

## Improvement of $\text{NO}_3^-$ Removal from Wastewater by Using Batch Electrocoagulation Unit with Vertical Monopolar Aluminum Electrodes

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This work investigates the possibility of removing nitrate ions ( $\text{NO}_3^-$ ) from wastewater by using monopolar vertical aluminum electrodes in a batch electrochemical unit. Variables studied were current density, initial  $\text{NO}_3^-$  concentration, initial solution pH, electrolysis time and anode diameter. The results show that up to 90% of  $\text{NO}_3^-$  can be removed in approximately 80 minutes. To throw some light on the economy of the process power consumption was measured against current density and percentage removal. The results show that the ratio (% removal/power consumption) dramatically decreased from 34.9 to 0.45 by increasing the current density from 3 to 13  $\text{mA/m}^2$  which suggests that the economy of the process is favored by low current densities.

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**Keywords:** Electrocoagulation, Nitrate removal, monopolar vertical electrode, Wastewater treatment.

### 1. INTRODUCTION

Industrial wastewater containing nitrate can cause serious health problems in humans. It can cause eutrophication problems of rivers, lakes and seas[1]. Nitrate is a stable and highly soluble ion with low potential for co-precipitation or adsorption. These properties make it difficult to be removed from water. Therefore, treatment for nitrate is typically very complicated and expensive. Existing methods of removing nitrate from wastewater include ion exchange, biological decomposition, chemical treatment, reverse osmosis, electrodialysis and catalytic denitrification. Although Ion exchange is very efficient process, it is fairly high in capital and operating costs, with undesirable high residual constituents such as chlorides and bicarbonates in the treated water, which must be removed prior to consumption[2-4]. Another method, is biological decomposition, which is a stable and extremely effective process in reducing nitrate by nearly 100% without using any undesirable

chemicals. Unfortunately, this process is generally time consuming, limited in temperature ranges, very costly and requires extensive maintenance. Therefore, it is utilized in most cases only for treating waste water for which the original nitrate concentration is sufficiently high [5]. Reverse osmosis and Electrodialysis [6] can be used to an efficiency of about 65% nitrate removal, however an extremely high cost is needed for energy input, thereby limiting its applications to mainly specialized industrial application. Other methods involve the use of metallic catalysts, such as palladium and rhodium. Horold et al [7] used a bimetallic catalyst with palladium and copper, activated by a fine stream of hydrogen gas, to convert nitrate to nitrogen. Reddy and Lin[8] developed an electro-catalytic reduction method with rhodium catalyst and a small electrical flow, and reported 80% nitrate removal from ground water in 6h. These methods can be operated in a wide range of temperatures and the costs are moderate. The only disadvantages are the difficulty in operation control, possible catalyst fouling, and the sensitivity of the process to environmental conditions [9]. Among the cheapest physico-chemical processes, which include chemical precipitation and electrocoagulation, the last one has several advantages, involving the ability to deliver a precise coagulant dose via control of the amount of applied electrical current, easy automation, low energy requirements [10], and the ability to destabilize, aggregate, and separate the pollutants in a single stage [11,12]. Electrocoagulation includes the in-situ generation of coagulants via the electro-dissolution of a sacrificial anode, which usually consists of iron or aluminium [12]. The interaction between the coagulant and the pollutant is the most complicated aspect in the electrocoagulation process. Once the coagulant metal is dissolved into water, it is hydrolyzed to form different hydroxo-metallic monomeric and polymeric species as well as metal hydroxide precipitates. The types and amounts of produced species primarily depend on the metal concentration and pH [13]. Likewise, the coagulation/destabilization mechanisms and removal efficiencies closely relate to the coagulant species present in the system [14]. Thus, it has been reported in the literature that nitrates can be removed from wastewater via their adsorption onto the surfaces of hydroxide precipitates, which are generated from metals and released by the electrodes [15-17]. From this point of view the aim of this work is to investigate the performance of an electrocoagulation unit with vertical monopolar aluminum electrodes operating in batch regime for the removal of nitrate from wastewater.

## 2. EXPERIMENTAL SETUP AND PROCEDURE

The experimental setup and electrical circuit used is shown in figure (1), the setup consisted of 1000 ml cylindrical glass container of 10 cm diameter and 15 cm height, two monopolar aluminum electrodes (cathode and anode) were placed vertically, with the anode at the center of the reactor parallel to the cathode to the wall of the cell. The cathode diameter was constant at 10 cm while anode diameter was changed from 0.8 to 1.2 cm. Before each run aluminum electrodes were immersed in diluted carbon tetrachloride solution for few minutes for removing greases, washed with distilled water, and finally connected to a D.C. power supply (15 volts, 10 A) fitted with a voltage regulator. A multirange ammeter was connected in series with the cell and a D.C. voltmeter was connected in parallel with the cell to measure its voltage. In each run 500 ml of synthetic solution of  $\text{KNO}_3$  with

initial  $\text{NO}_3^-$  concentration ranging from 150 to 1000 ppm and sodium chloride solution with constant concentration of 3.5% were placed at the electrolytic cell.  $\text{NO}_3^-$  concentrations for the fresh and treated solution were measured before and after each run by using a U.V. Spectrophotometer (UV-1800 SHIMADZU), 5 ml samples were drawn at different time intervals, diluted to 50 ml with distilled water, filtered to remove any possible interference from suspended particles, then acidified with 1 ml 1N HCl to prevent interference from hydroxides [18]. A calibration curve was prepared for the  $\text{NO}_3^-$  concentration range used, by adjusting the wave length at 220nm, this curve was used for finding out the  $\text{NO}_3^-$  concentration at any time. Many variables were investigated for its effect on the removal efficiency of the  $\text{NO}_3^-$  from wastewater such as, electrolysis time that ranged from 10 to 90 minutes, initial  $\text{NO}_3^-$  concentration from 150 to 1000 ppm, current density ranged from 3 to 13  $\text{mA}/\text{cm}^2$ , solution pH in the range from 3 to 12 and anode diameter from 0.8 to 2 cm were investigated.

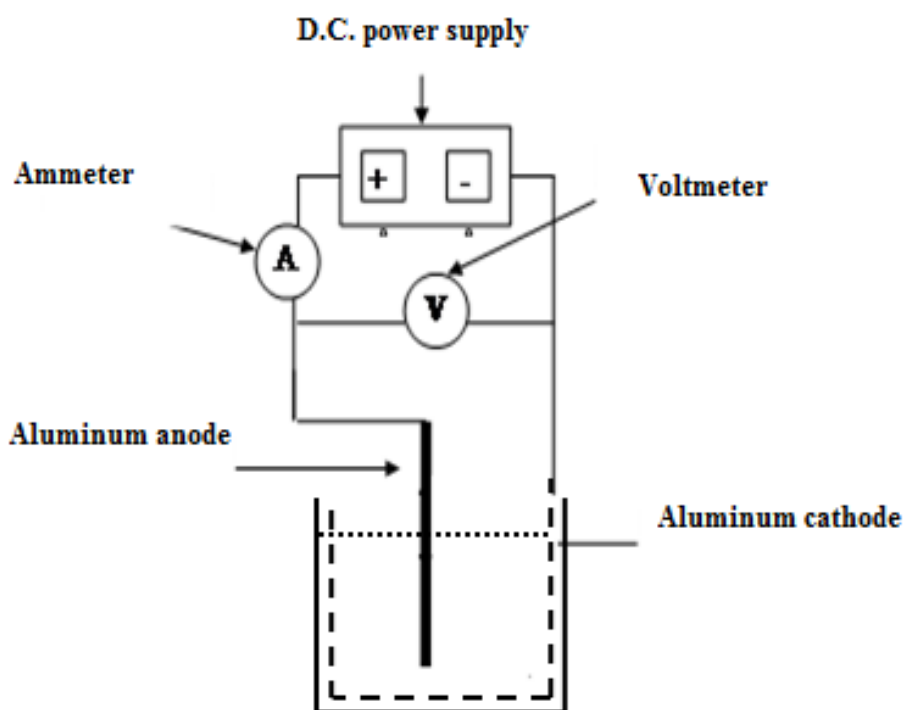
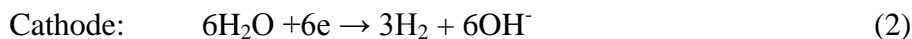
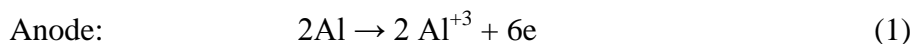


Figure 1. experimental setup.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Effect of current density

Figure (2) shows that the percentage removal of  $\text{NO}_3^-$  has been increased by increasing the current density within the range from 3 to 10  $\text{mA}/\text{cm}^2$ . These results can be explained by the fact that, increasing current density will increase the dissolution rate of aluminium electrode according to Faraday's law with the formation of  $\text{Al}(\text{OH})_3$  coagulant according to the reactions that:



The overall:



Increasing the rate of freshly formed amorphous  $\text{Al}(\text{OH})_3$  that have large surface area on which rapid adsorption of soluble  $\text{NO}_3^-$  and trapping of colloidal particles take place with a consequent removal of  $\text{NO}_3^-$  from wastewater. In addition the cathodically evolved  $\text{H}_2$  bubbles float  $\text{Al}(\text{OH})_3$  along with the adsorbed  $\text{NO}_3^-$  compounds to the upper surface of the solution. Besides, the rising  $\text{H}_2$  bubbles entrain solution in their wake [19]; the upward rising gas-liquid dispersion stirs the anode vicinity with a consequent decrease in the anode concentration polarization and the anode tendency to passivate. Increasing the current density above this range ( $10\text{ mA/cm}^2$ ) has decreased the percentage  $\text{NO}_3^-$  removal which may be ascribed to the possible passivation of anodic surface due to higher potential applied. Figure 2 also shows that increasing the electrolysis time has increased the %  $\text{NO}_3^-$  removal which can be attributed to fact that increasing the electrolysis time will certainly increase the available  $\text{Al}^{+3}$  according to Faraday's law, and consequently increase the amount of  $\text{Al}(\text{OH})_3$  which is responsible for  $\text{NO}_3^-$  removal.

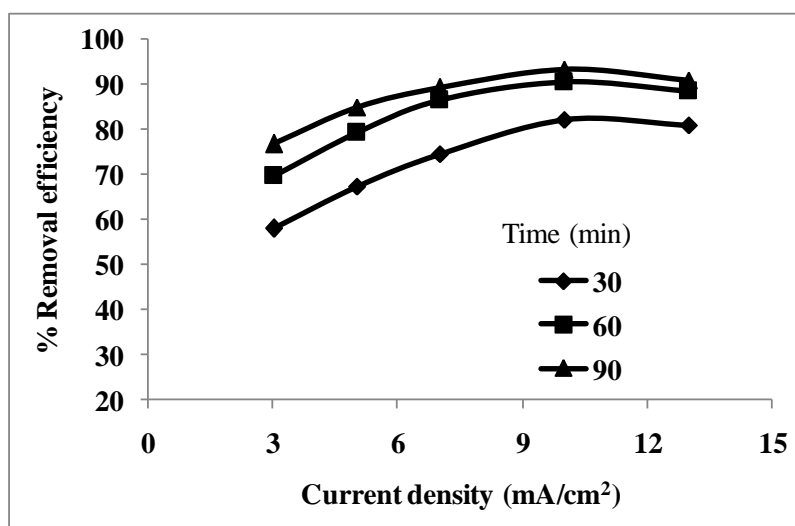


Figure 2. % Removal efficiency vs current density for different electrolysis time

### 3.2. Effect of initial $\text{NO}_3^-$ concentration

As shown in figure (3), the %  $\text{NO}_3^-$  removal efficiency decreased by increasing initial  $\text{NO}_3^-$  concentration in the range from 150 to 1000 ppm, this can be ascribed to the fact that, increasing  $\text{NO}_3^-$

ion concentration would probably increase activation polarization via adsorption on the anode and cathode with a consequent decrease in the rate of aluminum dissolution at the anode and hydrogen evolution at the cathode. In addition the figure(3) shows that at higher concentrations of NO<sub>3</sub><sup>-</sup> (1000 ppm) the removal rate approximately reached maximum value at certain period approximately 60 minutes, which can be ascribed to the fact that increasing the NO<sub>3</sub><sup>-</sup> concentration will block the adsorption sites of Al(OH)<sub>3</sub> rapidly and decreases its ability to adsorb more NO<sub>3</sub><sup>-</sup> ion.

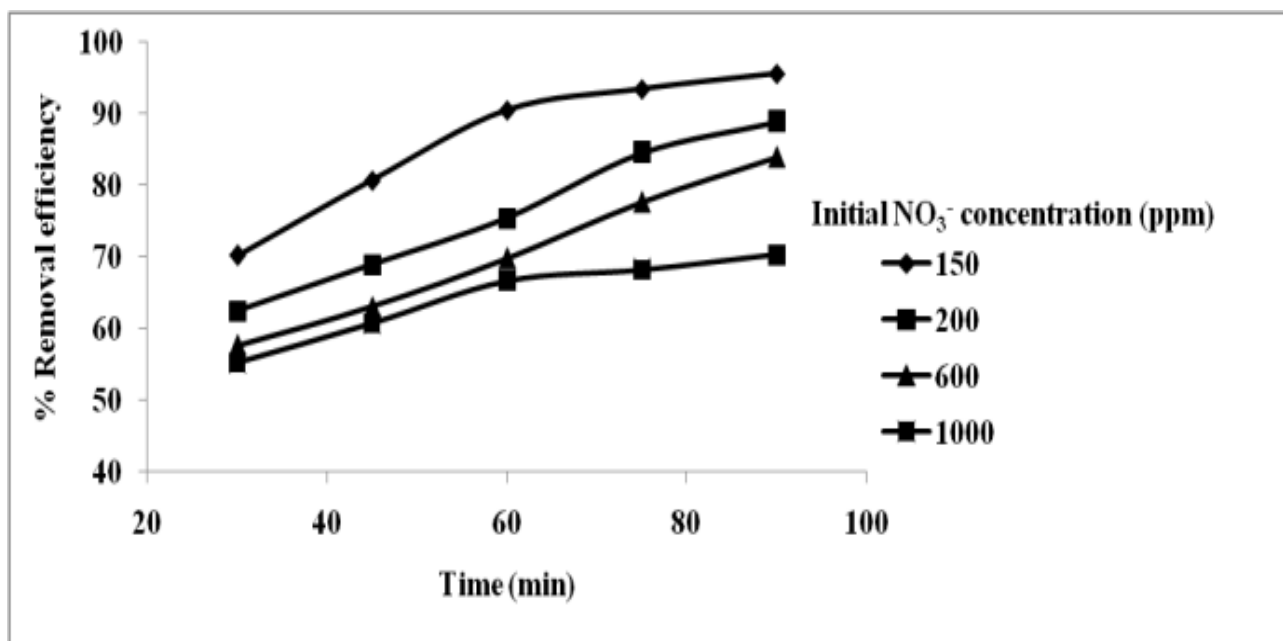


Figure 4. %Removal efficiency vs time for different initial NO<sub>3</sub><sup>-</sup> concentration

### 3.3. Effect of initial pH

It has to be mentioned that, depending on the pH of the aqueous medium other ionic species, such as dissolved Al (OH)<sup>2+</sup> and Al<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup> hydroxo complexes may also be present in the system. Anodic metal ions and hydroxide ions generated at the electrode surfaces react in the bulk wastewater to form various hydroxides and build up polymers [12]:



The suspended aluminum hydroxides can remove NO<sub>3</sub><sup>-</sup> from the solution by sorption, co-precipitation or electrostatic attraction, followed by coagulation [15]. Figure (5) shows that the % removal efficiency increased by increasing initial solution pH which can be ascribed to the fact that, increasing the solution pH can destroy the passive aluminium oxide layer that is formed at lower pH[4].

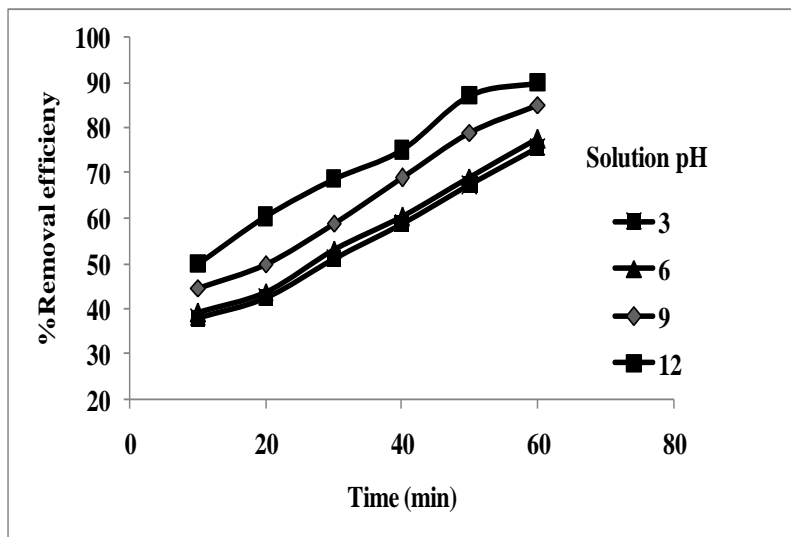


Figure 5. % Removal efficiency vs time at different solution pH

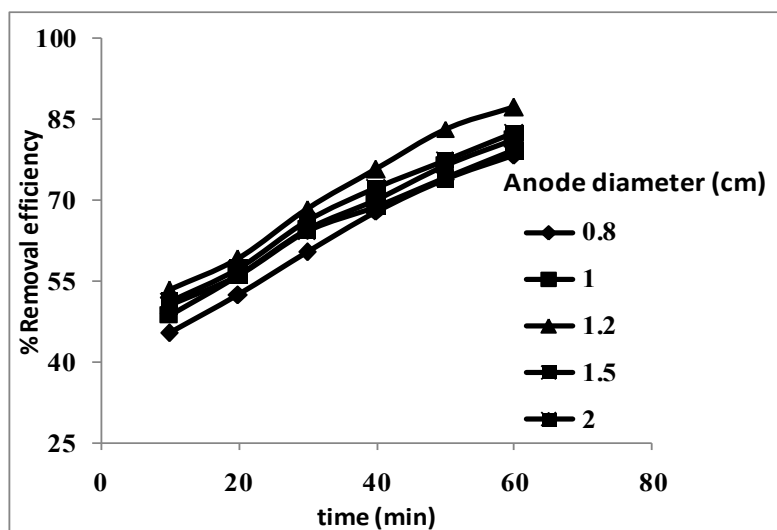


Figure 6. % Removal efficiency vs time at different anode diameter.

### 3.4. Effect of anode diameter

Figure (6) shows that increasing the anode diameter from 0.8 to 1.2 cm has increased the percentage removal of NO<sub>3</sub><sup>-</sup>, which can be ascribed to that, increasing the anode diameter will decrease the annular space between the anode and cathode that improves the agitation conditions within this region due to H<sub>2</sub> gas evolution at the cathode, which prevents accumulation of anodic and/or cathodic products at the electrodes surfaces which decreases polarization at both electrodes and improves the unit performance. Increasing the anode diameter above this limit was found to decrease the percentage removal of NO<sub>3</sub><sup>-</sup>, which can be ascribed to the fact that increasing the anode diameter will certainly increase the thickness of the diffusion layer that decreases the transfer of the ions generated from the anode surface to the solution bulk, which increases polarization and decreases the unit performance.

3.5. Electric power consumption

The electric power consumption of the process was calculated per m<sup>3</sup> of the waste solution using the equation that [20,21]:

$$P = EIt/V$$

Where P is the specific power consumption (W.h/m<sup>3</sup>). E is the cell voltage in volt (V), I is the current in ampere (A), t is the time of electrocoagulation in hour (h) and V is the solution volume in cubicmeter (m<sup>3</sup>). The time of operation was fixed at 60 min. As shown in figure (7), it is clear that increasing the current density will increase both power consumption and percentage removal efficiency.

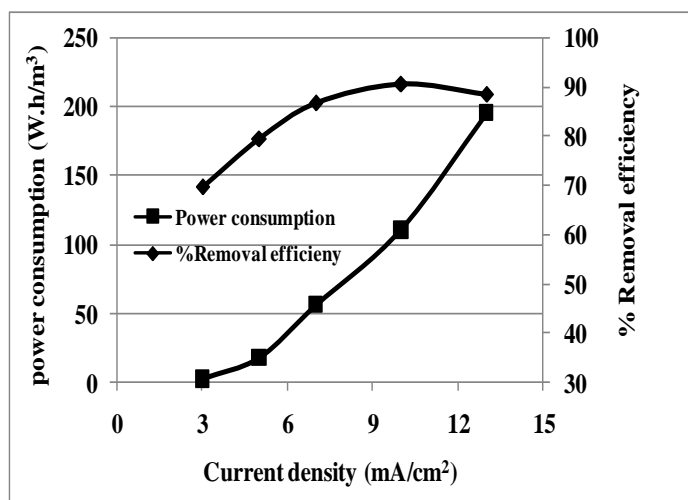


Figure 7. Power consumption and % removal efficiency vs current density

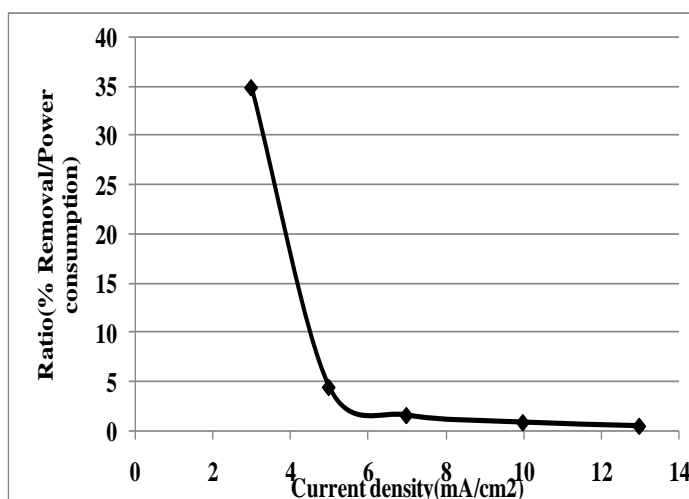


Figure 8. Ratio (% Removal efficiency/power consumption) vs current density

The increase in power consumption can be ascribed to the increased polarization on the two electrodes by increasing the current density [22].

To throw some light on the role of current density in the economy of the process the ratio (% removal efficiency/power consumption) was plotted versus current density as shown in figure (8), the results show that the ratio dramatically decreased from 34.9 to 0.45 by increasing the current density from 3 to 13 mA/m<sup>2</sup> which suggests that the economy of the process is favored by low current densities.

#### 4. CONCLUSIONS

Electrocoagulation was investigated for its performance in the removal of NO<sub>3</sub><sup>-</sup> from wastewater using vertical cylindrical monopolar aluminum electrodes in a batch electrocoagulation unit. The results show that, the % removal efficiency of the NO<sub>3</sub><sup>-</sup> has been increased by increasing the initial solution pH and increasing the current density up to 10 mA/cm<sup>2</sup>, above this range the % removal efficiency decreased by increasing the current density, and by increasing the anode diameter up to 1.2 cm while increasing the anode diameter above this limit was found to decrease the % removal efficiency. increasing initial NO<sub>3</sub><sup>-</sup> concentration will decrease the % removal efficiency. The results showed that 90% of the NO<sub>3</sub><sup>-</sup> can be removed within 80 minutes. In addition the power consumption for the unit was measured for different current densities. The results show that the ratio (% removal/power consumption) dramatically decreased from 34.9 to 0.45 by increasing the current density from 3 to 13 mA/m<sup>2</sup>, which suggests that the economy of the process is favored by low current densities.

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