colors, but also as an antimicrobial agent [12].

The nitrogen gas created by nitrate reduction in the presence of hydrogen gas, can be further used in the Haber process [13] to make ammonia. The agricultural sector, which may manufacture ammonia-based fertilizer, benefits indirectly from this process. The nitrogen supply in ammonia-based fertilizers is beneficial to plant uptake. Strong alkaline solutions are used in the nuclear industry to neutralize radioactive waste [14].

Caprolactam manufacture is gaining popularity since it is a necessary intermediary in the synthesis of nylon-6 fiber and resins. Caprolactam is made by combining hydroxylamine and cyclohexanone at early synthesis stages [15].

In medicine, where nitrous oxide (N<sub>2</sub>O), popularly known as laughing gas, is utilized for anesthetic uses, nitrate reduction is also important. As a pre-surgical treatment, patients are administered a low dose of N<sub>2</sub>O [16].

#### 1.3.2 Nitrate sources

Nitrate has no taste or smell. In water it can be detected via a chemical test. Nitrate is a major environmental pollutant, and it's usually linked to anthropogenic activity. Chemical fertilizer runoff, animal waste, septic tanks and municipality treatment

systems of sewage are all common causes of nitrate pollution. The major sources of nitrate pollution are fertilizers [17].

When home and industrial wastewaters are discharged into drinking water reservoirs, nitrogen compounds are major contaminants that create a variety of environmental issues [18]. The most stable of the nitrogen species is nitrate, which is formed by reaction of nitrogen, from ammonia or other sources, with aqueous oxygen [19].

Oxynitrogen compounds, such as nitrates and nitrites, can be found in drinking water from underground or surface sources. Agricultural runoff and fertilizers, chemical industry effluents, acid rain and naturally existing sources such as mineral deposits are also potential sources of these chemicals [20].

The pollution of nitrate and its derivatives stymies efforts to achieve a clean environment on a worldwide scale. The majority of pollution occurs on the surface and in groundwater as a result of a variety of reasons.

The high solubility of nitrates in water, as well as the reduction of nitrates by particular bacteria in food and the intestines, aids conversion to nitrite [21]. When nitrogencontaining chemicals enter water resources, they cause major problems such as eutrophication, degraded water quality, and potential health risks to humans and animals [22-24]. High levels of these substances cause eutrophication in ponds, rivers, lakes or seas, and negatively impact the biodiversity and human beings [25].

#### 1.3.3 Nitrate health risks and environmental concerns

Despite the low toxicity of nitrate in water it can be converted to nitrite by bacteria or reduction in vivo [26, 27]. Whereas, high levels of nitrogen-containing compounds in drinking water cause health problems such as cyanosis in children, cancer such as alimentary canal cancer, and liver damage [28, 29]. As a result, removing nitrate and nitrite from water samples is critical from a health and environmental standpoint [29].

The ion nitrate has been recognized as a possible health risk for newborns and pregnant women [30, 31]. This is due to the probable conversion of nitrate to nitrite ion in infants' stomachs, which can bind with infected newborns' haemoglobin, reducing oxygen transfer to the body's cells and resulting in a bluish skin color known as

methaemoglobinemia or the blue baby syndrome [32]. Furthermore, increasing nitrate has a negative impact on health by causing methemoglobinemia in children, hypertension, thyroid dysfunction, and the carcinogenicity of nitrosamine and nitrosamide [23, 33-36].

Under anaerobic conditions, nitrate enters the human intestine and is transformed to nitrite, which can cause methaemoglobinemia in babies [37-39]. Furthermore, because nitrosamines are the most potent carcinogens in animals, the synthesis of nitrosoamines from nitrite can lead to digestive tract malignancies [40].

Excessive nitrate levels in green vegetables can be caused by the overuse of nitrogen fertilizers. Nitrosamine, which predominantly affects the oesophagus and pharynx, can be transformed to a considerably more deadly nitrite and eventually to a carcinogenic nitrosamine [41] under specific conditions (gastrointestinal tract).

Human waste contributes a substantial amount of nitrogen to the environment. Fertilizers, animal waste, municipal and industrial wastes are also thought to be major contributors of nitrate contamination in groundwater [42, 43]. Chronic exposure to high doses of nitrate has been shown in animal experiments to diminish the intrathyroid iodine pool, making the gland more vulnerable to goitrogens, it causes abortion in brood animals in cattle [44].

Methaemoglobinaemia results from the combination of nitrite (which comes from nitrate reduction in our body) with haemoglobin in the red-blood cells to produce methaemoglobin, which strongly binds oxygen without releasing it, thus inhibiting oxygen transport [45]. Several research on the toxicity of nitrate on aquatic creatures have been undertaken, with the results indicating that nitrate interacts with hemoglobin, producing a lack of oxygen in their bodies (methaemoglobin) and eventually death [39].

The World Health Organization (WHO) has written rules to limit the nitrate concentration in drinking water to protect consumers from the negative effects of high nitrate intake. The nitrate standard for drinking water is 50 mg/L [46], and the European Union (EU) standard is half that amount [47]. Primary toxicity is the action of nitrate [48], which produces abdominal cramps, diarrhea, and vomiting when consumed in large amounts. Secondary toxicity occurs when nitrate is converted to nitrite.

Methemoglobinemia in babies has been linked to concentrations of more than 50 mg /L  $NO_3^{-1}$  in drinking water; the true toxin is nitrite, which is generated when gut bacteria reduce nitrate. Nitrite interacts with amines in an acidic environment to generate nitrosamines, which are carcinogens and mutagens [49].

#### **1.3.4 Nitrate treatment options**

Water needs treatment to meet allowed nitrate concentrations when nitrate levels are high. To remove nitrate from drinking water, the following treatment techniques have been explored or used: physicochemical [18, 28], chemical [28], electrochemical [28, 50, 51], biological methods [20, 28, 52], membrane based separation methods such as reverse osmosis [20, 53], nanofiltration [20], electrodialysis [20, 54-56], in addition to ion exchange [20, 51, 57], chemical reduction [20, 58] and electrochemical reduction [59-61].

#### **1.3.4.1 Biological method**

The most effective and cost-effective method for treating nitrate-containing wastewater is biological denitrification. This method can be used on any effluent as long as bacteria can thrive [61]. However, the inconsistency in the quality and quantity of industrial effluent has a significant impact on microbial activity. As a result, biological denitrification is not competitive with other nitrate removal techniques in industrial effluent. Another disadvantage of biological denitrification is the formation of sludge, which necessitates costly post-treatment difficulty [62, 63], creates organic residues and demands extensive maintenance and continued supply of organic matters [64]. It is only useful at concentrations less than 1000 mg  $1^{-1}$  [28].

#### **1.3.4.2** Physicochemical method

Secondary brine wastes are produced by physicochemical procedures such as: ion exchange [65], reverse osmosis [66] and electrodialysis [67]. Therefore, the nitrates are only separated and not completely eliminated [50]. Membrane processes have several drawbacks, including expensive installation and maintenance costs, brine creation, and membrane sensitivity [59].

#### **1.3.4.3 Chemical method**

Hazardous bi-products, such as nitrite ions and ammonia are produced via chemical techniques, which necessitate the use of huge amounts of metals [68, 69] or hydrogen gas as a reducing agents, which are costly problematic [68].

#### **1.3.4.4** Chemical reduction method

Chemical reduction is a viable nitrate-removal approach. The conversion of nitrate to non-toxic nitrogen is the most significant benefit of this method [70-72]. Electrochemical removal was suggested as a treatment alternative to various chemical denitrification procedures, such as metal-based or catalytic hydrogen-based reductions, among chemical technologies [59, 73-75]. At low concentrations, the nitrate ion is chemically stable. Moreover, speeding up its chemical reduction demands the use of catalysts (to speed up the reaction) in addition to special temperatures and pressures [76].

#### 1.3.4.5 Electrochemical denitrification method

There are three common electrochemical nitrate removal methods: Electroreduction (ER), electrodialysis (ED) and electrocoagulation (EC). ER and EC can convert nitrate to harmless nitrogen, but ED is primarily based on physical processes like adsorption and migration. Because of its excellent nitrate removal efficiency and lack of fouling or scaling formation, the ER approach is suitable for high salinity wastewater. The EC technique can be applied to water. The ED approach is effective in the treatment of drinking water [61]. The key advantages of electrochemical technologies are their simplicity, the absence of sludge creation, and the absence of the need for ongoing maintenance or chemicals [77-79]. Electrochemical technologies have already proven to be effective in wastewater treatment since they are inexpensive, quick, and direct [80-82].

#### **1.4 Electrochemical reduction**

The right removal method must be adopted to fulfill the specific requirements of each process application while also being ecologically friendly [20]. Recently, electrochemical reduction, which is effective method for nitrate removal, attracted special attention. Compared to other methods such as biological ones, electrochemical technology is more time effective, easy to operate and needs no organic materials [83-85], when the parameter effects and interactions are thoroughly examined even with high nitrate removal yields [86], no post-treatment is required, and the reactor architecture is simple and does not require a start-up phase [59], lowering investment costs. One of the most environmentally safe and selective methods is electrochemical reduction of nitrates. This process is being studied using various transition metals [87].

#### 1.4.1. Examples of electrode materials

For nitrate removal from water, many electrode materials were used, such as: Pd [88], Cu [89], Ag [90], Ni [91], Rh [92], Sn [93], Pb [94], alloys (such as CuPt [95], CuSn [28]), PdRh1.5/Ti [96], Cu–Zn [97], Cu–Ni [98], Rh–Ni [99], Sn–Pd [100], Ag–Pd[5], Ag–Pt–Pd [5], Pd–Co–Cu [101] alloy and aluminum [28]. It should be noticed that some of the materials are costly and should be avoided.

#### 1.4.2. Aluminum

Aluminum is a common element on the planet. It can be found in various forms in most rocks and soils, as well as in gemstones such as topaz and garnet. It's present in plants and in all of the world's water [102], it is a metal with a low density and good electrical conductivity; yet, electroplating on it is difficult due to its affinity for oxygen, which results in a protective oxide covering that is not conducive to adhesion. Normally, this oxide protects aluminum against corrosion, but when highly corrosive media are utilized, it may be essential to supplement this natural protection with a metallic coating. A deposit may be employed to strengthen the superficial hardness against abrasive friction in specific instances. At the very least, a brilliant deposit might be justified for a decorative reason [103].

#### **1.5 Objectives of the present work**

#### 1.5.1 Strategic objectives

Nitrate pollutes various water sources, which is becoming a big issue in Palestine. As a result, the overarching purpose of this study was to develop a realistic and cost-effective method of lowering nitrate concentrations in drinking water that might be implemented in Palestine and other places.

#### **1.5.2 Technical objectives**

The aim of this work is to develop an environmentally friendly method for water purification from the hazardous nitrate that is harmful for humans. While doing so, a number of technical objectives will be targeted:

- Aluminum films modified with Graphite, Graphene, Copper, Graphite/Copper and Copper/Graphite will be prepared.
- 2- Comparatively study the reduction efficiency of the different electrodes. The electrode that demands lowest applied potential and achieves higher reduction rates will be of more interest to us. Moreover, effect of treatment on aluminum electrode stability will also be assessed.
- 3- Characterization of the prepared Aluminum films modified will be done.
- Effects of time, initial nitrate concentration, stability and the electrode material will be studied.

#### 1.6 What is new in this work?

1- What has been done on Al modification for nitrate electrochemical removal?

Al sheets modified with zeolites have been effective in removing fluoride ions from water [102]. A unique organic-modified aluminum manganese bimetal oxide (OABO) adsorbent was developed to remove nitrate and phosphate ions from wastewater and lower the risk of eutrophication. As a result, OABO has a lot of potential for removing nitrate and phosphate from water.

The maximum adsorption quantities of NO<sub>3</sub><sup>-</sup>N and PO<sub>4</sub><sup>3-</sup>P were 19.45 mg/g and 33.16 mg/g, respectively. This adsorbent can be regenerated and reused for 5 cycles [103].

For simultaneous phosphate and ammonium removal, a natural zeolite (Z-N) rich in clinoptilolite was modified (Z-Al) by including hydrated aluminum oxide (HAlO).

The phosphate sorption capacity improves from 0.6 mg-P/g for Z-N to 7.0 mg-P/g for Z-Al, whereas the ammonium sorption capacity decreases somewhat from 33 mg-N/g for Z-N to 30 mg-N/g for Z-Al.

With regeneration cycles, the zeolite phosphate capacity was shown to be reduced [104].

For ceftazidime adsorption, three impregnated activated carbon IAC (AC-Cu, AC-Fe, and AC-Al) enhanced by Fe, Cu and Al were utilized.

The maximum adsorption quantities of ceftazidime on AC-Cu derived by a pseudosecond order kinetic model at different temperatures were 200.0 mg g<sup>-1</sup> (298 K), 196.1 mg g<sup>-1</sup> (303 K), and 185.2 mg g<sup>-1</sup> (185.2 K) (308 K). It was significantly greater than AC-Fe and AC-AI [105].

An electrocoagulation process improvement for hydrogen recovery and nitrate removal from water. An anode and cathode made of aluminum alloy with a surface area of  $2 \text{ dm}^2$  were employed.

The maximum removal effectiveness of 95.9% was attained at a current density of 0.25  $A/dm^2$  and a pH of 7.0, according to the findings. The energy yield of created hydrogen was 54% of the electrocoagulation process' electrical energy demand. Electrocoagulation could be a valuable technology for treating water used in power plants. The aluminum hydroxide produced in the cell absorbs the nitrate in the water and reduces it to a safe level, making it drinkable [106].

2- What has not been done?

- 1- Electrochemical removal from water of nitrates by modified aluminum electrode was not studied.
- 2- Modified aluminum electrode to remove nitrates from water was nor described.

Therefore, the present work involves the following novel aspects:

- 1. Preparation of modified aluminum with graphite for nitrate electrochemical removal.
- 2. Preparation of modified aluminum with graphene for nitrate electrochemical removal.
- 3. Preparation of modified aluminum with copper nanoparticles for nitrate electrochemical removal.

- 4. Preparation of modified aluminum with copper/graphite for nitrate electrochemical removal.
- 5. Preparation of modified aluminum with graphite/copper nanoparticles for nitrate electrochemical removal.

#### 1.7. Assumptions

- 1) It is assumed that coating the Al metal with graphite will stabilize its surface.
- 2) Graphite is a conducting material which allows charge transfer between Al and the solution nitrate ions, but it may increase resistance and inhibit nitrate removal.
- 3) Graphite has higher specific surface area than Al sheets. Therefore, graphite will increase interaction with nitrate ions.
- 4) Coating Al surface with Cu nanoparticles will increase nitrate ion reduction due to its high conductivity and nano-size nature.
- 5) Coating Al with graphene may increase surface area and nitrate removal, if resistance at Al-solution interface does not increase.

### Chapter Two Experimental Work

#### 2.1 Chemicals and Reagents

Sodium nitrate, Sodium sulfate, 1 mol/L Hydrochloric acid, Phenol (89%), 95% v/v Ethyl alcohol, Sodium pentacyanonitrosylferrate (III) dehydrate, Sodium hydroxide, Trisodium citrate, Sodium hypochlorite, anhydrous ammonium chloride, Phosphoric acid (85%), Sulfanilamide, N-(1-Naphthyl)ethylenediamine dihydrochloride, Toluene, Sodium nitrite, Graphite, Graphene, Copper sulfate and Sulfuric acid were purchased from local market.

#### 2.2 Calibration curve

#### 2.2.1 Calibration curve for NO<sub>3</sub>-

- A) NaNO<sub>3</sub> stock solution (1000 ppm) was prepared by the addition of 0.1371g NaNO<sub>3</sub> to 100 ml water.
- B) Working solutions (200 ppm) was prepared by the dilution of 1000 ppm of NaNO<sub>3</sub> stock solution in 100.0 ml water.
- C) To the prepared solutions (0, 10, 12, 14, 18, 20) ppm from working solution was added HCl (1 mol/L) in a ratio of 1 ml HCl per 50.0 ml.
- D) UV-Vis spectra were measured for samples on a Shimadzu UV-1800 at (200-400) nm.

#### 2.2.2 Calibration curve for NH4<sup>+</sup>

- A) A stock solution was prepared by the addition of phenol (11.1 ml, 89%) to Ethyl alcohol (95% v/v) to reach a volume of 100.0 ml in volumetric flask.
- B) Sodium nitroprusside (0.5% w/v) was prepared by dissolving sodium nitroprusside (0.5000 g) in deionized water (100.0 ml).
- C) Alkaline citrate was prepared by dissolving trisodium citrate (200.0000 g) and sodium hydroxide (10.0000 g) in deionized water to reach 1000.0 ml.
- D) Oxidizing solution was prepared by mixing alkaline citrate solution (100.0 ml) with sodium hypochlorite (25.0 ml).

- E) Stock solution of aqueous ammonium chloride was prepared by dissolving anhydrous NH<sub>4</sub>Cl (3.8190 g) in water, and was diluted to 1000.0 ml.
- F) Intermediate solution (100 ppm) was prepared by the dilution of 1000 ppm of stock solution in 100.0 ml water.
- G) The intermediate solutions with concentrations of (0, 1, 2, 4, 5, 7 ppm) were prepared. Then phenol (0.4 ml), Sodium nitroprusside (0.4 ml) and oxidizing solution (1.0 ml) to 10.0 ml of each sample of the intermediate solutions, were added. Then the samples were covered with paraffin wrapper film, and stored in closed storage with dim light at room temperature for minimum 1 hr.
- H) UV-Vis spectra were measured for all samples on a Shimadzu UV-1800 at 640 nm and the absorption was plotted vs. concentration to make the calibration curve.

#### 2.2.3 Calibration curve for NO<sub>2</sub>-

- A) Color reagent was prepared by adding water (800.0 ml), phosphoric acid (100.0 ml, 85%) and sulfanilamide (10.0000 g). After sulfanilamide was dissolved completely, *N*-(1-naphthyl)-ethylenediamine dihydrochloride (1.0000 g) was added. The mixture was stirred to dissolution, then diluted with water to 1000.0 ml.
- B) Stock solution was prepared by the dissolving NaNO<sub>2</sub> (1.2320 g) in water and diluted to 1000.0 ml.
- C) Standard solution (100 ppm) was prepared by the dilution of 1000 ppm of stock solution in 100.0 ml water
- D) Prepared (0, 0.1, 0.02, 0.03, 0.04, 0.05) ppm from standard solution and added color reagent to it in a ratio of 1.0 ml color reagent per 25.0 ml. Samples were covered with paraffin wrapper film, then the color was developed at room temperature from 10 min to 2h.
- E) Finally, UV-Vis spectra were measured for samples on a Shimadzu UV-1800 at 543 nm to construct the calibration curve (absorption vs concentration).

#### **2.3 Electrode preparation**

#### 2.3.1 Aluminum preparation

The pieces of aluminum sheet were used with dimensions of  $(1 \text{ cm} \times 5 \text{ cm} \times 0.225 \text{ mm})$ .

#### 2.3.2 Aluminum films modified with Graphite preparation

The aluminum piece was scratched with sand paper (with 120 particles/cm<sup>2</sup>, each particle with ~0.9 mm in diameter) in order to rough the surface and to remove any other oxides and doodled on aluminum with a pencil (graphite).

#### 2.3.3 Aluminum films modified with Graphene preparation

The aluminum piece was crushed with glass paper in order to clean it and added 2.0000 g graphene with 5.0 ml toluene and mixed them by sonicater. Then, it was painted on a piece of aluminum and annealed at 300 °C under N<sub>2</sub> using an oven.

#### 2.3.4 Aluminum films modified with Copper preparation

The aluminum piece was crushed with glass paper in order to clean it. Copper solution was prepared by added 10.0000 g copper sulfate (CuSO<sub>4</sub>) and 15.0 ml concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) in 100.0 ml distilled water. Then, the aluminum piece was dipped in the copper solution and dried for a minute.

#### 2.3.5 Aluminum films modified with Copper /Graphite preparation

Aluminum films modified with Copper was prepared using the same procedure and doodled on it with a pencil (graphite).

#### 2.3.6 Aluminum films modified with Graphite/Copper preparation

Aluminum films modified with Graphite was prepared using the same procedure, then it was dipped in the copper solution and dried for a minute.

#### 2.4 Electrode characterization

#### 2.4.1 XRD

X-Ray Diffraction was used to determine the crystal structure and particle size of the prepared electrodes: aluminum films modified with copper, aluminum films modified with graphite and aluminum films modified with copper /graphite. The measurements were made at UAE University, Al Ain, UAE.

#### 2.4.2 UV-Vis spectroscopy

The UV-Vis spectra have been measured for solutions of different prepared electrodes on a Shimadzu UV-1800. The spectra were measured using a Perkin Elmer LS50 Luminescence spectrometer. Solution samples of different prepared electrode were excited at (200-400) nm for  $NO_3^-$ , 640 nm for  $NH_4^+$  and 543 nm for  $NO_2^-$ .

#### 2.5 Electrochemical reduction experiment

NaNO<sub>3</sub> solution (1000 ppm) was prepared by the addition of 1.3710 g NaNO<sub>3</sub> in 1000.0 ml distilled water, it was diluted to 100 ppm in 500.0 ml distilled water and added it 3.5510 g Na<sub>2</sub>SO<sub>4</sub>. 70.0 ml of the solution was put in a 100.0 ml glass beaker, then it was reduced using a potentiostat device under N<sub>2</sub> gas for the first five minutes at -1.8 volt and taken (1- 2) ml of the solution every quarter of an hour for 1.5 h. Samples solution were diluted and analyzed using UV-Vis spectrophotometer. The reduction efficiency was calculated from these data.

#### 2.6 Effect of parameter

#### 2.6.1 Effect of the electrode material

Electrochemical reduction experiments were done using different prepared electrodes: aluminum films, aluminum films modified with graphite, aluminum films modified with graphene, aluminum films modified with copper, aluminum films modified with graphite/copper and aluminum films modified with copper /graphite by a potentiostat device for 1.5 h. The best electrode has been selected to assess the impacts of concentration and time.

#### 2.6.2 Effect of initial nitrate concentration

Electrochemical reduction experiments were done using different concentrations (40, 50, 100. 150 and 200 ppm) for aluminum film modified with copper by a potentiostat device for 1.5 h.

#### 2.6.3 Effect of time

Electrochemical reduction experiments were made using different period of time (0, 105, 210, 315 and 420 minutes) for aluminum film modified with copper by a potentiostate device for 7 h.

#### 2.6.4 Stability study

Electrochemical reduction experiments were done for aluminum film modified with copper by a potentiostat device for 1.5 h. Then, the same electrode was washed and used again for an additional 1.5 h.

#### 2.7 Ions analysis

The solutions were taken after completing the reduction experiments, then the ions were determined in the water after treating it in the Water and Environmental Research Center using an inductively coupled plasma/mass spectrometry (ICP-MS). The same method was described to determine the trace elements by (ICP-MS) device.

### Chapter Three Results and Discussion

In this work different electrodes were used for electrochemical reduction of nitrate in water. These catalyst electrodes are aluminum films, aluminum films modified with graphite, aluminum films modified with graphene, aluminum films modified with copper, aluminum films modified with graphite/copper and aluminum films modified with copper /graphite. Different factors affecting electrochemical reduction were studied.

#### 3.1 Calibration curve

The Calibration curve of  $NO_3^-$ ,  $NH_4^+$ ,  $NO_2^-$  are shown in Figure(1), (2) and (3) respectively.

#### Figure 1

Calibration curve for NO3<sup>-</sup> determination



Calibration curve for NH4<sup>+</sup> determination



#### Figure 3

Calibration curve for NO2<sup>-</sup> determination



#### 3.2 Electrode characterization

#### **3.2.1 X-Ray Diffraction (XRD)**

As per pervious research [107]. it was shown in Figure (4) XRD patterns for pure Alsheet, diffraction signals of (111), (200), (220), (311), (400) at  $2\theta = 38.52$ , 44.76, 65.14, 78.26 and 99.11, respectively, match Al sheet.

Particle size was determined using the Debye Scherrer, Equation (1):

$$d = \frac{0.9\,\lambda}{\beta\,\cos\theta} \tag{1}$$

Where, d is particle size (Å);  $\lambda$  is X-ray wavelength from source = 1.45 Å;  $\beta$  is fullwidth at half-maximum for signal in radians;  $\theta$  is diffraction angle (degree).

#### Figure 4

XRD patterns measured for pure Al electrode [107].



Figure (5) shows XRD patterns for Al-graphite. Sharp signals indicated crystallinity. Diffraction signals of (111), (200), (311) at  $2\theta = 38.74$ , 43.06 and 76.24, respectively, match Al structure [108]. Diffraction signals of (002), (004) at  $2\theta = 26.32$  and 54.1, respectively, match graphite structure [109], and the signal of (104) at  $2\theta = 36.1$  match Al<sub>2</sub>O<sub>3</sub> structure [110]. Signals showing some broadening indicate smaller particle size of Al-graphite.

Average particle size of Al crystallite inside were measured. In Al-graphite electrode average particle size of Al was 21.1250 nm, average particle size of graphite was 18.9950 nm and particle size of Al<sub>2</sub>O<sub>3</sub> was 19.9500 nm.



XRD patterns measured for Al-graphite electrode.

Figure (6) shows XRD patterns for Al-Cu/graphite. Sharp signals indicate crystallinity structure. Diffraction signals of (111), (200), (311) at  $2\theta = 38.96$ , 43.22 and 76.98, respectively, match Al structure [108]. signals of (110), (002) at  $2\theta = 32.24$  and 34.12, respectively, match CuO structure [111], signals of (002), (004) at  $2\theta = 26.34$  and 54.3, respectively match graphite structure [109], and signal of (104) at  $2\theta = 36.3$  match Al<sub>2</sub>O<sub>3</sub> structure [110].

In Al-Cu/graphite electrode average particle size of Al was 63.1570 nm, average particle size of graphite was 55.9200 nm, and particle size of Al<sub>2</sub>O<sub>3</sub> was 57.3600 nm.

#### Figure 6



XRD patterns for Al- Cu/graphite.

Figure (7) shows XRD patterns for Al-Cu. Sharp signals were indicated crystallinity structure. Diffraction signals of (110), (002), (020), (202) at  $2\theta = 32.6$ , 34.54, 53.96 and 58.1, respectively, match CuO structure [111], diffraction signals of (110), (311) at  $2\theta = 36.78$  and 73.16, respectively, match Cu<sub>2</sub>O structure [112], diffraction signal of (200) at  $2\theta = 50.169$  match Cu structure [113], signals of (111), (200), (311) at  $2\theta = 38.72$ , 43.00 and 76.16, respectively, match Al structure [108]. and signal of (104) at  $2\theta = 36.121$  match Al<sub>2</sub>O<sub>3</sub> structure [110]. It signals show some broadening indicate smaller particle size of Al-Cu.

In Al- Cu electrode average particle size of Al was 18.2150 nm, particle size of Cu was 11.31 nm, average particle size of CuO was 16.3125 nm, average particle size of Cu<sub>2</sub>O was 17.7500 nm, and average particle size of Al<sub>2</sub>O<sub>3</sub> was 19.0500 nm.

#### Figure 7





Results for particle sizes for Al-graphite, Al-Cu/graphite and Al-Cu are summarized in Table (1) as shown below.

#### Table 1

Electrode	Crystallite size (nm) for various materials								
	Al	Cu	Graphite	CuO	Cu <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>			
Al-graphite	21.1250	-	18.9950	-	-	19.9500			
Al- Cu/graphite	63.1570	-	55.9200	-	-	57.3600			
Al-Cu	18.2150	11.3100	-	16.3125	17.7500	19.0500			

Particle sizes for Al-graphite, Al-Cu/graphite and Al-Cu.

#### 3.3 Electrochemical reduction experiment

#### **3.3.1 Electrochemical reduction on Al**

Figure (8) shows a loss in NaNO<sub>3</sub> of  $3.80 \times 10^{-4}$  M. For the NO<sub>2</sub><sup>-</sup> there was production amount of  $2.10 \times 10^{-4}$  M, but there was no indication for NH<sub>4</sub><sup>+</sup>. The difference between both NaNO<sub>3</sub> and NO<sub>2</sub><sup>-</sup> was due to the time the experiment took place, where NaNO<sub>3</sub> done in 90 min, while NO<sub>2</sub><sup>-</sup> was done in 60 min.

#### Figure 8

*Nitrate reduction of nitrate ions on Al electrode. Experimental conditions were: initial nitrate 0,00118 M, applied potential -1.8 V, time 1.5 h, and at room temperature.* 



#### 3.3.2 Electrochemical reduction on Al-graphite

Figure (9) shows a loss in NaNO<sub>3</sub> of  $5.40 \times 10^{-4}$  M. For the NO<sub>2</sub><sup>-</sup> there was production amount of  $4.50 \times 10^{-4}$  M. For NH<sub>4</sub><sup>+</sup> the production value was  $2.80 \times 10^{-4}$  M. The results show that the removed nitrate ion is converted to ammonium and nitrite ions with no nitrogen production. The above results mean that both Al and Al-Graphite electrodes are not good electrodes for removal of nitrate, since nitrite and ammonium ions are produced with no nitrogen.

Nitrate reduction of nitrate ions on Al-graphite electrode. Experimental conditions were: initial nitrate 0,00118 M, applied potential -1.8 V, time 1.5 h, and at room temperature.



#### 3.3.3 Electrochemical reduction on Al-graphene

Figure (10) shows a loss in NaNO<sub>3</sub> of  $3.90 \times 10^{-4}$  M. For the NO<sub>2</sub><sup>-</sup> there was production amount of  $3.70 \times 10^{-4}$  M, while for NH<sub>4</sub><sup>+</sup> the production value was 74.00×10<sup>-4</sup> M. The results indicate that the Al-graphite removes more nitrate ions than Al-graphene does.

#### Figure 10

Nitrate reduction of nitrate ions on Al-graphene electrode Experimental conditions were: initial nitrate 0,00118 M, applied potential -1.8 V, time 1.5 h, and at room temperature.



#### 3.3.4 Electrochemical reduction on Al-Cu

Figure (11) in Appendix (A) shows a loss in NaNO<sub>3</sub> of  $8.70 \times 10^{-4}$  M. For the NO<sub>2</sub><sup>-</sup> there was production amount of  $1.10 \times 10^{-4}$  M, while for NH<sub>4</sub><sup>+</sup> the production value was  $3.79 \times 10^{-4}$  M. We notice that in this experiment the loss NaNO<sub>3</sub> is more than the other above Electrochemical reduction experiments. Based on earlier literature [114-116], the

difference between the nitrate loss  $(8.70 \times 10^{-4} \text{ M})$  and the total nitrite and ammonium ion production  $(4.89 \times 10^{-4} \text{ M})$  is due to N<sub>2</sub> gas production  $(3.81 \times 10^{-4} \text{ M})$ . This proves that the electrode Al modified with Cu the best choice to produce nitrogen gas from nitrate ions.

#### 3.3.5 Electrochemical reduction on Al-Cu-graphite

Figure (12) in Appendix (A) shows a loss in NaNO<sub>3</sub> of  $7.60 \times 10^{-4}$  M. For the NO<sub>2</sub><sup>-</sup> there was production amount of  $1.20 \times 10^{-4}$  M, while for NH<sub>4</sub><sup>+</sup> the production value was  $8.30 \times 10^{-4}$  M. There is error in measurements, since total nitrite and ammonium ion concentrations are slightly more than nitrate ion loss, However, the results show that the Al-Cu-Graphite electrode is more efficient than Al, Al-Graphite and Al-Graphene in removing nitrate ions, but it does not yield nitrogen. On the other hand, the Al-Cu electrode is more efficient than Al-Cu-Graphite in production.

#### 3.3.6 Electrochemical reduction on Al-graphite-Cu

Figure (13) in Appendix (A) shows a loss in NaNO<sub>3</sub> of  $6.20 \times 10^{-4}$  M. For the NO<sub>2</sub><sup>-</sup> there was production amount of  $4.10 \times 10^{-4}$  M, while there was no indication for NH<sub>4</sub><sup>+</sup>. Based on literature [114-116] it is expected that the difference between the nitrate ion loss and the nitrite ion production, which is equal to  $(2.10 \times 10^{-4} \text{ M})$ , is due to N<sub>2</sub> gas. The reason for the production of N<sub>2</sub> gas was due to modification of Al with graphite/Cu where the Cu was on the external surface of the electrode.

Results for all studied electrodes are summarized in Table (2) for comparison. As shown in Table (2) it is found that Al-Cu is the best electrode in nitrate electrochemical reduction. The electrode activity in removing nitrate was for various electrodes deceased as: Al-Cu > Al-Cu/graphite > Al-graphite/Cu > Al-graphite > Al-graphene > Al. The Al and the Al-Graphene are least active electrode. Al-Cu is most active in nitrate removal and in selectivity to producing N<sub>2</sub> gas, followed by Al-graphite/Cu. Moreover, the Al-Cu showed least NO<sub>2</sub><sup>-</sup> production, which is another feature for Al-Cu electrode since NO<sub>2</sub><sup>-</sup> is not desired at all. In case of the Al-Cu electrode, the remaining nitrate ion concentration is  $3.10 \times 10^{-4}$  M, with is ~19 ppm and much lower than the WHO allowed value (50 ppm). More comparisons between types of electrodes is presented in Section 3.4.1 below.

#### Table 2

Nitrate ion electro-reduction results using various types of electrodes. Experimental conditions: Initial nitrate  $11.80 \times 10^{-4}$  M, applied potential - 1.8 V and at room temperature.

Electrode	Remaining nitrate (M×10 <sup>-4</sup> )	Degradation%	Removed Nitrate (M×10 <sup>-4</sup> )	Resulting NO2 <sup>-</sup> (M×10 <sup>-4</sup> )	$\begin{array}{c} \textbf{Resulting} \\ \textbf{NH4}^+ \\ \textbf{(M\times10^{-4})} \end{array}$	N <sub>2</sub> (M×10 <sup>-4</sup> )
Al	8.00	32.20	3.80	2.10	0	0
Al-graphite	6.40	45.76	5.40	4.50	2.80	0
Al-graphene	7.90	33.05	3.90	3.70	0.74	0
Al-Cu	3.10	73.73	8.70	1.10	3.79	3.81
Al-Cu/graphite	4.20	64.40	7.60	1.20	8.30	0
Al-graphite/Cu	5.60	52.54	6.20	4.10	0	2.10

#### **3.4 Effects of reaction parameters**

#### 3.4.1 Effect of the electrode material

As shown in the Figure (14) in Appendix (A) below, the best electrode for nitrate reduction was Al-Cu with electrochemical reduction of  $8.70 \times 10^{-4}$  M from originally  $11.80 \times 10^{-4}$  M. This means that the removal% was 73.73%. The Al-Cu-graphite comes in second with electrochemical reduction of  $7.60 \times 10^{-4}$  M, where the removal% was 64.40%. The Al-graphite-Cu comes after with electrochemical reduction of  $6.20 \times 10^{-4}$  M, where the removal% was 52.54%. Al-graphite comes in  $4^{th}$  with electrochemical reduction of  $5.40 \times 10^{-4}$  M and removal% of 45.76%. That is followed by Al-graphene with electrochemical reduction  $3.90 \times 10^{-4}$  M and removal% of 33.05%. The least effective was the Al electrode (unmodified) was the worst case with electrochemical reduction  $3.80 \times 10^{-4}$  M with degradation ratio 32.20%.

The modification of Al was to prevent it from corrosion and improve the electrochemical reduction.

As the most effective electrode is Al-Cu, this is understandable. The Cu are nanoparticles which should have electroreduction catalytic activity. With their small sizes, they are expected to have high relative surface areas which increases activity. The Graphite and Graphene were added to increase adsorption of nitrate and to increase removal efficiency due to their high surface areas. But their effects on the Al-Cu electrode are not positive, as the carbon materials may also increase resistance which lowers efficiency. However, the carbon materials have positive effects on the naked Al sheets since both increased nitrate ion removal, presumably by increased surface area and adsorption of nitrate.

Since the Al-Cu electrode is the most active electrode among the series, all other reactions have been performed using this electrode only.

#### 3.4.2 Effect of initial nitrate concentration

Figure (15) in Appendix (A) shows that with lower initial nitrate concentration the removal% value increases. Where the removal% was (78.72%, 74.57%, 71.18%, 60.79% and 47.66%) for  $(4.70 \times 10^{-4}, 5.90 \times 10^{-4}, 11.80 \times 10^{-4}, 17.60 \times 10^{-4} \text{ and } 23.50 \times 10^{-4}$  M), respectively. However, with higher initial nitrate concentration, both the removed nitrate amount and the initial rate increase. Kinetic study has been made here to find the rate constant and the rate law with respect to the nitrate.

To study kinetic of nitrate electro chemical reduction we apply the following equation (2) for the rate law:

$$Rate = k[A]^n$$
(2)

where k is the rate constant, A is the molar concentrations of reactant (in our case is NO<sub>3</sub><sup>-</sup>), **n** must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed

Based on Figure (15) the initial rate values were calculated for various initial nitrate concentrations, as shown in Table (3). Then, a plot of Ln (initial rate) vs. Ln (initial concentration) was made as shown in Figure (16) in Appendix (A) at higher concentration than Figure (17) in Appendix (A). The slope in Figure (12) is 0.9015 in which means that the reaction order with respect to nitrate is 0.9015, this value is approximately first order, but it is lower order with higher nitrate concentration as Figure (16). From the interception with the y-axis in Figure (17), the value for Ln(k) was -5.5074, which means that the value for the rate constant was  $(4.06 \times 10^{-3} \text{ s}^{-1})$ 

#### Table 3

Conc (M×10 <sup>-4</sup> )	Ln[NO <sub>3</sub> <sup>-</sup> ]	Initial rate	Ln(initial rate)
4.70	-7.663	0.00000411	-12.40
5.90	-7.435	0.00000488	-12.23
11.80	-6.742	0.00000933	-11.58
17.60	-6.342	0.00001190	-11.34
23.50	-6.053	0.00001240	-11.30

*Values of Ln (rate initial) and Ln [NO* $_3$ <sup>-</sup>].

#### 3.4.3 Effect of time

To check the impact of time on Al-Cu the experiment was conducted for seven hours, the electrochemical reduction for NaNO<sub>3</sub> was 96.61% which is a good value that indicate the possibility to completely remove NaNO<sub>3</sub> from water in enough time.

The Figure (18) in Appendix (A) also shows that  $NO_2^-$  ion is produced at the beginning, then it starts to disappear to yield more of  $NH_4^+$  ions. After some time, the  $NH_4^+$  ions themselves start to disappear with time. This is important to explain mechanism of the electroreduction reaction process. At first stage, the nitrate ions are converted to nitrite ions, which are then converted to ammonium ions. The nitrite ions are reduced again to yield nitrogen gas at the cathode. The ammonium ions are also oxidized to nitrogen gas at the anode. Similar mechanisms have been reported earlier [114-116].

The results confirm the importance of using Al-Cu electrode to remove nitrate ions from water. Moreover, the resulting nitrite and ammonium ions are also removed in the electrochemical cell during the process with time. The dominant product in the process is nitrogen gas, which is a safe product.

#### **3.4.4 Electrode stability and recovery**

Figure (19) in Appendix (A) shows the possibility to recover and reuse Al-Cu electrode for more than one time. The electrochemical reduction has been performed on one fresh electrode and on a recovered electrode for only 90 min in each case. This is important for practical purposes. The Figure shows lowering in electrode efficiency on reuse, but still functions. More study is needed to assess stability of the Al-Cu electrode on recovery and reuse.

#### **3.5 Ion analysis**

In order to find stability of electrodes to dissociation under electrochemical reduction of nitrate ion, the working solutions were analyzed for various metal ions. As noted in Table (4) the level of Al concentration in the solutions for all electrodes after electrochemical reduction process were within the recommended levels given by WHO. For As, Ba, Be, B, Pb, Mn, Ni, Cr concentration in the solutions for all electrodes after electrochemical reduction process were on the recommended levels given by WHO. The modification electrodes show lower concentration for these ions in comparison with the naked Al electrode.

The level of Cd concentration is more than the recommended levels by WHO. Its noted that the concentration of Cd in Al electrode is less than the concentration of modified Al electrodes, except for Al-Cu electrode which caused lower Cd ion production. Thus, the Al-Cu electrode is a good electrode, and it is preferred to use in electrochemical reduction experiments. This is in addition to other advantages discussed above namely: efficiency and selectivity to nitrogen production.

The level of Cu ion concentration, resulting after using naked Al sheet, is more than the recommended levels by WHO. The Al-Cu modification of Al electrode showed much lower Cu ion concentration than the naked Al electrode itself. This means that copper atoms inside the naked Al sheet are being protected by sheet modification.

#### Table 4

Ions	Al Conc. Mean (ppm)	Al-graphite Conc. Mean (ppm)	Al-graphene Conc. Mean (ppm)	Al-Cu Conc. Mean (ppm)	Al-Cu/graphite Conc. Mean (ppm)	Al-graphite/Cu Conc. Mean (ppm)	Allowed limit (ppm)	Ref
Al	0.006436	0.027671	0.007043	0.019525	0.026047	0.024917	0.1 - 0.2	[117]
As	0.000228	0.000144	0.000076	0.000127	0.000115	0.000115	0.01	[118]
Ba	0.001738	0.000734	0.001361	0.000715	0.000514	0.001339	0.7	[118]
Be	0.000105	0.000097	0.000059	0.0000091	0.000115	0.000107	0.012	[119]
В	0.056150	0.014314	0.010977	0.016373	0.031944	0.018966	0.5	[118]
Cd	0.025513	0.039100	0.000201	0.006026	0.003337	0.011782	0.003	[120]
Cr	0.006971	0.004731	0.004612	0.008759	0.006702	0.005198	0.05	[118]
Co	0.000123	0.000071	0.000053	0.000056	0.000086	0.000068	No guideline	[121]
Cu	0.738106	0.473987	0.043153	0.200867	0.961467	0.148896	0.005	[122]
Fe	0.020238	0.023711	-0.016571	0.017302	0.030777	0.008163	No guideline	[123]
Pb	0.001647	0.000232	0.000011	0.0000109	0.001370	0.000113	0.01	[124]
Mn	0.000510	0.000279	0.000081	0.000245	0.000376	0.000170	0.4	[118]
Ni	0.001616	0.001799	0.000176	0.001058	0.001491	0.001126	0.07	[125]
Se	0.008765	0.089453	0.072912	0.022502	0.082951	0.030475	0.01	[118]
Zn	0.476606	0.305779	0.373889	0.226507	1.218722	0.106618	No guideline	[121]

Ion analy	sis	for Al	sheet	and	modifi	ed Al	electrode	s experiments
								· · · · <b>·</b> · · · · · · · · · · · · · ·

#### **3.6 Conclusions**

The present study has successfully shown that modified Al sheet electrode can be useful in removing nitrate ions from water by electroreduction. A number of electrodes have been modified with graphite, graphene, graphite with Cu, and Cu with graphite. The following conclusions have been found:

- 1. Al-Cu electrode was the most effective electrode for nitrate removal and can remove the nitrate ions almost completely if given enough time. This electrode is recommended for further study and assessment.
- 2. Using Al modification lowers its dissolution in the reaction medium.
- 3. In case of Al-Cu electrode, N2 gas results as the predominant product, which is another value for the electrode. The electrode is therefore efficient and selective to nitrogen.
- 4. The nitrate reduction reaction is approximately first order (0.9015) with respect to nitrate concentration, and lower order with higher nitrate concentration. The rate constant is approximately  $(4.06 \times 10^{-3} \text{ s}^{-1})$ .

- 5. The Al-Cu electrode can be recovered and reused. More study is needed in this area.
- 6. The treatment method of nitrate contaminated water by Al-Cu electrode seems to be effective, economic and simple.

#### 3.7 Recommendations for future study in this lab:

- As the Al-Cu showed promising results, it is necessary to do more research on Al-Cu electrode in nitrate ion reduction in water.
- 2. It is also necessary to use aluminum sheets that include low concentrations of foreign metals such as Cd and others.
- 3. More study on recovering and reusing the Al-Cu electrode is necessary to study.

List	of	Abbı	evia	tions

Abbreviation	Meaning
ER	Electroreduction
ED	Electrodialysis
EC	Electrocoagulation
OABO	Organic-modified aluminum manganese bimetal oxide
HAIO	Hydrated aluminum oxide
UV-Vis	Ultraviolet Visible
XRD	X-Ray Diffraction
ICP-MS	Inductively coupled plasma/mass spectrometry
WHO	World Health Organization

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#### Appendices

#### Appendix A

#### **Figures**

#### Figure 11

Nitrate reduction of nitrate ion on Al-Cu electrode. Experimental conditions were: initial nitrate 0,00118 M, applied potential -1.8 V, time 1.5 h, and at room temperature.



#### Figure 12

*Nitrate reduction of nitrate ion on Al-Cu-graphite electrode. Experimental conditions were: initial nitrate 0,00118 M, applied potential -1.8 V, time 1.5 h, and at room temperature.* 



Nitrate reduction of nitrate ion on Al-graphite-Cu electrode. Experimental conditions were: initial nitrate 0,00118 M, applied potential -1.8 V, time 1.5 h, and at room temperature.



#### Figure 14

*Effect of the electrode material on nitrate ion removal. Experimental conditions were: Initial nitrate 0,00118 M, applied potential - 1.8 V and at room temperature.* 



Effect of the nitrate ion concentration on electrochemical reduction. Experimental conditions were:  $\overset{}{\longrightarrow}$  Initial nitrate  $4.70 \times 10^{-4}$  M,  $\overset{}{\longrightarrow}$  Initial nitrate  $5.90 \times 10^{-4}$  M,  $\overset{}{\longrightarrow}$  Initial nitrate  $11.80 \times 10^{-4}$  M,  $\overset{}{\longrightarrow}$  Initial nitrate  $17.60 \times 10^{-4}$  M,  $\overset{}{\longrightarrow}$  Initial nitrate  $23.50 \times 10^{-4}$  M, applied potential - 1.8 V, time 1.5 h and at room temperature.



#### Figure 16

Plot of Ln (initial rate) vs Ln(nitrate concentration) in electrochemical reduction at high concentration. Experimental conditions were: Applied potential - 1.8 V, time 1.5 h and at room temperature.



*Plot of Ln(initial rate) vs Ln(nitrate concentration) in electrochemical reduction at low concentration. Experimental conditions were: Applied potential - 1.8 V, time 1.5 h and at room temperature.* 



#### Figure 18

*Effect of time on NO<sub>3</sub>-NO<sub>2</sub>-N-NH<sub>4</sub> electro-reduction. Experimental conditions were: Initial nitrate 0,00118 M, applied potential - 1.8 V, time 7 h and at room temperature.* 



Al-Cu electrode performance after recovery in nitrate ion removal. -1) for fresh electrode, and -2) for recovered electrode. Experimental conditions were: Initial nitrate 0,00118 M, applied potential - 1.8 V, time 1.5 h and at room temperature.





# الاختزال الكهروكيميائي لأيون النترات باستخدام الألمنيوم المعدل كحفاز : طريقة حديثة لتنقية المياه

إعداد شروق عيد محمد عيد

إشراف أ. د. حكمت هلال

قدمت هذه الرسالة استكمالا لمتطلبات الحصول على درجة الماجستير في الكيمياء، من كلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس- فلسطين.

# الاختزال الكهر وكيميائي لأيون النترات باستخدام الألمنيوم المعدل كحفاز : طريقة حديثة لتنقية المياه

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#### الملخص

الخلفية: أن تلوث المياه السطحية والجوفية بالنترات هو مشكلة في العديد من الأماكن العالم ، مما لها من آثار ضارة على صحة الإنسان والبيئة ، وكانت الممارسات البشرية الخاطئة ، سواء كانت صناعية أو زراعية ، في رفع نسبة التلوث المسموح بها في الماء بحسب منظمة الصحة العالمية (WHO), وعلينا ايجاد حل لهذه المشكلة.

الهدف: فقد كان هدفنا الرئيسي من هذه الدراسة هو تطوير طريقة بسيطة وعملية وفعالة من حيث التكلفة لتقليل تركيزات النترات في المحاليل المائية.

AI- المعدل: AI- واقطاب مختلفة من AI المعدل: AI واقطاب مختلفة من AI المعدل: AI- واقطاب مختلفة من AI-Graphite المعدل: AI-Graphite-Cu ، AI-Cu-Graphite ، AI-Cu ، AI-Graphene ، Graphite

النتائج: كانت النواتج هي  $^{-}NO_2$  و  $^{+}NH_4$  ومن المتوقع أن ينتج  $N_2$ . وكان القطب الأكثر كفاءة هو AI النتائج: كانت النواتج هي  $^{-}NO_2$  وكفاءة إزالة النترات 73.73%. وقد أجريت تجربة جميع الأقطاب الكهريائية على -1.8 فولت.

الخلاصة: من خلال دراسة آليات الاختزال على Al-Cu ، تشير النتائج إلى أن الاختزال الكهربائي Al-Graphite يكون تقريبًا من الدرجة الأولى فيما يتعلق بالنترات. تم قياس XRD لـ Al-Cu و Al-Cu في Al-Cu النترات يكون تقريبًا من الدرجة الأولى فيما يتعلق بالنترات. تم قياس ARD لـ Al-Cu في ما-Cu الفول العديد من المتغيرات على كفاءة القطب Al-Cu في اختزال أيون النترات، مثل الوقت وتركيز النترات الأولي. وتم أيضا دراسة ثباتية القطب ونوع القطب تحت الخروف التجربة. كما تم دراسة إمكانية إعادة استخدام القطب الكهربى Al-Cu أيون النترات، مثل الوقت وتركيز النترات الأولي. وتم أيضا دراسة ثباتية القطب ونوع القطب تحت الخروف التجربة. كما تم دراسة إمكانية إعادة استخدام القطب الكهربى Al-Cu مرة أخرى.

الكلمات المفتاحية: تلوث المياه، منظمة الصحة العالمية، تركيز النترات، أقطاب الألمنيوم المعدلة، تجارب الاختزال الكهروكيميائي